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# A revised description of the binary $\text{CaCl}_2\text{-H}_2\text{O}$ chemical system up to solution-mineral equilibria and temperatures of $250^\circ\text{C}$ using Pitzer equations. Extension to the multicomponent $\text{HCl-LiCl-NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$ system.

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## Abstract

Calcium chloride is a highly soluble chemical compound involved in variable amounts in many natural and industrial environments. The description of its chemical properties and mineral-solution equilibrium conditions must cover a wide range of temperatures and chemical compositions, including saline solutions. This article reports an improved model for the thermodynamic accurate description of the  $\text{CaCl}_2\text{-H}_2\text{O}$  chemical system according to the Pitzer formalism from 25 to  $250^\circ\text{C}$ , over the whole concentration range between pure water and the solubility of salts (up to 30 M). It accounts for the aqueous speciation of the  $\text{CaCl}_2$  electrolyte, according to the partial molar properties of the  $\text{Ca}^{2+}$ ,  $\text{CaCl}^+$ ,  $\text{CaCl}_2^0$  and  $\text{Cl}^-$  aqueous species described by the HKF theory. The numerical stability, resulting from the lowered ionic strength in comparison to full dissociation, facilitates the development of temperature-dependent models for ternary systems containing the main major cations:  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ .

## Keywords

Thermodynamic modeling; aqueous electrolytes; Pitzer equations; HKF theory; Partial dissociation

### 1. Introduction

Calcium chloride is a chemical compound involved in variable amounts in many natural and industrial environments. Due to its high solubility in water, its natural occurrences mostly concern saline deposits associated with hydrothermal systems [1]. Such deposits are often described as evaporites [2–4],

whose deposition mechanisms have been widely studied in regard to secular variations in seawater chemistry or the formation of basinal brines [5–8]. These deposits can also result from the hydration of mantle rock minerals, like enstatite, when deep hot waters of marine origin flow within their porosity. Such water-rock interactions, which result in the transformation of primary mantle rocks into serpentinites, could be responsible for the formation of Salt Giants [3,9–12]. Such formations are characterized by the presence of relatively thick layers of tachyhydrite ( $\text{CaCl}_2 \cdot (\text{MgCl}_2)_2 \cdot 12\text{H}_2\text{O}$ ), a very soluble salt that is not stable in the current most arid environments in the world. The  $\text{CaCl}_2$ -rich hot waters associated with these hydrothermal systems are often recorded in fluid inclusions, which are used to investigate the past conditions of temperature, pressure and chemistry [13,14]. In some specific contexts of the Earth's deep crust, where temperatures and pressures are relatively high (above  $350^\circ\text{C}$  and 200 bars), the hydrolysis of  $\text{CaCl}_2$  is thought to be responsible for the generation of significant amounts of HCl [15]. In other specific environments located in Proterozoic sedimentary basins,  $\text{CaCl}_2$ -rich brines may be responsible for the alteration of monazite minerals contained in high-grade uranium deposits [16].

Industrial applications of calcium chloride, including thermal processes, are numerous [1,17,18] because of the combination of its hygroscopic character, heat of hydration, the low to medium melting points of its hydrates and its low material costs. Beyond the conventional applications like deicing, dust control and road stabilization, the physical and chemical properties of aqueous  $\text{CaCl}_2$  and its solid hydrates are useful for phase change material, desiccants, heat pumps and refrigeration, and thermal energy storage [19–21].  $\text{CaCl}_2$  can also be used to tune the crystallinity of some minerals, like  $\text{Mg}(\text{OH})_2$ , which is produced for specific applications for instance as a flame retardant filler [22]. Mixed with other chemical compounds, it is also used as a coagulant to prevent silica scaling in the surface installation of geothermal plants [23,24], or in wells where geothermal fluids undergo significant temperature variations during ascent in the production well and during reinjection. For all the aforementioned applications, the supply of  $\text{CaCl}_2$  in its various forms is provided by sufficient production based on the

refining of natural brines [25], the reaction of calcium hydroxide with ammonium chloride in Solvay soda production, and the reaction of hydrochloric acid with calcium carbonate [18].

In addition, depending on the chemical composition of the pore brine in a reservoir rock targeted for CO<sub>2</sub> geological storage, CaCl<sub>2</sub> may influence the solubility of the gas [26–29].

Due to the variety of uses and occurrences of CaCl<sub>2</sub> in natural and industrial environments with, in some instances, environmental and economic issues, it is necessary to have a reliable description of its chemical properties and solid-gas-solution equilibrium conditions over a wide range of temperatures and chemical compositions, including saline solutions. In this context, the objective of this work was to improve the thermodynamic description of the CaCl<sub>2</sub>-H<sub>2</sub>O chemical system according to a combined Pitzer-HKF formalism from 0 to 250°C, over the whole concentration range between pure water and the solubility of salts, and to extend its application to ternary systems containing the main major cations: H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>.

## 2. Theoretical background and methodology

Despite important advances previously made by numerous researchers, the CaCl<sub>2</sub>-H<sub>2</sub>O system still needs improvement. For instance, the model of Li et al. [30] based on the Pitzer-Simonson-Clegg equations, is able to describe reliably the solution properties and solid-liquid equilibria over a wide range of temperatures and concentrations of binary aqueous chloride systems, including CaCl<sub>2</sub>. Yet, the description of more complex systems is still necessary, and should rely on thermodynamic models implemented in modelling tools that can be used by a large scientific community. The Pitzer equations belong to these models as they are implemented in several geochemical and reactive transport simulation tools [31–33], and as they were often used to calculate the properties of the CaCl<sub>2</sub>-H<sub>2</sub>O system as described hereafter. In the original philosophy of the Pitzer approach [34,35], aqueous electrolytes are assumed to be fully dissociated and mutual influences between solutes are described by specific interaction parameters that affect ion activity coefficients rather than by aqueous complexation constants. This helped to improve the description of a number of saline aqueous systems

up to salinities of c.a.  $6 \text{ mol}\cdot\text{kg}^{-1}$ . In order to extend the range of concentrations to higher values and to consider pH-sensitive chemical systems and weak electrolytes, it was found necessary to introduce the possibility of considering partial dissociation or aqueous complex formation [36–38]. The corresponding Pitzer equations are summarized in the supplementary materials (Appendix 1). Other options proposed to extend the description of solution properties to higher concentrations included the use of additional ionic strength-dependent specific interaction parameters [39–42], and a mole fraction description of the concentrations [43]. However, considering partial dissociation has advantages that led us to select this option. Indeed, describing the formation of aqueous complexes is inherently consistent with the Debye-Hückel theory, which applies to dilute aqueous solutions. Thus, considering partial dissociation brings consistency as a continuum between concentrated and dilute systems where the effects of ionic strength dominate the ion-specific interactions. In addition, when partial dissociation is taken into account, the number of “free” water molecules remaining in the brine is larger than in the full dissociation case and, thus, the aqueous solution “status” can be maintained up to higher concentrations. At the same time, the ionic strength of the brine increases less when partial dissociation is considered, which contributes to stabilizing the solvation of the Pitzer equations. Moreover, solution properties like density, heat capacity and enthalpy should be better described when considering the contribution of the various complexes or ion pairs, the standard properties of which differ from the simple weighted sum of the fully dissociated species. Despite these advantages, one must acknowledge that this option also has significant drawbacks due to the semi-empirical character of the Pitzer equations. In particular, increasing the variety of aqueous species increases the number of specific interaction parameters to consider when parameterizing the Pitzer equations. The risk is generating an exponentially growing dataset of interaction parameters, which poses an open question. In addition, the use of aqueous complexation constants determined for dilute solutions to constrain the estimation of specific interaction parameters for higher concentrations may be tricky. In some cases, a value different from that determined for dilute solutions, and thus with a questionable

physical meaning, had to be proposed, as previously done by Møller [44] for the  $\text{CaSO}_4^0$  ion pair, and as illustrated in the following.

The  $\text{CaCl}_2\text{-H}_2\text{O}$  chemical system is concerned by these evolutions of the Pitzer equations since the solubility of antarcticite ( $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ ) is  $7.3 \text{ mol}\cdot\text{kg}^{-1}$  at  $25^\circ\text{C}$ , and that of the stable salt ( $\text{CaCl}_{2,\text{cr}}$ ) at  $250^\circ\text{C}$  is about  $30.8 \text{ mol}\cdot\text{kg}^{-1}$  according to Pitzer and Oakes [45]. This led Sterner et al. [46] to revise the previous thermodynamic models developed in particular by Møller [44] and Greenberg and Møller [47]. Sterner et al. [46] proposed 4 models based on the different evolutions of the Pitzer equations: (i) the basic Pitzer equation, (ii) the Pitzer equation augmented by an ionic strength-dependent third virial contribution, (iii) the Pitzer equation together with equilibria involving the formation of  $\text{CaCl}^+$  and  $\text{CaCl}_2^0$ , and (iv) the simultaneous combination of all of the above.

Unsurprisingly, the two first models of Sterner et al. [46] could not satisfactorily describe the osmotic coefficient data over the whole range of temperatures and concentrations. Models (iii) and (iv) did much better with an advantage for model (iv) because of its greater numerical stability, especially at high temperatures and concentrations. Interestingly, the authors considered a limited number of temperature-dependent interaction parameters for their models based on the partial dissociation hypothesis. Indeed, only 9 parameters per temperature were necessary in model (iii), namely the aqueous complex formation constants of  $\text{CaCl}^+$  and  $\text{CaCl}_2^0$  from  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , the binary interaction parameters  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C^\phi$  for the  $\text{Ca}^{2+}\text{-Cl}^-$  and  $\text{CaCl}^+\text{-Cl}^-$  ion pairs and the mutual binary interaction  $\lambda$  for the  $\text{CaCl}_2$  aqueous complex. In model (iv), the  $C_1^\phi$  parameter was added to account for the ionic strength-dependent term of the interaction between  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , and between  $\text{CaCl}^+$  and  $\text{Cl}^-$ . Then, the temperature variation of each interaction parameter or formation constant was fitted with 3 coefficient temperature functions.

More recently, Lach et al. [48] proposed a new set of interaction parameters to include experimental solution heat capacity data as additional constraints to the optimization procedure. However, the concentration of  $\text{CaCl}_2$  was limited to  $7 \text{ mol}\cdot\text{kg}^{-1}$  and temperatures were comprised between 0 and

75°C. Because of this limited concentration range, the authors could describe both the osmotic coefficient and solution heat capacity of  $\text{CaCl}_2$  aqueous solutions by considering full dissociation of the electrolyte. Then Lassin et al. [49] introduced the  $\text{CaCl}_2^0$  ion pair to extend the description of the osmotic coefficient data at 25°C beyond the solubility limit of antarcticite, in the metastability domain of the aqueous solution (up to 11 mol·kg<sup>-1</sup>). This made it possible to determine new interaction parameters for describing solution properties (activity coefficients and water activity) and salt solubilities in the multicomponent H-Li-Na-K-Ca-Mg-Cl-H<sub>2</sub>O system, but at 25°C only.

Considering partial dissociation is actually constrained by the standard partial thermodynamic properties of the solutes, which depend on temperature and pressure. A convenient way to describe such a dependency is to use an equation of state that relates the standard partial molar volume of the aqueous species to the temperature and the pressure. In the present work, the robust, well-known and well-documented revised-HKF theory is applied [50–52]. The combined use of the revised HKF-theory and of the Pitzer equations has been previously described in the literature and proved to be a powerful approach able to cover very large conditions of temperatures and concentrations [53–57]. The geochemical calculation code used in the present work is PHREESCALE [48,58], which is an evolution of PhreeQC [31], software that is widely used in the geochemical modelling community.

The general description of the model development performed in the present work is extensively detailed in the supplementary materials (Appendix 2). Regardless of the formation constants of the aqueous complexes which were set according to [59], 12 specific interaction parameters were found necessary to reproduce the osmotic coefficient data, each parameter being variable with temperature (in Kelvin) according to the following expression (equation (1)) implemented in PhreeSCALE:

$$Y(T) = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6\ln(T) \quad (1)$$

For all Y parameters, which are presented in Table 1, the  $a_4$  coefficient was set to 0. The number of digits of the parameters reported in Table 1 is very large but, at the highest concentrations and temperatures, the computation is very unstable and truncations may lead to failures.



Table 1 – Temperature-dependent Pitzer interaction parameters estimated in this work (unless indicated otherwise) to describe the  $\text{CaCl}_2\text{-H}_2\text{O}$  binary system and the  $\text{HCl-CaCl}_2\text{-H}_2\text{O}$ ,  $\text{LiCl-CaCl}_2\text{-H}_2\text{O}$ ,  $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ ,  $\text{KCl-CaCl}_2\text{-H}_2\text{O}$ , and  $\text{MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$  ternary systems<sup>a,b</sup>

Parameter		$a_1$	$a_2$	$a_3$	$a_5$	$a_6$
<b>CaCl<sub>2</sub>-H<sub>2</sub>O system</b>		0 < T < 250°C				
$\beta^{(0)}$	$\text{Ca}^{2+}\text{-Cl}^-$	2.64951	-7.76412E-3	8.55745E-06	-240.83888	0
$\beta^{(0)}$	$\text{CaCl}^+\text{-Cl}^-$	1.69861	-5.11886E-3	3.94991E-06	1.01651	0
$\beta^{(1)}$	$\text{Ca}^{2+}\text{-Cl}^-$	9.78521	-9.136031E-3	0	-1572.72024	0
$\beta^{(1)}$	$\text{CaCl}^+\text{-Cl}^-$	-1.30849	7.491923E-3	0	0	0
$C^\phi$	$\text{Ca}^{2+}\text{-Cl}^-$	4.43923E-2	-1.97602E-4	2.08590E-07	9.89356E-1	0
$C^\phi$	$\text{CaCl}^+\text{-Cl}^-$	-7.74506E-2	2.64517E-4	-2.28284E-07	-2.51838E-1	0
$\lambda$	$\text{CaCl}_2^0\text{-Cl}^-$	3.43665	-1.36667E-2	1.37988E-05	1.29783	0
$\lambda$	$\text{CaCl}_2^0\text{-Ca}^{2+}$	7.25380E-1	-2.98981E-3	2.08541E-06	-6.19108E-2	0
$\lambda$	$\text{CaCl}_2^0\text{-CaCl}^+$	-310.67494	-1.19739E-1	3.23404E-05	7337.89850	56.017375
$\theta$	$\text{Ca}^{2+}\text{-CaCl}^+$	-16.66512	4.71423E-2	-4.34747E-05	1925.51497	0
$\mu$	$\text{CaCl}_2^0\text{-CaCl}_2^0\text{-CaCl}_2^0$	2.9	0	0	0	0
$\zeta$	$\text{CaCl}_2^0\text{-CaCl}^+\text{-Cl}^-$	-0.21759	-7.72569E-4	1.60629E-06	100.84472	0
<b>HCl-CaCl<sub>2</sub>-H<sub>2</sub>O system</b>		25°C	Consistent with the HCl-H <sub>2</sub> O parameters from [60]			
$\theta^c$	$\text{H}^+\text{-Ca}^{2+}$	9.68627E-2	0	0	0	0
$\theta$	$\text{H}^+\text{-CaCl}^+$	7.50E-03	0	0	0	0
$\psi$	$\text{H}^+\text{-Ca}^{2+}\text{-Cl}^-$	-1.01797E-03	0	0	0	0
$\psi$	$\text{H}^+\text{-CaCl}^+\text{-Cl}^-$	-1.80E-03	0	0	0	0
<b>LiCl-CaCl<sub>2</sub>-H<sub>2</sub>O system</b>		10 < T < 50°C	Consistent with the LiCl-H <sub>2</sub> O parameters from [61]			
$\theta$	$\text{Li}^+\text{-Ca}^{2+}$	0.02578	0	0	0	0
$\theta$	$\text{Li}^+\text{-CaCl}^+$	-0.07	0	0	0	0
$\psi$	$\text{Li}^+\text{-Ca}^{2+}\text{-Cl}^-$	0	0	0	0	0
$\psi$	$\text{Li}^+\text{-CaCl}^+\text{-Cl}^-$	5.04638	-1.76648E-2	2.04973E-05	-475.1255	0
<b>NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system</b>		18 < T < 130°C	Consistent with the NaCl-H <sub>2</sub> O parameters from [44]			
$\theta^c$	$\text{Na}^+\text{-Ca}^{2+}$	0.05	0	0	0	0
$\theta$	$\text{Na}^+\text{-CaCl}^+$	-0.05	0	0	0	0
$\psi$	$\text{Na}^+\text{-Ca}^{2+}\text{-Cl}^-$	5.6136E-2	-4.1646E-4	6.7532E-07	0	0
$\psi$	$\text{Na}^+\text{-CaCl}^+\text{-Cl}^-$	6.3123E-2	-4.7242E-4	7.6190E-07	0	0
<b>KCl-CaCl<sub>2</sub>-H<sub>2</sub>O system</b>		18 < T < 200°C	Consistent with the KCl-H <sub>2</sub> O parameters from [47]			
$\theta^c$	$\text{K}^+\text{-Ca}^{2+}$	0.1156	0	0	0	0
$\theta$	$\text{K}^+\text{-CaCl}^+$	2.28922	-2.56619E-3	0	-582.8673	0
$\psi$	$\text{K}^+\text{-Ca}^{2+}\text{-Cl}^-$	7.23166	-2.1006E-2	2.0230E-05	-839.19018	0
$\psi$	$\text{K}^+\text{-CaCl}^+\text{-Cl}^-$	-0.19453	2.24792E-4	0	44.60541	0
<b>MgCl<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O syst.</b>		25 < T < 110°C	Consistent with the MgCl <sub>2</sub> -H <sub>2</sub> O parameters from [48]			
$\theta$	$\text{Mg}^{2+}\text{-Ca}^{2+}$	0.05	0	0	0	0
$\theta$	$\text{Mg}^{2+}\text{-CaCl}^+$	7.0589E-3	1.200E-5	0	0	0
$\psi$	$\text{Mg}^{2+}\text{-Ca}^{2+}\text{-Cl}^-$	1.84775E-1	-6.15313E-4	0	0	0
$\psi$	$\text{Mg}^{2+}\text{-CaCl}^+\text{-Cl}^-$	-2.62484E-1	1.47044E-3	-2.0487E-06	0	0

<sup>a</sup>: the coefficient  $a_4$ , of the temperature dependence function given in the text, is set to 0 for all interaction parameters — <sup>b</sup>:ternary interaction parameters involving the  $\text{CaCl}_2^0$  aqueous species were all set to 0 and are not reported in this table (see text for more details) — <sup>c</sup>: valid up to 250°C.

The formation and individual standard properties of the aqueous complexes,  $\text{CaCl}^+$  and  $\text{CaCl}_2^0$ , are given in Table 2. The formation properties (e.g.  $\log K$ , the logarithm of the thermodynamic constant of any reaction) depend on temperature according to equation (2):

$$\log K = A + BT + C/T + D \log(T) + E/T^2 \quad (2)$$

with T in Kelvin

$\log K$  are used to calculate the aqueous speciation while the individual standard properties (HKF parameters) are used to calculate the thermal and volumetric properties of the solutes and, then, of the aqueous solution [58].

Once solution properties are described satisfactorily over the whole range of temperatures and concentrations, including the liquid-vapor equilibrium at saturation with the stable salts [30,62], the solubility product of these salts can be deduced from the calculated ion activity product of the corresponding dissolution reaction. The temperature function coefficients obtained this way are reported in Table 3.

After the binary  $\text{CaCl}_2\text{-H}_2\text{O}$  system has been fully parameterized, the study can focus on the ternary systems (i.e. with an additional cation among Li, Na, K and Mg) using the same methodology. However, much fewer solution properties have been measured in mixed systems and the most abundant information in the literature comes from solubility measurements. The temperature range of available data varies with the system. Most of these data could be reproduced satisfactorily using cation-cation ( $\theta$ ) and cation-cation-anion ( $\psi$ ) interaction parameters (Table 1) and solubility products of salts (Table 3).

Table 2 – Formation reaction ( $\log K$ , Equation (2)) and individual properties (HKF parameters\*) of the aqueous complexes of the  $\text{CaCl}_2\text{-H}_2\text{O}$  system.

Reaction	A	B	C	D	E
$\text{Ca}^{2+} + \text{Cl}^- = \text{CaCl}^+$	784.30407	1.29811E-1	-43492.573	-285.72525	2630012

$\text{Ca}^{2+} + 2 \text{Cl}^- = \text{CaCl}_2^0$	1562.1171	2.55796E-1	-85801.168	-569.81877	5221187.6E		
Species	$a_1$	$a_2$	$a_3$	$a_4$	$c_1$	$c_2$	$\omega$
Source: [59]							
$\text{Ca}^{2+}$	-0.81E-1	-30.34E+2	22.16	-10.37E+4	37.66	-10.55E+4	5.17E+5
$\text{Cl}^-$	1.687	20.09E+2	23.28	-11.91E+4	-18.41	-23.91E+4	6.09E+5
$\text{CaCl}^+$	1.13587	-4.8103E+2	25.9195	-11.4282E+4	87.3782	2.1928E+4	2.0343E+5
$\text{CaCl}_2^0$	2.602	30.99E+2	11.85	-12.91E+4	100.25	13.69E+4	-0.159E+5

\*:  $a_1$  ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{bar}^{-1}$ );  $a_2$  ( $\text{J}\cdot\text{mol}^{-1}$ );  $a_3$  ( $\text{J}\cdot\text{K}\cdot\text{mol}^{-1}\cdot\text{bar}^{-1}$ );  $a_4$  ( $\text{J}\cdot\text{K}\cdot\text{mol}^{-1}$ );  $c_1$  ( $-\text{mol}^{-1}\cdot\text{K}^{-1}$ );  $c_2$  ( $\text{J}\cdot\text{K}\cdot\text{mol}^{-1}$ );  $\omega$  ( $\text{J}\cdot\text{mol}^{-1}$ )

Table 3 – Solubility products (log K, Equation (2))<sup>a</sup> of the various salts estimated in this work.

Salt and dissolution reaction	A	B·10 <sup>3</sup>	C	E	T range (°C)
Antarcticite $\text{CaCl}_2\cdot 6\text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + 6\text{H}_2\text{O}$	29.9618	-39.6182	-4331.89	0	0-30
$\alpha$ - $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$ (ghiaraitite) $\text{CaCl}_2\cdot 4\text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + 4\text{H}_2\text{O}$	-21.2256	41.7284	4099.02	0	25-46
$\beta$ - $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$ $\text{CaCl}_2\cdot 4\text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + 4\text{H}_2\text{O}$	7.43447	-7.72095	0	0	25-43
$\gamma$ - $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$ $\text{CaCl}_2\cdot 4\text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + 4\text{H}_2\text{O}$	-8.0835	17.6240	2385.79	0	25-40
$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ (sinjarite) $\text{CaCl}_2\cdot 2\text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + 2\text{H}_2\text{O}$	25.5584	-27.4357	-5833.03	812151	20-177
$\text{CaCl}_2\cdot \text{H}_2\text{O}$ $\text{CaCl}_2\cdot \text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + \text{H}_2\text{O}$	13.53563	-18.64790	0	0	175-190
$\text{CaCl}_2\cdot 1/3\text{H}_2\text{O}$ $\text{CaCl}_2\cdot 0.33\text{H}_2\text{O} = \text{CaCl}^+ + \text{Cl}^- + 0.33\text{H}_2\text{O}$	15.12605	-20.80292	0	0	190-233
$\text{CaCl}_2$ $\text{CaCl}_2 = \text{CaCl}^+ + \text{Cl}^-$	16.52931	-23.03200	0	0	225-250 <sup>b</sup>
$\text{LiCl}\cdot\text{CaCl}_2\cdot 5\text{H}_2\text{O}$ $\text{LiCl}\cdot\text{CaCl}_2\cdot 5\text{H}_2\text{O} = \text{Li}^+ + \text{Ca}^{2+} + 3\text{Cl}^- + 5\text{H}_2\text{O}$	51.8798	-0.08461	-4919.4	0	$\leq 25$
Tachyhydrite $\text{CaCl}_2(\text{MgCl}_2)_2\cdot 12\text{H}_2\text{O} = \text{CaCl}^+ + 2\text{Mg}^{2+} + 5\text{Cl}^- + 12\text{H}_2\text{O}$	80.0289	-0.12865	-7611.7	0	25-110
$(\text{CaCl}_2)_2\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ $(\text{CaCl}_2)_2\text{MgCl}_2\cdot 6\text{H}_2\text{O} = 2\text{CaCl}^+ + \text{Mg}^{2+} + 4\text{Cl}^- + 6\text{H}_2\text{O}$	15.90	0	0	0	110
$\text{KCl}:\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ $\text{KCl}:\text{CaCl}_2\cdot 2\text{H}_2\text{O} = \text{K}^+ + \text{CaCl}^+ + 2\text{Cl}^- + 2\text{H}_2\text{O}$	13.60481	-0.01934	0	0	45-95
$\text{KCl}:\text{CaCl}_2\cdot \text{H}_2\text{O}$ $\text{KCl}:\text{CaCl}_2\cdot \text{H}_2\text{O} = \text{K}^+ + \text{CaCl}^+ + 2\text{Cl}^- + \text{H}_2\text{O}$	14.493	-0.02000			95-110
$\text{KCl}:\text{CaCl}_2$ $\text{KCl}:\text{CaCl}_2 = \text{K}^+ + \text{CaCl}^+ + 2\text{Cl}^-$	17.15829	-0.02548	0	0	$\geq 110$

<sup>a</sup>: the D coefficient was found to be always 0 — <sup>b</sup>: temperature region actually not correctly described by the model

### 3. Results and discussion

#### a. The binary $\text{CaCl}_2\text{-H}_2\text{O}$ system

- *Osmotic coefficient*

Osmotic coefficients calculated over the whole range of concentrations comprised between pure water and saturation with respect to solid salt, from 25 to 250°C, are compared to experimental values in Figure 1. Very good agreement was found both at low and high concentrations over the whole temperature range. However, some discrepancies can be observed between the model and the values recommended by Pitzer and Oakes [45], at 50, 100 and 150°C. We note that the values recommended at 150°C are superimposed on the experimental values measured later by Gruskiewicz and Simonson [63] at 140°C, the latter being correctly described by the model.

At higher temperatures (*i.e.*, 160, 180 and 225°C) the model also closely matches the experimental values obtained by Gruskiewicz and Simonson [63], which were not used in the optimization procedure as was explained previously.

At 25°C, the values recommended by Pitzer and Oakes [45] are consistent with those recently measured by Azougen et al. [64], which are also consistent with the critically selected experimental data and smoothed values recommended by Rard and Clegg [65].

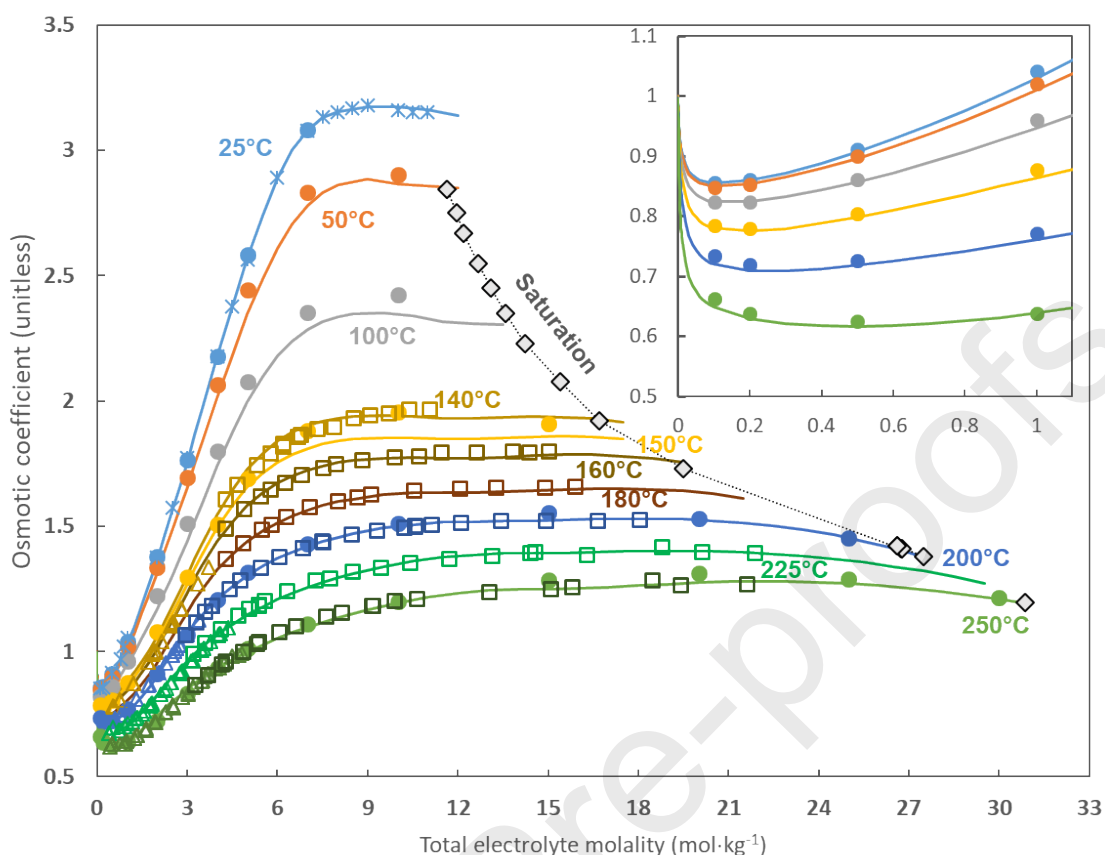


Figure 1 – Osmotic coefficient of  $\text{CaCl}_2$  aqueous solutions as a function of electrolyte concentration, over the temperature range 25-250°C. Symbols represent experimental data; filled circles and diamonds: [45]; stars: [64]; squares: [63]; triangles: [66]. Lines represent calculated values (this work).

These observations suggest that the values recommended by Pitzer and Oakes [45] at 50, 100 and 150°C should be considered with caution and that new experimental data should be acquired to fix this issue.

- *Thermal properties*

The set of interaction parameters developed in this work is temperature dependent. This means that thermal properties of the aqueous solutions can be calculated with PhreeSCALE and compared to experimental data.

Perron et al. [67] measured apparent heat capacities at 25°C and Ananthaswamy and Atkinson [68] report experimental measurements of heat capacities and apparent enthalpies of  $\text{CaCl}_2$  aqueous

solution at 25 and 50°C. Saluja et al. [69] and Gao et al. [70] measured heat capacities for  $\text{CaCl}_2$  concentrations up to 6 M and temperatures up to 100°C.

Literature and calculated values of heat capacity can be compared in Figure 2. Heat capacity is correctly described up to 4 M and between 25 and 100°C. Out of this range, significant discrepancies appear. Furthermore, despite the order of magnitude being correct, the apparent enthalpy is systematically underestimated by the model, by a factor of about 1/3 (not shown).

Many parameters can explain these discrepancies. Indeed, the solution heat capacity depends on the standard partial molar heat capacity of the solutes, the aqueous speciation and the apparent heat capacity. The apparent enthalpy and the apparent heat capacity depend on derivatives of the excess Gibbs energy with respect to temperature, which also depend on the aqueous speciation [71]. Any of these contributions can be a source of error that is difficult to evaluate. The standard partial molar heat capacity of the  $\text{CaCl}^+$  and  $\text{CaCl}_2^0$  aqueous species were estimated by Sverjensky et al. [59], using empirical equations. No experimental data is available to check the aqueous speciation calculated in the present work, especially at high salinity. The experimental apparent enthalpy data are available on a narrow range of temperatures and concentrations. Thus, they can only have a small weight on the parameter estimation procedure, compared to the much more numerous osmotic coefficient data. This indicates that there is still room for further improvements of the model.

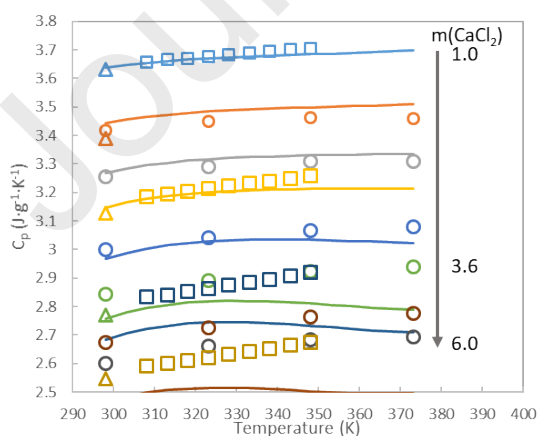


Figure 2 – Heat capacity of  $\text{CaCl}_2$  aqueous solutions as a function of temperature for different electrolyte concentrations between 1 and 6 M. Symbols represent experimental data [67,69,70] and lines represent the model (this work).

- *Aqueous speciation*

The identification of different solutes for the  $\text{CaCl}_2\text{-H}_2\text{O}$  system directly addresses the question of their distribution within the aqueous solution, depending on the total electrolyte concentration and on the temperature. Details are given in the supplementary materials (Appendix 3, including Figure A3-3). Results indicate the predominance of the  $\text{Ca}^{2+}$  (and  $\text{Cl}^-$ ) aqueous species at low to moderate concentrations (*i.e.*, never above 9 M of total  $\text{CaCl}_2$ ), mostly at low temperatures (below  $150^\circ\text{C}$ ).  $\text{Ca}^{2+}$  is progressively replaced by  $\text{CaCl}^+$ , which remains the predominant species over the whole range of concentrations and temperatures. This replacement occurs at lower concentrations as temperature increases.

With this model, the  $\text{CaCl}_2^0$  species always remains in the minority, which may explain its relative instability at the highest concentrations and temperatures.

- *Salt solubility*

Solubility calculations were performed in the binary  $\text{CaCl}_2\text{-H}_2\text{O}$  system as a function of temperature to provide additional insights into the reliability of the model. This was done in two steps. First, the ionic activity products were calculated at the saturation points defined according to the smoothed recommended values of Pátek et al. [72] who worked extensively on the collection and critical selection of existing solubility data. These ionic activity products were then used to fit temperature-dependent solubility products for each  $\text{CaCl}_2\cdot n\text{H}_2\text{O}$  solid salt (with  $n = 0, 1/3, 1, 2, 4, 6$ ) in their respective temperature domain of stability. Finally solid-aqueous solution equilibrium calculations were performed to check the ability of the model to reproduce the  $\text{CaCl}_2\text{-H}_2\text{O}$  phase diagram.

Because  $\text{CaCl}^+$  is the major aqueous species in the saturation domain, it is more relevant to write the dissolution reactions of salts with respect to this species, instead of  $\text{Ca}^{2+}$ . Indeed, especially at high temperature and very high total electrolyte concentration,  $\text{Ca}^{2+}$  becomes a trace species, which brings instability to the mineral-solution equilibrium calculations. It was found that a simple Van't Hoff

approximation could be applied for most hydrates to fit the temperature dependence of the solubility product in the temperature range of interest. The corresponding coefficients are reported in Table 3. The log K values at 25°C for antarcticite ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ),  $\alpha$ - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  (or ghiaraite) and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (or sinjarite) compare very well with those proposed by Lassin et al. [49], which are 3.915, 5.27, and 7.35, respectively.

Results of the solubility calculations as a function of temperature are plotted in Figure 3. Very good agreement was achieved for the hydrates containing 6 down to 1/3 water molecules, i.e. from 20°C to 230°C. Above this, discrepancies can be observed between the recommended and the calculated solubility of  $\text{CaCl}_2$ .

An additional criterion is used in the literature to check the quality of the model. It is based on the vapor pressure above solutions saturated with  $\text{CaCl}_2$  salts as a function of temperature. Details are given in the supplementary materials (Appendix 4) and results confirm the quality of the model in its temperature range of validity.



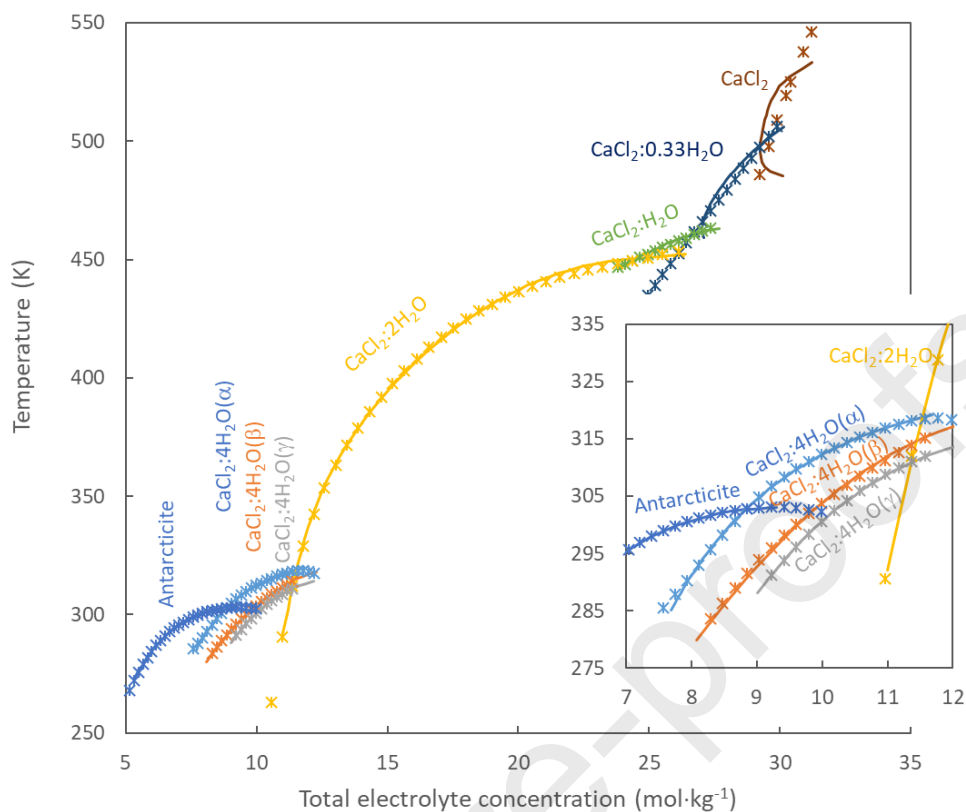


Figure 3 – Solubility of  $\text{CaCl}_2$  hydrates as a function of temperature. Stars represent the smoothed recommended values of Pátek et al. [72] and lines represent the model calculations (this work).

Finally, the model developed in this work is able to describe most of the available experimental osmotic coefficient data very satisfactorily, which makes it almost unique in the literature. In addition, it describes the solubility of the various hydrates up to a temperature of  $230^\circ\text{C}$  and a total electrolyte concentration of  $29.5 \text{ mol}\cdot\text{kg}^{-1}$ . However, the model presents several weaknesses regarding its ability to describe derived solution properties like heat capacity and enthalpy. Furthermore, the aqueous speciation calculated at high concentrations and temperatures can be questionable as the presence of larger amounts of the  $\text{CaCl}_2^0$  aqueous species could be expected.

Further verifications and developments are conducted in the next sections based on the description of aqueous solution properties (like isopiestic properties) and solid-solution equilibria in ternary systems, which were previously studied at  $25^\circ\text{C}$  by Lassin et al. [49] who did not consider the  $\text{CaCl}^+$  aqueous

species in their model. New results are presented below, and the updated and temperature-dependent interaction parameters and solubility products are given in Table 1 and Table 3, respectively. Note that, because the  $\text{CaCl}_2^0$  aqueous species remains minor in the  $\text{CaCl}_2\text{-H}_2\text{O}$  binary system for every conditions of temperature and concentration, it was found that the specific ternary interaction parameters involving this species (namely,  $\lambda$ ,  $\zeta$ ,  $\eta$  and  $\mu$  parameters) could be set to 0 for all the ternary systems studied in this work. Thus, to save space, they are not reported in Table 1.

#### b. The HCl- $\text{CaCl}_2\text{-H}_2\text{O}$ system

For this ternary system, experimental data are available at 25°C only. Modeling results are compared to these published data in Figure 4 for the mean activity coefficient of aqueous HCl, and in Figure 5 for the solubility of calcium chloride hydrates as a function of HCl concentration. With a new  $\sigma$  value of 0.00435 instead of 0.00222 (see the supplementary materials, Appendix 5), it appears that the mean activity coefficient of HCl is slightly better described by the previous model of Lassin et al. [49], despite 4 ternary interaction parameters, instead of 2, being used in the new model. The solubility of antarcticite is better described by the new model (new  $\sigma = 0.01811$  compared with 0.02242) like that of the di-hydrate (new  $\sigma = 0.01730$  compared with 0.02468), whereas that of the tetra-hydrate is better described by the previous model (new  $\sigma = 0.02318$  compared with 0.01425), especially at high HCl contents. It should be noted that the solubility product of the salts is now constrained by the recommended values of Pátek et al. [72], which was not the case in the previous model.

It must be highlighted here that the aqueous speciation of the  $\text{CaCl}_2$  electrolyte is affected by the chemical composition of the brine mixture and temperatures. Indeed, the speciation in the ternary HCl- $\text{CaCl}_2\text{-H}_2\text{O}$  systems but also in all the other systems presented hereafter (i.e.  $\text{MCl}_n\text{-CaCl}_2\text{-H}_2\text{O}$  with  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Mg}$ ) differs from the one presented for the binary  $\text{CaCl}_2\text{-H}_2\text{O}$  system in Figure A3-3 (Appendix 3, Supplementary materials). This speciation is graphically presented for each system in the supplementary materials (Appendix 6). Together with what follows, it illustrates that the proposed model is able to describe satisfactorily the solution properties and solution-solid equilibria while considering the chemical complexity of the aqueous mixtures.

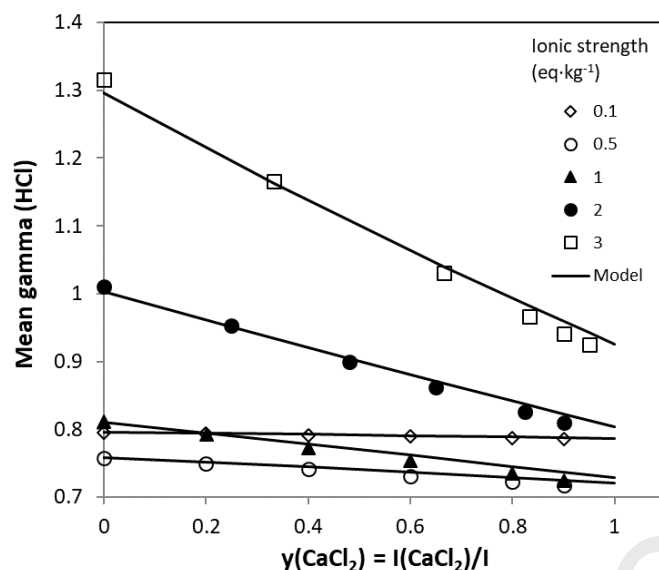


Figure 4 – Mean activity coefficient of HCl in HCl-CaCl<sub>2</sub> aqueous mixtures at 25°C, as a function of CaCl<sub>2</sub> ionic strength fraction,  $y(\text{CaCl}_2)$ , for ionic strengths comprised between 0.1 and 3.0 eq kg<sup>-1</sup>. The symbols represent experimental measurements from [73]; the lines represent modeling results.

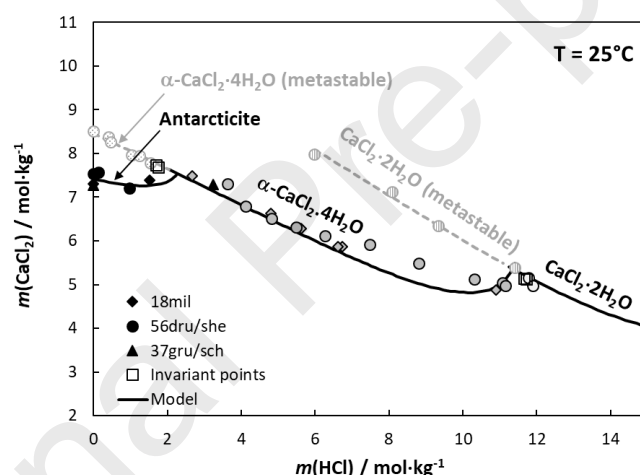


Figure 5 – Solubility diagram for the H-Ca-Cl-H<sub>2</sub>O system, at 25°C. Symbols: experimental data, with circles from [74], diamonds from [75], and triangles from [76]. The black symbols represent antarcticite solubility, the dark gray symbols represent CaCl<sub>2</sub>·4H<sub>2</sub>O solubility, and the light gray symbols represent CaCl<sub>2</sub>·2H<sub>2</sub>O solubility. The solid symbols represent stable minerals while the dotted or hatched symbols designate metastable minerals. The empty squares indicate the invariant points identified by [75] and [76]. The lines represent the solubilities of the stable salts (solid lines) and of the metastable salts (dashed lines) according to model calculations.

### c. The LiCl-CaCl<sub>2</sub>-H<sub>2</sub>O system

Only three interaction parameters were needed to describe this system, namely  $\theta(\text{Li}^+/\text{Ca}^{2+})$ ,  $\theta(\text{Li}^+/\text{CaCl}^+)$ , and  $\psi(\text{Li}^+/\text{CaCl}^+/\text{Cl}^-)$ . This represents a simplification with respect to our previous 25°C model, which required 6 non-zero interaction parameters [49]. The results are close to those obtained

previously. Thus, they are plotted in the supplementary materials (Appendix 7), Figure A7-5 for iso-water activity data and in Figure A7-6 for solubility at 25°C. Nevertheless, the new model is apparently less accurate for the solubility of antarcticite (new  $\sigma = 0.02392$  compared with 0.01381). This can be explained by the fact that the solubility of this mineral now takes into account the value recommended by Pátek et al. [72]. For other salts, the new model is either equivalent (for  $\alpha$ -CaCl<sub>2</sub>·4H<sub>2</sub>O and LiCl·H<sub>2</sub>O; new  $\sigma = 0.02313$  and 0.03903 compared with 0.01686 and 0.03344, respectively) or slightly better (for the double salt LiCl·CaCl<sub>2</sub>·5H<sub>2</sub>O; new  $\sigma = 0.01520$  compared with 0.03436). Note that the new log K(25°C) value for this salt is 10.155, which compares well with the value of 10.27 estimated in the previous study, and with the value of 10.60 that was proposed by Christov et al. [77].

Only two sets of solubility data were found for temperatures above 25°C, namely 40 and 50°C [78,79]. In addition, Xu et al. [80] recently produced vapor-liquid equilibrium data for LiCl-CaCl<sub>2</sub> aqueous mixtures, from 50 to 150°C. The latter set of data covers the whole range of mixture fractions from the binary LiCl to the binary CaCl<sub>2</sub> brines, for total Cl concentrations comprised between 15 and 20 mol·kg<sup>-1</sup>. Unfortunately, a preliminary test showed a strong inconsistency between the experimental vapor pressure at equilibrium with the binary LiCl brines and the values calculated with our model. As our LiCl-H<sub>2</sub>O model had been thoroughly tested up to 250°C against large sets of solution properties and solid-liquid equilibrium data [61], it is beyond the scope of this study to perform further verifications. Thus, it was decided to leave these data aside. Yet, it is worth mentioning that the calculated vapor pressures above the binary CaCl<sub>2</sub> brine are consistent with the experimental data of Xu et al. [80].

Nevertheless, good agreement was achieved between experimental solubility data and the model at 40 and 50°C (Figure 6-C,D) using constant  $\theta$  parameters for Li<sup>+</sup>/Ca<sup>2+</sup> and Li<sup>+</sup>/CaCl<sup>+</sup> interactions and a temperature-variable Li<sup>+</sup>/CaCl<sup>+</sup>/Cl<sup>-</sup> interaction parameter  $\psi$  (Table 1). At 40°C (Figure 6-C), calculations suggest that, in the region of low LiCl concentrations, the experimental data of Blidin [78] describe the metastable solubility of the  $\beta$ -CaCl<sub>2</sub>·4H<sub>2</sub>O solid salt rather than the stable solubility of the  $\alpha$ -CaCl<sub>2</sub>·4H<sub>2</sub>O salt.

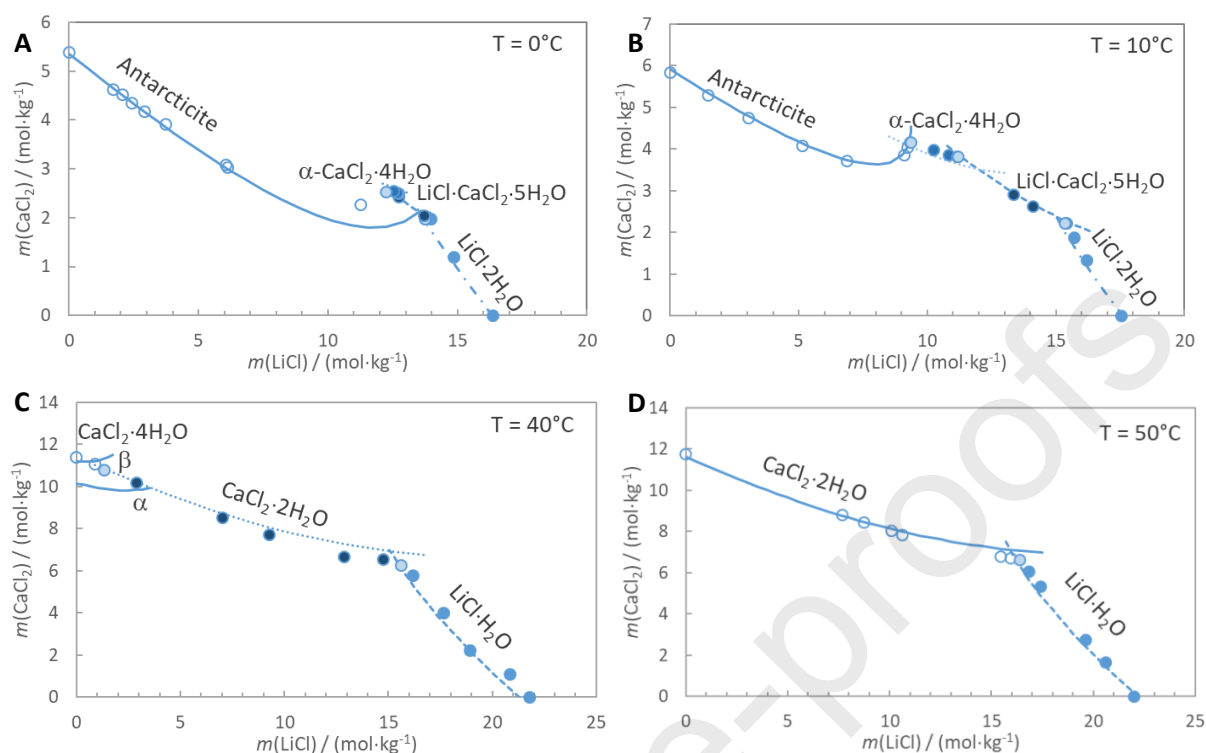


Figure 6 – Solubility diagrams in the LiCl-CaCl<sub>2</sub>-H<sub>2</sub>O system at 0°C (A), 10°C (B), 40°C (C) and 50°C (D). Symbols: experimental data from [78], [79] and [81]; lines: calculated values with our model.

In addition, Wang et al. [81] and Zeng et al. [79] also produced solubility data at 0 and 10°C, respectively. Figure 6-A,B shows the possible extension of our model below 25°C, down to 0°C. Note that, at these temperatures, the authors did not specify the polymorph of the calcium chloride tetrahydrate that was formed during their experiment. Calculations suggest that the  $\alpha$  polymorph is the possible candidate. However, at 0°C, in the narrow range of LiCl concentrations comprised between 11 and 14 M, the model correctly describes the solubility of  $\alpha$ -CaCl<sub>2</sub>·4H<sub>2</sub>O and LiCl·CaCl<sub>2</sub>·5H<sub>2</sub>O but as metastable phases. Indeed, in this region, the calculated stability of antarcticite appears exaggerated compared to the experimental data of Wang et al. [81]. To reproduce the solubility of the LiCl:CaCl<sub>2</sub>:5H<sub>2</sub>O double salt that is also observed at 25°C (Figure A7-6, Appendix 7, Supplementary materials), a temperature dependence of its solubility product was proposed (Table 3).

#### d. The NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system

As for the previous ternary system, results for this chemical system at 25°C are plotted in Figure A7-7 (Appendix 7, Supplementary materials), showing a very good match between calculated and experimental data. At this temperature, the new model is equivalent to the previous one for the solubility of antarcticite (new  $\sigma = 0.03249$  compared with 0.02735) and of halite (new  $\sigma = 0.16983$  compared with 0.17787).

Solubility data between 18 and 130°C were found in the literature (Figure 7), mostly in the collections of Zdanovskii et al. [82], Linke [83] and Silcock [84], but also in more recent works by Yang et al. [85]. However, while most of the data collected by Zdanovskii et al. [82] are fairly consistent for each temperature, those from Yang et al. [85] at 75°C show very different behavior (Figure 7-C). Because of the very large stability domain of the CaCl<sub>2</sub>·2H<sub>2</sub>O salt, in comparison with the observations made by all the other authors, and at different temperatures, these data were excluded from the optimization procedure.

The results shown in Figure 7 were obtained by using constant  $\theta(\text{Na}^+/\text{Ca}^{2+})$  and  $\theta(\text{Na}^+/\text{CaCl}^+)$ , and temperature-variable  $\psi(\text{Na}^+/\text{Ca}^{2+}/\text{Cl}^-)$  and  $\psi(\text{Na}^+/\text{CaCl}^+/\text{Cl}^-)$  parameters.

Experimental heat capacity data were also found in the literature. Saluja et al. [69] measured heat capacities of mixtures for ionic strengths comprised between 3 and 5 eq·kg<sup>-1</sup>, temperatures between 25 and 100°C, and a pressure of 0.6 MPa. These data could not be used as constraints for the optimization procedure of the model, but can be used for checking as illustrated in Figure 8.

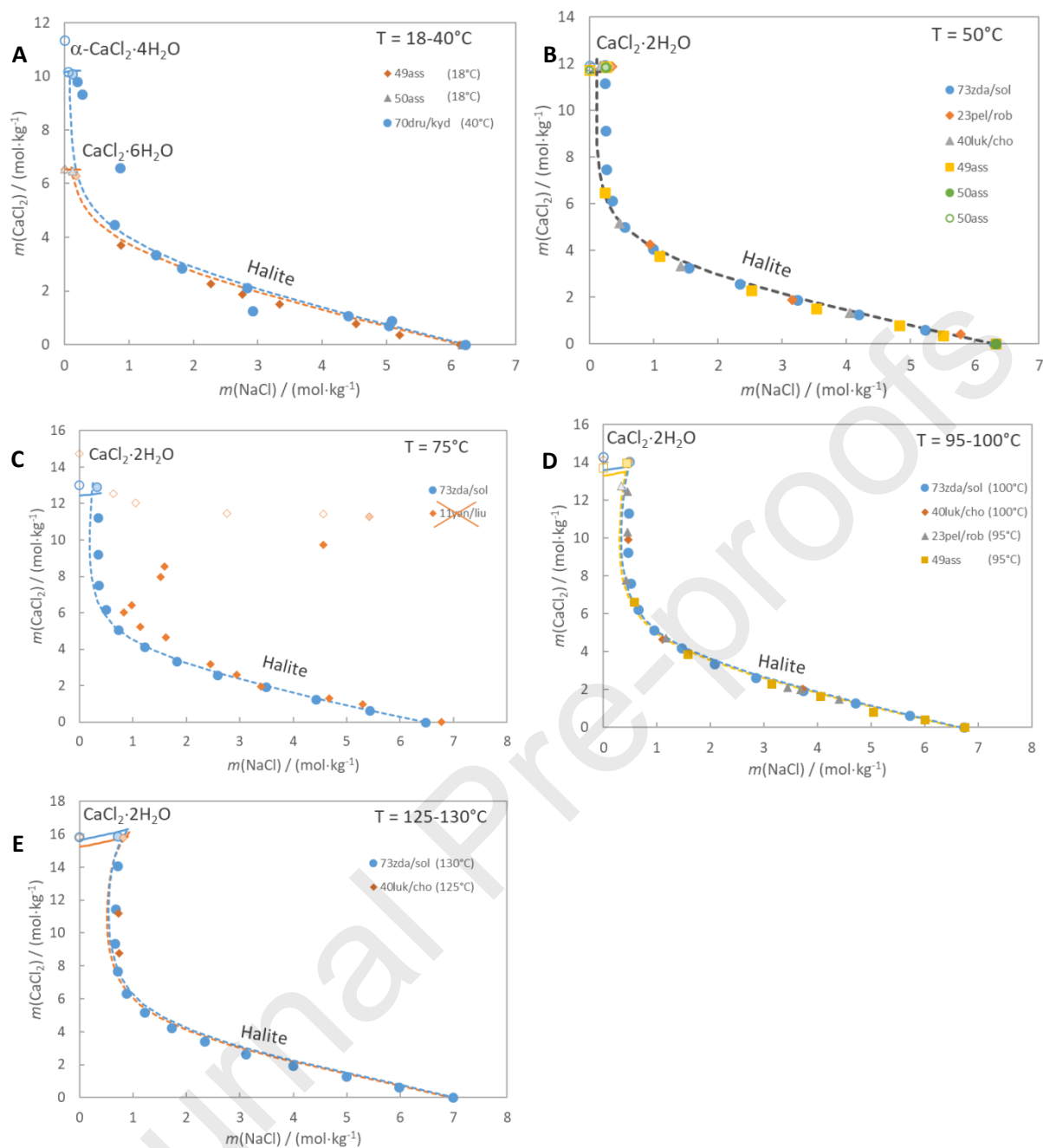


Figure 7 – Solubility diagrams in the NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system at 18 and 40°C (A), 50°C (B), 75°C (C), 95 and 100°C (D) and 125 and 130°C (E). Symbols: experimental data collected and recommended by [82] and from [85]; lines: values calculated with our model.

The comparison of calculated heat capacity with experimental values shows that the data points are distributed below the first bisector. A number of them accumulate along this line, which represents equality of calculated and experimental values. Moreover, the quasi vertical distribution of the points suggests that the heat capacity may be independent of the mixture composition in some specific

conditions only. As this is questionable, we conclude that some experimental issues may have occurred during the work of Saluja et al. [86] and, therefore, new experimental data are needed for further verifications.

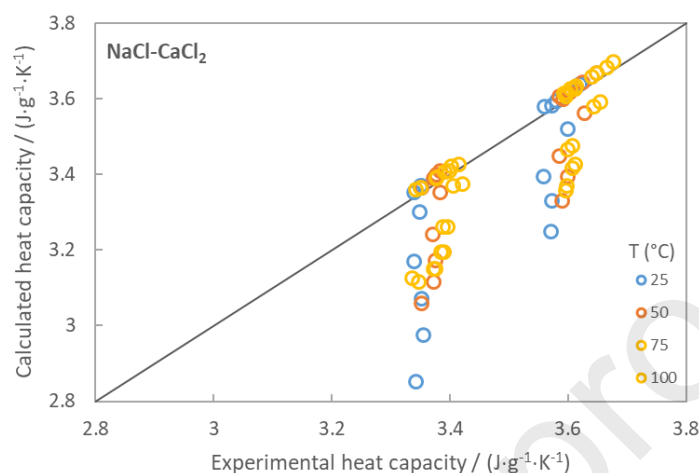


Figure 8 – Calculated vs. experimental heat capacity of NaCl-CaCl<sub>2</sub> aqueous mixtures, at various temperatures and for ionic strengths comprised between 3 and 5 eq·kg<sup>-1</sup>. Experimental data of [86].

#### e. The KCl-CaCl<sub>2</sub>-H<sub>2</sub>O system

Here again, results for this chemical system at 25°C are plotted in Figure A7-8 (Appendix 7, Supplementary materials), showing a very good match between calculated and experimental data. At this specific temperature, the new model is equivalent to the previous one for the solubility of antarcticite (new  $\sigma = 0.02111$  compared with 0.01940) and of sylvite (new  $\sigma = 0.03736$  compared with 0.03497).

Solubility data between 18 and 250°C were found in the literature (**Error! Reference source not found.**), mostly in the collections of Zdanovskii et al. [82], Linke [83] and Silcock [84], as for the previous chemical system. Yang et al. [85] also produced solubility data at 75°C. Contrary to the NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system, double salts can form but their identification seems to be challenging. Indeed, among the various authors reported by Zdanovskii et al. [82], Lightfoot and Prutton [87,88] reported the 2KCl:CaCl<sub>2</sub>:2H<sub>2</sub>O hydrated double salt at 75 and 95°C while Assarsson [89] and Sveshnikova [90,91] reported the KCl:CaCl<sub>2</sub> anhydrous double salt for temperatures between 37.8, 43.4, 50 and 95°C. In



addition, Bergman and Kuznetsova [92] observed two polymorphs of this anhydrous double salt, the  $\alpha$  being stable between 50 and 150°C, and the  $\beta$  being stable above these temperatures. Other authors cited in Zdanovskii et al. [82] did not identify any double salts, but various hydrates of the simple  $\text{CaCl}_2$  salt, instead [93,94]. Yang et al. [85] did not observe any double salt at 75°C either.

These contradictory observations in fact give some freedom for the model development because several options for the mineralogical control of the chemical composition of the saturated solution can be tested. Finally, it was found that temperature variation had to be implemented for three interaction parameters and that three double salts were necessary to fully describe the solubility diagrams of the  $\text{KCl-CaCl}_2\text{-H}_2\text{O}$  system from 18 to 200°C, as shown in **Error! Reference source not found.**. The three interaction parameters are  $\theta(\text{K}^+/\text{CaCl}^+)$ ,  $\psi(\text{K}^+/\text{Ca}^{2+}/\text{Cl}^-)$  and  $\nu(\text{K}^+/\text{CaCl}^+/\text{Cl}^-)$ .

The three double salts are  $\text{KCl:CaCl}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{KCl:CaCl}_2\cdot \text{H}_2\text{O}$  and  $\text{KCl:CaCl}_2$ , which are stable between 40 and 95°C, 95 and 100°C, and above 100°C, respectively. They were determined according to the slope and the curvature of the solubility line given by their chemical composition, which better described the experimental data point than any other chemical composition (among those proposed by the various authors cited above).

**Error! Reference source not found.**-A shows that the model can extend to temperatures lower than 25°C and illustrates that it can help discriminate between experimental data sets. More specifically, the data from Mazzetti (1929, cited in Zdanovskii et al. [82]) should be discarded from the recommended values.

At high temperatures (**Error! Reference source not found.**-G), the new thermodynamic model can be applied up to salt solubility and 200°C, except in the region where the less hydrated  $\text{CaCl}_2$  salts are stable. At even higher temperatures, the model becomes unstable and it cannot be used to describe salt solubility. It could however be used at these temperatures for describing solution properties of moderate salinity.

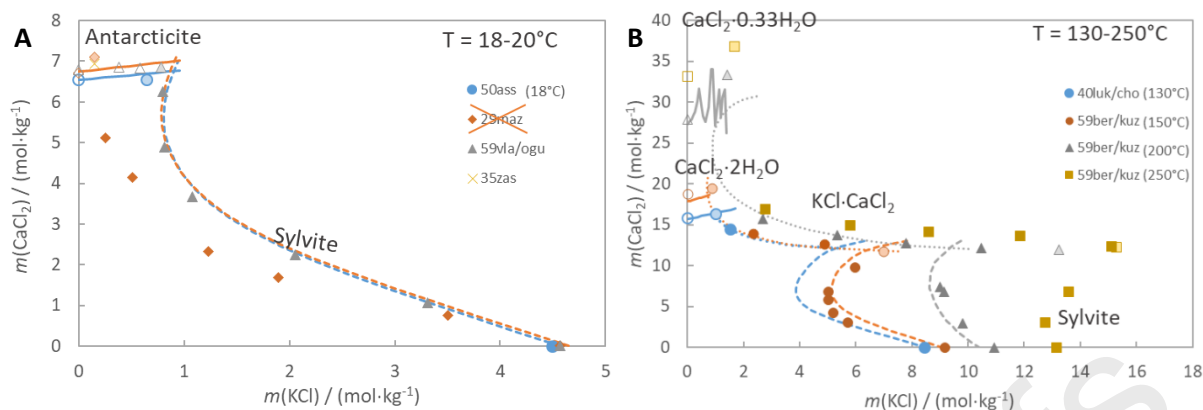


Figure 9 – Solubility diagrams in the KCl-CaCl<sub>2</sub>-H<sub>2</sub>O system at 18 and 20°C (A), and 130 to 250°C (B). Symbols: experimental data collected and recommended by [82] and from [85]; lines: calculated values with our model.

#### f. The MgCl<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O system

Both isopiestic and solubility data at 25°C were correctly described over the whole range of compositions, as shown in Figure A7-9 (Appendix 7, Supplementary materials). The solubility product of tachyhydrite had to be slightly revised in order to fit the corresponding solubility data points. The revised value is 16.42 (see Table 3), which compares quite well with the previous value of 17.05 proposed by Christov [95]. The consequence is that the new model better describes the solubility of tachyhydrite (new  $\sigma = 0.07569$  compared with 0.08376). The solubility of antarcticite is also improved (new  $\sigma = 0.00470$  compared with 0.00902) whereas for other salts, the new model is either equivalent (for  $\alpha$ -CaCl<sub>2</sub>·4H<sub>2</sub>O and bischofite: new  $\sigma = 0.04667$  and 0.04689 compared with 0.03907 and 0.03892, respectively).

For this system, solubility data can be found in the literature up to 110°C, essentially in the collections of Zdanovskii et al. [82], Linke [83] and Silcock [84]. This chemical system is characterized by an extended region where the solubility is controlled by tachyhydrite at all temperatures (Figure 10). At 110°C, however, an additional double salt appears in the solubility diagram. Its chemical composition is 2CaCl<sub>2</sub>:MgCl<sub>2</sub>:6H<sub>2</sub>O.

To describe the solid-liquid equilibria of this chemical system (Figure 10), the temperature variability of the three interaction parameters  $\theta(\text{Mg}^{2+}/\text{CaCl}^+)$ ,  $\psi(\text{Mg}^{2+}/\text{Ca}^{2+}/\text{Cl}^-)$  and  $\psi(\text{Mg}^{2+}/\text{CaCl}^+/\text{Cl}^-)$  had to be

implemented. It was not possible to define a temperature function for the  $2\text{CaCl}_2:\text{MgCl}_2:6\text{H}_2\text{O}$  since it was observed for one temperature only. Its solubility product determined at  $110^\circ\text{C}$  is reported in Table 3.

Solution data were also found in the literature: Saluja et al. [86] provided the heat capacity of  $\text{MgCl}_2$ - $\text{CaCl}_2$  aqueous mixtures for ionic strengths comprised between 2.7 and  $4.8 \text{ eq}\cdot\text{kg}^{-1}$ , temperatures between  $25$  and  $100^\circ\text{C}$ , and a pressure of  $0.6 \text{ MPa}$ . In addition, Christov [95] performed isopiestic measurements for  $\text{MgCl}_2$ - $\text{CaCl}_2$  aqueous mixtures of ionic strengths between  $3.7$  and  $5.9 \text{ eq}\cdot\text{kg}^{-1}$ , at  $50^\circ\text{C}$ . The chemical compositions of these aqueous mixtures are far from the solubility limits of the system. They do not bring strong constraints to the optimization procedure of the model and, consequently, they were used only for checking as illustrated in Figure 11. Here, contrary to the  $\text{NaCl}$ - $\text{CaCl}_2$ - $\text{H}_2\text{O}$  system, all the heat capacity data points line up along the first bisector and thus indicate a good match between calculated and experimental values (Figure 11-A). As expected, the calculated isopiestic lines also fit the experimental data points (Figure 11-B).

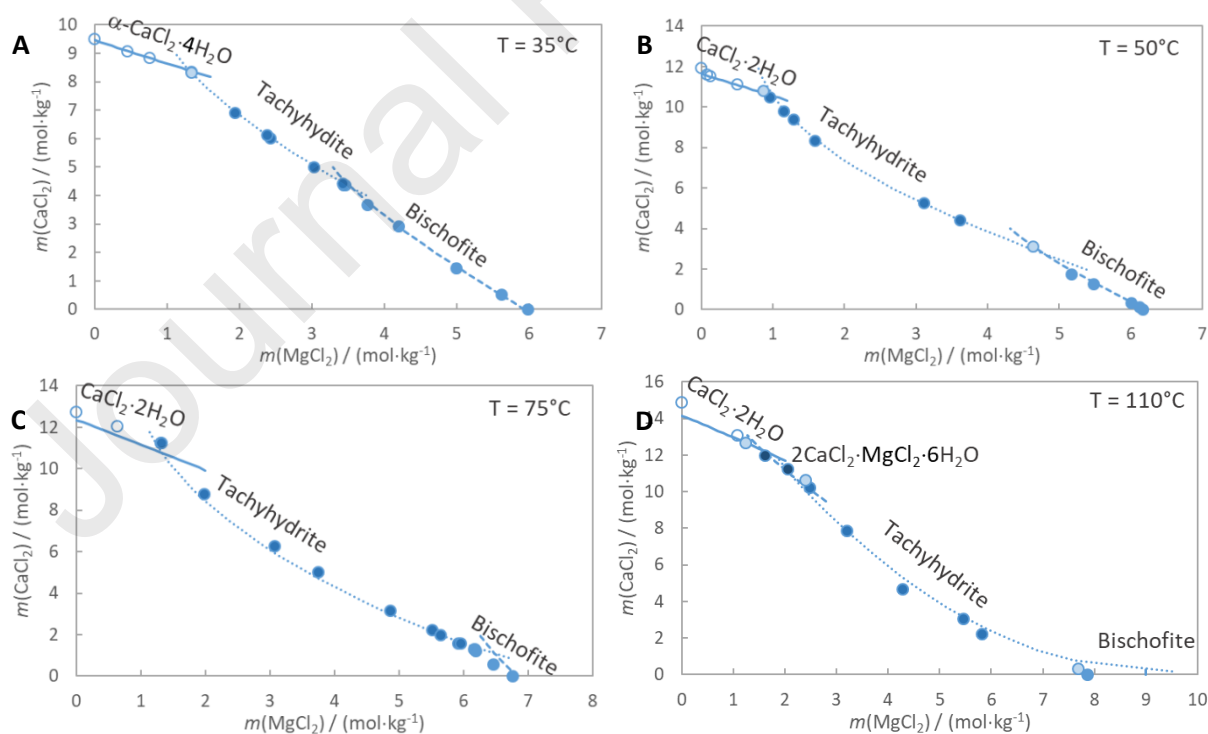


Figure 10 – Solubility diagrams in the  $\text{MgCl}_2$ - $\text{CaCl}_2$ - $\text{H}_2\text{O}$  system at  $35^\circ\text{C}$  (A),  $50^\circ\text{C}$  (B),  $75^\circ\text{C}$  (C), and  $110^\circ\text{C}$  (D). Symbols: experimental data collected by [82] and [83] ; lines: calculated values with our model.

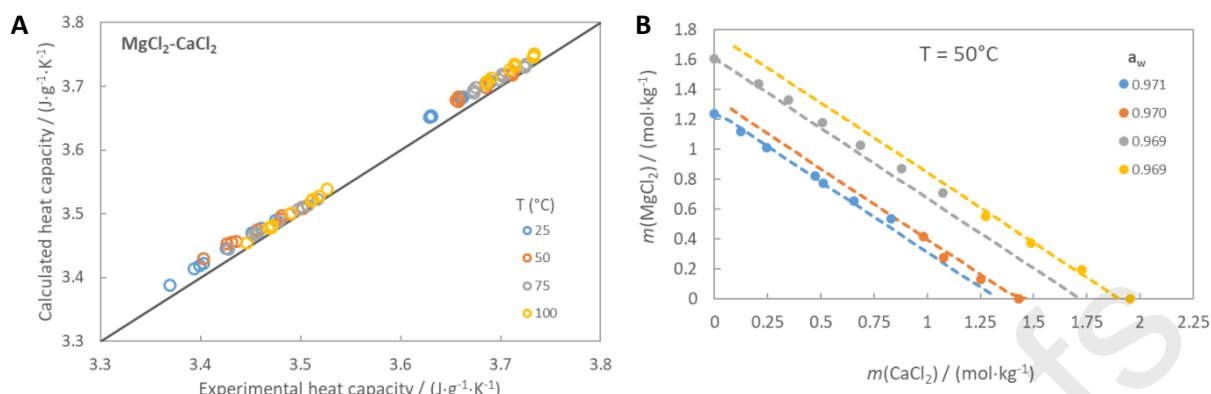


Figure 11 – Calculated vs. experimental heat capacity of MgCl<sub>2</sub>-CaCl<sub>2</sub> aqueous mixtures, at various temperatures and for ionic strengths comprised between 3 and 5 eq·kg<sup>-1</sup> (A), and isopiestic data (B). Experimental heat capacities are taken from [86] and isopiestic measurements from [95].

#### 4. Conclusion

A new thermodynamic model has been developed in the framework of the combined HKF-Pitzer equations in order to describe solution properties and phase diagrams of aqueous chloride systems bearing calcium, up to elevated temperatures. This model accounts for the aqueous speciation of the CaCl<sub>2</sub> electrolyte, according to the partial molar properties of the Ca<sup>2+</sup>, CaCl<sup>+</sup>, CaCl<sub>2</sub><sup>0</sup> and Cl<sup>-</sup> aqueous species described by the HKF theory.

As a result, the CaCl<sup>+</sup> aqueous complex and the Cl<sup>-</sup> anion are the main species of the CaCl<sub>2</sub> electrolyte in most of the investigated conditions of temperature and chemical composition of the system. Despite the complexity induced by partial dissociation, the number of additional ternary interaction parameters needed for describing the chemical behavior of ternary systems remains reasonably limited.

The model applies up to 250°C in the binary CaCl<sub>2</sub> aqueous systems. It can also apply to ternary systems containing other major alkaline and alkaline earth cations, namely Li, Na, K and Mg, up to temperatures generally above 100°C. The model becomes unstable for ternary systems and temperatures above 200°C at high concentrations (close to the solubility limits). Therefore, it needs improvements, but at

this time and to our knowledge it is the only model with such capabilities that can be used with a free geochemical code like PhreeSCALE. As such, it extends the range of application to hydrothermal environments in the domain of geosciences, or to specific industrial issues dealing with chloride brines like the geological storage of CO<sub>2</sub> in deep saline aquifers.

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

**CRedit author statement**

**Arnault Lassin:** Data curation, Model development, Writing- Original draft preparation

**Laurent André:** Supervision, Model validation, Writing- Reviewing

**A revised description of the binary  $\text{CaCl}_2\text{-H}_2\text{O}$  chemical system up to solution-mineral equilibria and temperatures of  $250^\circ\text{C}$  using Pitzer equations. Extension to the multicomponent  $\text{HCl-LiCl-NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$  system.**

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**Highlights:**

- Combined use of Pitzer and HKF theories to describe the binary  $\text{CaCl}_2\text{-H}_2\text{O}$  system including partial dissociation
- Description of the osmotic coefficient and salt solubility up to  $250^\circ\text{C}$  and 30 M
- Extended description of solution properties and salt solubility to the  $\text{HCl-LiCl-NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$  multicomponent system, up to high temperatures
- Applicability to natural (hydrothermal, geothermal) and industrial contexts