

Water Rock Interaction [WRI 14]

# Thermodynamic behavior of $\text{FeCl}_3\text{-H}_2\text{O}$ and $\text{HCl-FeCl}_3\text{-H}_2\text{O}$ systems - a Pitzer model at 25 °C

L. André<sup>a\*</sup>, C. Christov<sup>b</sup>, A. Lassin<sup>a</sup> and M. Azaroual<sup>a</sup>

<sup>a</sup>BRGM, Water, Environment, Ecotechnology Division, 3 Avenue Claude Guillemin 45060 Orléans Cedex 1, France.

<sup>b</sup>GeoEco Consulting 2010, San Diego, California, USA, and Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.

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## Abstract

Most of the speciation models of aqueous electrolyte systems are based on the “ion pairing and complexing approach”. They are only suitable for aqueous solutions with ionic strengths lower than about  $1 \text{ eq.kg}_w^{-1}$ . For highly saline solutions, an approach based on “specific-ion interactions” (the so-called “Pitzer approach”) provides much more accurate results.

Various thermodynamic databases supporting the “Pitzer approach” exist, but they are often inconsistent and poorly documented. The number of chemical elements is limited because of the difficulties inherent to producing relevant experimental data for wide ranges of temperature, ionic strength, pH, and for low solubility metals and hydroxides, and also because of the difficulty in evaluation of consistent and accurate values for interaction parameters.

This study presents a new set of parameters using the standard Pitzer formalism that is able to model the behavior of Fe-rich solutions and solid-liquid equilibria in binary  $\text{FeCl}_3\text{-H}_2\text{O}$  and mixed  $\text{HCl-FeCl}_3\text{-H}_2\text{O}$  systems at 25 °C. The new binary and mixing interaction parameters are adjusted in order to fit various independent experimental activity (water activity, osmotic coefficients) and ferric chloride salts solubility data. This work allows updating and improving thermodynamic databases for Fe(III) systems in order to simulate the complex geochemical behaviour of solutions and gas-brine-rock interactions in various applications in the geosciences or industrial processes.

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\* Corresponding author. Tel.: +33 (0) 238 64 31 68; fax: +33(0) 238 64 37 19.

E-mail address: [l.andre@brgm.fr](mailto:l.andre@brgm.fr)

## 1. Introduction

Knowledge of the thermodynamic behavior of saline multicomponent aqueous systems is important in industrial processes as well as in geosciences. Increasing use of such non-conventional water resources needs development of robust geochemical models for describing and predicting chemical reactions within these particular media (dissolution/precipitation of salts, evaporation...). The Pitzer approach, usually quoted to describe such complex systems, is suitable to deal with major elements in brines. But, some systems are poorly documented and the Pitzer databases have to be continuously improved to integrate new chemical species and interaction parameters.

This study focuses on very acidic systems and on the efforts made to define the interactions of Fe(III) species within the H-Fe-Cl-H<sub>2</sub>O system at 25°C.

## 2. Bibliography and critical selection of experimental data

The H-Fe(III)-Cl-H<sub>2</sub>O system was investigated by numerous authors both the experimental and numerical aspects. For the experimental part, water activity data are presented for the binary FeCl<sub>3</sub>-H<sub>2</sub>O system [1-2], as well as in mixed HCl-FeCl<sub>3</sub>-H<sub>2</sub>O solutions [3-6]. In these works, water activities were measured in solutions up to concentrations of 7 and 4 m for HCl and FeCl<sub>3</sub>, respectively.

Thermodynamic models for the Fe(III) chloride binary system, based on the Pitzer formalism, were developed by various authors, each of them establishing a different set of parameters [7-10]. It should be noted that to accurately describe the activity properties of FeCl<sub>3</sub>-H<sub>2</sub>O system at high molality, the models used the extended Pitzer approach with four binary parameters ( $\beta^0$ ,  $\beta^1$ ,  $\beta^2$ ,  $c^*$ ) [8-9]. The model of Marion [10] extends to low temperature the 25°C model of Christov [9]. All these models [8-10] give a very good agreement with both osmotic coefficients, water activity, and FeCl<sub>3</sub>:6H<sub>2</sub>O<sub>(cr)</sub> solubility data in pure water at 25°C {m(sat) = 6.1 mol.kg<sub>w</sub><sup>-1</sup> at 25°C}. A model for the mixed HCl-FeCl<sub>3</sub>-H<sub>2</sub>O system was also developed by [8], which can describe accurately the solubility of FeCl<sub>3</sub>:6H<sub>2</sub>O<sub>(cr)</sub> up to 5 M of HCl.

However, in mixed hydrochloric solutions the solubility of the ferric chloride salt increases sharply with increasing HCl concentration [11-12]. According to the experimental solubility data, in addition to hexahydrate (FeCl<sub>3</sub>:6H<sub>2</sub>O<sub>(cr)</sub>), low crystal hydrates (FeCl<sub>3</sub>:3.5H<sub>2</sub>O, FeCl<sub>3</sub>:2.5H<sub>2</sub>O, FeCl<sub>3</sub>:2H<sub>2</sub>O) and double salt (FeCl<sub>3</sub>.HCl.2H<sub>2</sub>O) precipitate from saturated mixed HCl-FeCl<sub>3</sub>-H<sub>2</sub>O solutions. These low crystal hydrates have extremely high solubilities, greater than 13 mol.kg<sub>w</sub><sup>-1</sup> in solutions with relatively low acidity (between 1 and 5 mol.kg<sub>w</sub><sup>-1</sup> of HCl). Such solubility corresponds to an ionic strength greater than 75 m, if the salt is assumed totally dissociated. This extremely high solubility of ferric chloride salts in mixed systems leads to limitations of the solid-liquid equilibrium models for the FeCl<sub>3</sub>-H<sub>2</sub>O system available from the literature [7-9]. Current binary and ternary parameters are not sufficiently “robust” and the models are not able to reproduce accurately such salt solubilities.

Within this study we evaluate new sets of pure electrolyte parameters of Fe(III)-Cl interactions, which are valid up to a very high molality supersaturated (with respect to the stable FeCl<sub>3</sub>:6H<sub>2</sub>O<sub>(cr)</sub> solid) FeCl<sub>3</sub>-H<sub>2</sub>O solutions. The new FeCl<sub>3</sub>-H<sub>2</sub>O binary parameters are then used to develop a high molality solid-liquid equilibrium model for mixed HCl-FeCl<sub>3</sub>-H<sub>2</sub>O system. Two ferric chloride salts (FeCl<sub>3</sub>:3.5H<sub>2</sub>O and FeCl<sub>3</sub>:2.5H<sub>2</sub>O) are added to the database and their respective equilibrium constants at 25°C are also determined. The defined parameters are developed for the PHREEQC geochemical code [13], and according to the specific formalism implemented in the program.

### 3. Results of numerical modeling

#### 3.1. Binary parameters for $\text{FeCl}_3\text{-H}_2\text{O}$ system

The new set of parameters for the binary  $\text{FeCl}_3\text{-H}_2\text{O}$  system is established using the experimental data given in [1-2]. The estimation procedure is described in [14]. As done in [8-9], a 4-parameter approach is applied, which allows fitting the osmotic coefficient data without considering the existence of a complex species in solution (as  $\text{FeCl}_3^{2+}$ ,  $\text{FeCl}_2^+$ ,  $\text{FeCl}_3(\text{aq})$ , as suggested in [4-5]).

The resulting parameterization gives good agreement with experimental osmotic coefficients data ( $\sigma = 0.0106$ ). The new model permits inclusion of three ferric chloride minerals (Table 1), which precipitate in the  $\text{FeCl}_3\text{-H}_2\text{O}$  system at extremely high molality ( $> 16$  m). The calculated equilibrium constants give  $m(\text{sat})$  predictions which are in excellent agreement with experimental solubility data (Table 1).

Table 1. Experimental and predicted solubilities of ferric chloride salts in binary  $\text{FeCl}_3\text{-H}_2\text{O}$  system at 25°C

Solid phases	Experimental $m(\text{sat})$ (mol/kg <sub>w</sub> ) in [12]	Calculated $m(\text{sat})$ (mol/kg <sub>w</sub> ) (this study)
$\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$	6.05	6.05
$\text{FeCl}_3 \cdot 3.5 \text{H}_2\text{O}$	13.04	13.26
$\text{FeCl}_3 \cdot 2.5 \text{H}_2\text{O}$	16.10	16.12

#### 3.2. Ternary parameters for $\text{HCl-FeCl}_3\text{-H}_2\text{O}$ system

The ternary interaction parameters ( $\Theta_{\text{H-Fe}}$  and  $\Psi_{\text{H-Fe-Cl}}$ ) are evaluated using the experimental  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})$  solubility data in  $\text{HCl-FeCl}_3\text{-H}_2\text{O}$  system [3]. The  $\text{HCl-H}_2\text{O}$  parameterization (binary parameters) is issued from [15] and it is valid up to  $\approx 20$  m at 25°C [16]. The new mixed system parameterization provides a very good agreement between model predictions and:

- *the water equi-activity measurements* (Fig. 1a). The established parameterization gives very good agreement both in high and low concentration solutions;
- *the composition of invariant (eutonic) solutions*. The new set of parameters can reproduce the measured composition of eutonic solutions with a maximum difference in molality of about 5% (Table 2);
- *the measured pH of acid solutions* (Fig. 1b), even in the range of negative values of pH.

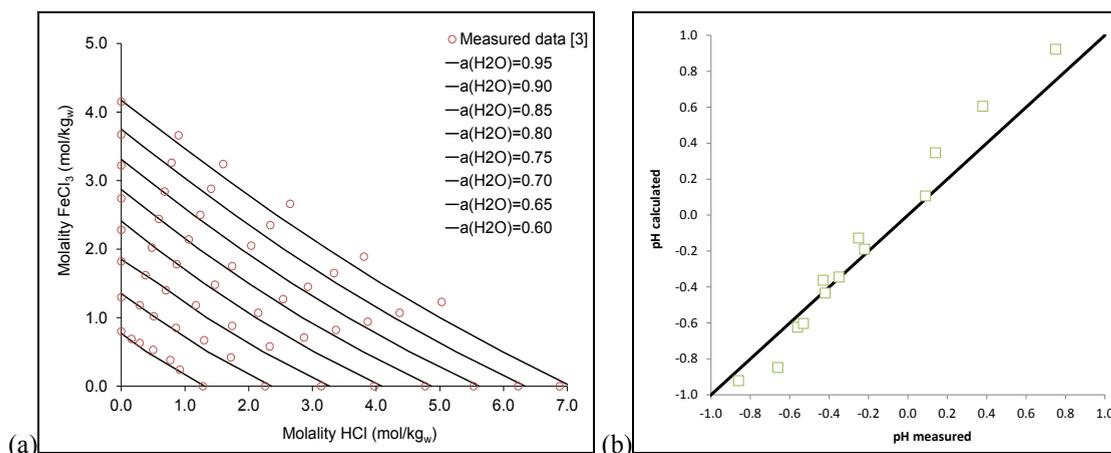


Fig. 1 In HCl-FeCl<sub>3</sub>-H<sub>2</sub>O solutions at 25°C: (a) A comparison between experimental (red circles, [3]) and calculated (solid lines) water activities; b) A comparison between calculated (solid line) and measured (open squares, [17]) pH values.

Table 2. Experimental and predicted composition of invariant points in HCl-FeCl<sub>3</sub>-H<sub>2</sub>O systems at 25°C

Solid phases	Experimental data [11-12]		Calculated results (This study)		
	HCl (mol/kgw)	FeCl <sub>3</sub> (mol/kgw)	HCl (mol/kgw)	FeCl <sub>3</sub> (mol/kgw)	Ionic strength
FeCl <sub>3</sub> ·6H <sub>2</sub> O + FeCl <sub>3</sub> ·3.5H <sub>2</sub> O	1.29	13.18	1.29	12.47	75.8
FeCl <sub>3</sub> ·3.5H <sub>2</sub> O + FeCl <sub>3</sub> ·2.5H <sub>2</sub> O	4.16	16.51	4.16	17.47	109.0

#### 4. Concluding remarks

The set of parameters established in this work is suitable to reproduce water characteristics of ferric chloride solutions both at low and high ionic strengths. This new set of parameters can represent the composition of highly saline solutions up to the eutonic points of hydrated ferric chloride salts in the mixed HCl-FeCl<sub>3</sub>-H<sub>2</sub>O system. All binary and mixed solution interaction parameters and equilibrium constants of Fe(III) minerals are coherent, and therefore can be used to determine the activities of dissolved species up to the salt solubility concentrations. The models have been developed in order to update the PHREEQC code. The presented parameterization can be used without any additional adjustments to determine the solution behaviour of more complex Fe(III) systems, as well as to develop a solubility model for a very important geochemical Fe(III) hydroxides minerals in high salinity solutions.

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