Thermodynamic model for solution behavior and solid-liquid equilibrium in Na-Al(III)-Fe(III)-Cr(III)-Cl-H$_2$O system at 25°C

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Abstract: *The knowledge of the thermodynamic behavior of multicomponent aqueous electrolyte systems is of main interest in geo-, and environmental-sciences. The main objective of this study is the development of a high accuracy thermodynamic model for solution behavior, and highly soluble M(III)Cl$_3$(s) (M= Al, Fe, Cr) minerals solubility in Na-Al(III)-Cr(III)-Fe(III)-Cl-H$_2$O system at 25°C. Comprehensive thermodynamic models that accurately predict aluminium, chromium and iron aqueous chemistry and M(III) mineral solubilities as a function of pH, solution composition and concentration are critical for understanding many important geochemical and environmental processes involving these metals (e.g., mineral dissolution/alteration, rock formation, changes in rock permeability and fluid flow, soil formation, mass transport, toxic M(III) remediation). Such a model would also have many industrial applications (e.g., aluminium, chromium and iron production, and their corrosion, solve scaling problems in geothermal energy and oil production). Comparisons of solubility and activity calculations with the experimental data in binary and ternary systems indicate that model predictions are within the uncertainty of the data. Limitations of the model due to data insufficiencies are discussed. The solubility modeling approach, implemented to the Pitzer specific interaction equations is employed. The resulting parameterization was developed for the geochemical Pitzer formalism based PHREEQC database.*

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Introduction

The construction of thermodynamic models for accurate description of the thermodynamic behavior of highly saline solutions represents a challenge, because of their wide applicability in different industrial and geosciences domains s.a. exploitation of geothermal brines from deep reservoirs, CO_2 storage in saline reservoirs, development of nuclear waste storage strategies, extraction of valuable resources from saline lakes, desalination of sea waters, and others. All these field-applications require the necessity to use a consistent geochemical modeling approach permitting full and correct description of such complex systems. The major characteristic of used approach is its ability to predict correctly the chemical behavior of complex brines at various conditions, i.e. composition, temperature and pressure changes, and up to high concentration, including stable and metastable salt precipitation. Therefore, the use of such approach can considerably reduce the laboratory experiments and field works. Geochemical calculations and modeling results are strongly dependent on the model solution and solid phase parameters and experimental database used in parameterization. The traditional activity models (as the extended Debye-Hückel model, Davis model), commonly implemented in geochemical calculation codes, are not able to represent the interactions between all solution species, limiting their applications to dilute solutions, generally up to the salinity of sea water. To describe behavior of highly saline solutions, a specific and robust approach is needed, which includes all possible solution species and interactions in solutions, as well as all experimentally determined equilibrium solids. The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer [1,2] represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic models. It was showed that the Pitzer approach could be expanded to accurately calculate solubilities in complex brines and to predict the behavior of natural fluids at standard temeperature[3-5] , as well as at wide range of temperatures from 0° to 300^oC [6-9] , and from extremely low [10-12] to very high concentration of solutions [8,9,35]. However, the existing Pitzer's databases have different limitations as the number of implemented solution species and precipitating solids, the temperature and concentration ranges of application. This is why a permanent updating work must be done in order to increase their applicability, and consequently the quality of predicted results.

This paper continues our series () concerning parameterization of Pitzer approach based comprehensive models which can assist in the development of a complex thermodynamic database that can accurately predict the chemical behavior of aluminium Al^{3+} [10-17], chromate (CrO_4) [18], dichromate (Cr_2O_7) [19,20], and Iron (as Fe^{2+} [21], and Fe^{3+} [21,35] solution species and minerals in a sea-type natural fluid systems. The main objective of this study is the development of a high accuracy thermodynamic model for solution behavior, and highly soluble $M(III)Cl_3(s)$ (M= Al, Fe, Cr) minerals solubility in Na-Al(III)-Cr(III)-Fe(III)-Cl-H_2O system at 25°C. Sodium chloride fluids constitute most of the deep groundwater resources. Comprehensive thermodynamic models that accurately predict aluminum, chromium and iron aqueous chemistry and M(III) mineral solubilities as a function of pH, solution composition and concentration are critical for understanding many important geochemical and environmental processes involving these metals (e.g., mineral dissolution/alteration, rock formation, changes in rock permeability and fluid flow, soil formation, mass transport, toxic M(III) remediation). Such a model would also have many industrial applications (e.g., aluminum, chromium and iron production, and their corrosion).

The originality of this study is to compare activity and solubility behavior in binary and ternary subsystems with participation of all three trivalent cations and to use some analogies between these different systems, when experimental data are missing, in order to estimate new interaction parameters. This study focuses on the (i) test and validation of previously determinate parameters for binary $M(III)Cl_3$ -H_2O systems, and (ii), evaluation of new mixing parameters for all 6 ternary subsystems,

using new available experimental solubility and activity data. Then, the completed full parameterization for the system under study will be introduced to widely used by modelers PHREEQC code [22].

2. Thermodynamic calculation code

In this work, the calculations are performed with the geochemical code PHREEQC [22] including Pitzer's equations from PHRQPITZ code [23]. In their program [3,4], coded Pitzer equations for the calculation of Θ parameters which accounts for cation-cation and anion-anion interactions with equation resolution, which is slightly different than the resolution procedure proposed by Pitzer [1, 24]. For Θ parameters, Pitzer [24] found that some additional terms should be included to account unsymmetrical mixing effects in ternary systems when cation, or anion pairs have different charge, It is of main importance especially when one ion has a charge of three units or more. The complete expression for $\Phi_{\iota\varphi}{}^{\Phi}$ is given below:

$$\Phi_{ij}^{\Phi} = \Phi_{ij} + \text{I}.\Phi'_{ij}$$
$$\text{where} \quad \Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I)$$
$$\text{and} \quad \Phi'_{ij} = {}^{E}\theta'_{ij}(I)$$
$$\text{giving} \quad \Phi_{ij}^{\Phi} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I)$$

The terms $^{E}\Theta_{ij}(I)$ and $^{E}\Theta'_{ij}(I)$ account for the electrostatic unsymmetrical mixing effects and depend only on the charges of the ions i and j, the total ionic strength and the solvent properties E and d_w (hence, on the temperature and pressure). According to [24] $^{E}\Theta_{ij}(I)$ and $^{E}\Theta'_{ij}(I)$ are zero when ij cation or anion have the same charge. For the unsymmetrical pairs of cations or unsymmetrical pairs of anions, the resolution of such equation implies the use of integrals $J_0(x)$ and $J_1(x)$, which can be calculated according to different ways. Pitzer [24] proposed a numerical integration to solve it, whereas Harvie [25] resolved it by using two Chebyshev polynomial approximations. However, test calculations of [25] showed a little difference from more simplified approximations to $J_0(x)$ and $J_1(x)$ given by Pitzer [24].

Consequently, caution should be exercised in using parameters issued from published studies: values of Θ_{ij} must be compatible with the binary parameters (β^0, β^1, β^2 and c^{Φ}) but also, for their use with PHREEQC code, their determination must include the higher-order electrostatic terms discussed above. It should be noted that, values of $\square_{ij}$ evaluated by [26], and Pitzer [2] do not include the higher-order electrostatic terms for unsymmetrical cations pairs and anions pairs. Therefore, previously evaluated mixing parameters cannot be directly introduced in PHREEQC code calculations without validation, and eventually without some modifications. This is the reason why some parameters issued in published papers are re-estimated in this study. For more information about the resolution differences between the Pitzer's approach [24] and the Harvie's approach [25], the reader can refer to the user's guide of PHRQPITZ (Plummer et al. [23].

3. Model Parameterization

The system Na-Al(III)-Cr(III)-Fe(III)-Cl-H_2O have been investigated according to the following scheme [5,8,9,19] evaluation of not-concentration restricted (β^0, β^1, (β^2) and C^{φ}) parameters for binary systems NaCl-H_2O, AlCl$_3$-H_2O, FeCl$_3$-H_2O, and CrCl$_3$-H_2O, and determination of the chemical potential of solids precipitating from saturated binary solutions; determination of mixing parameters, i.e. evaluation of the following parameters: A) θ(Na,Al), and ψ(Na,Al,Cl) for ternary system NaCl-AlCl$_3$-H_2O; B) θ(Na,Fe), and ψ(Na,Fe,Cl) for ternary system NaCl-FeCl$_3$-H_2O; C) θ(Na,Cr), and ψ(Na,Cr,Cl) for ternary system NaCl-CrCl$_3$-H_2O; D) θ(Al,Fe), and ψ(Al,Fe,Cl) for ternary system AlCl$_3$-FeCl$_3$-H_2O; E) θ(Al,Cr), and ψ(Al,Cr,Cl) for ternary system AlCl$_3$-CrCl$_3$-H_2O, and F) θ (Cr,Fe), and ψ(Cr,Fe,Cl) for ternary system CrCl$_3$-FeCl$_3$-H_2O. Determination of chemical potential of solids, crystallizing in ternary systems. Plot phase diagrams for ternary sub-systems and validate the models. Water activity, osmotic

coefficients and salt solubility are solution properties, which are used for binary and mixing parameter's estimation [13].

In constructing the model of the quinary Na-Al(III)-Cr(III)-Fe(III)-Cl-H$_2$O system at 25 °C, the Debye-Huckel constant (A$^\varphi$) at 25°C is taken from [8], Table 1 and equals to 0.391475. It is calculated from temperature function given in [6,7]. Pure electrolyte parameters of Na-Cl interactions at 25 °C and solubility product of halite are calculated from temperature functions given in [6] and in acid-base model of [7]. Evaluations of the remaining model parameters are discussed in the sections below.

3.1. NaCl-AlCl$_3$-H$_2$O system

Christov [14] evaluate binary parameters for AlCl$_3$-H$_2$O system at 25 °C, using osmotic coefficients data up to supersaturated solutions: from Mason [43] between 0 and 1.7 mol.kg^{-1}, and from Mikulin [27] between 2 and 3.44 mol.kg^{-1}. These parameters are directly used to develop a solid-liquid equilibrium model for quaternary K-Mg-Al-Cl-H$_2$O system at 25 °C [14]. The binary parameters published by [14,20] are tested here using our new calculation PHREEQC code. These parameters give a very good agreement between experimental φ data and model predictions up to molality of saturation (see Fig. 1a below). Therefore, these parameters and solubility product for AlCl$_3$, 6H$_2$O(s) (from [14,20]) are selected without any modification in construction of mixing Na-Al-Cl-H$_2$O model.

Christov et al. [10] develop a temperature variable ((0 to 100) °C) model for H-Na-K-Al-Cl-H$_2$O system. The T-variation model for Na-Al-Cl-H$_2$O sub-system have been costructed without using solubility data in this ternary. The model used constant with temeprature θ(Na,Al) parameter from Palmer and Wesolowski [28] (equals to 0.335), and T-variation ψ(Na,Al,Cl) parameter (equals to 0.0653 at 25°C). Note that [28] determine the constant θ(Na,Al) value using their own extremely low gibbsite solubility data in sodium chloride media. Christov et al. [10] evaluate T-variation ψ(Na,Al,Cl) parameter by ploting polythermal diagram for Na-K-Al-Cl-H$_2$O system. After that, [11,12] used the mixing θ(Na,Al) and ψ(Na,Al,Cl) parameterization establishe in [10] to develop a T-variation model for gibbsite and boehmite solubility in NasCl solutions. As a first step in a new Na-Al-Cl-H$_2$O model development we test the parameterization of [10] using available solubility data. Two sets of experimental data from Farelo et al. [29] and Sarkarov et Mironova [30] are used in this test. With [10] mixing parameters, the agreement between experiments and calculation data is good (dashed line on Fig. 1b). It shoud be notted that the accepted θ(Na,Al) value in [28] and [10] is mach higher, compare to other θ(Na,M) values for Na$^+$-M^{3+} common anion chloride and sulfate systems (see Table 3 in [5]). Our preliminary modeling study on the development of model for corresponding sulfate system Na-Al-SO$_4$-H$_2$O shows that θ(Na,Al) parameter from [28] can not fit well the solubility data in this ternary. In a series of papers Christov [14], developed a solid-liquid equilibrium model, which includes all ternary subsystems within K-Mg-Al-Cl-SO$_4$-H$_2$O, Na-K-NH$_4$-Al-Cr-SO$_4$-H$_2$O [15-17] and Na-K-Mg-Fe(III)-Cl-SO$_4$-H$_2$O [21] systems. The author found that for all considered ternary chloride (1-1)+(3-1) and (1-2)+(3-2) sulfate mixtures a θ(Na,M(III)) value equals to (-0.07) gives a very good agreement between experimental solubility data in mixed ternary and quaternary systems, and model predictions. Therefore, in this study we develop a new Na-Al-Cl-H$_2$O model accepting θ(Na,Al) value equals to (-0.07). Then, the ψ(Na,Al,Cl) parameter's value is adjusted to fit experimental data (solid line on Figure 1b). The calculation and experiments are in a very good agreement. The calculated coordinates of the invariant point (halite + AlCl$_3$.6H$_2$O(s) are also coherent with the measured data given by Farelo et al. [29].
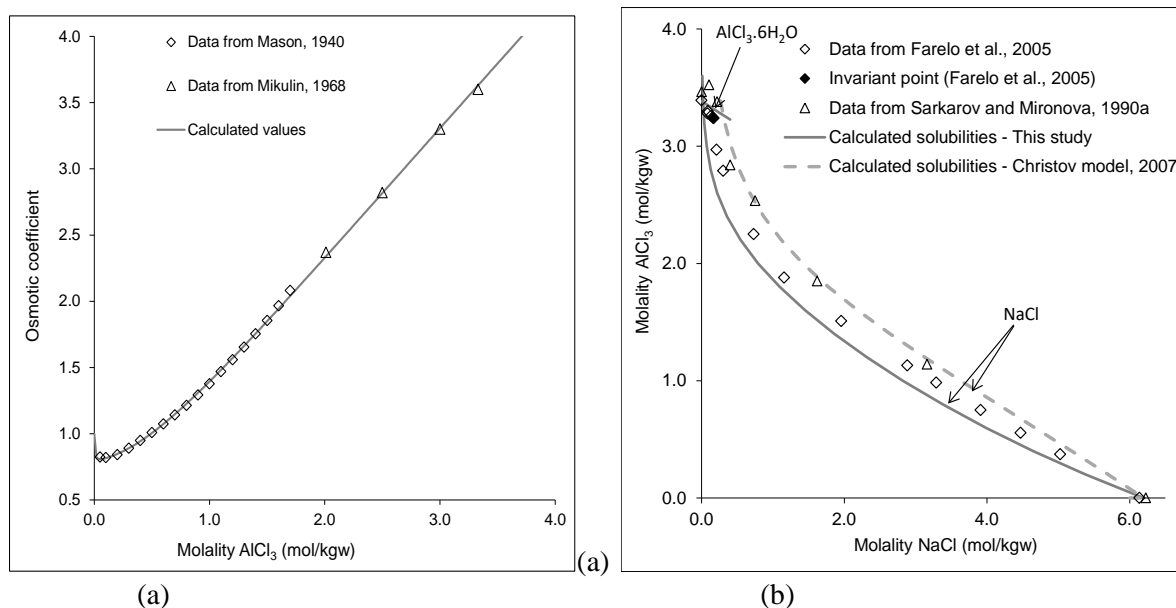
(a)

(b)

Fig. 1. (a) Calculated (lines) and experimental (symbols) osmotic coefficients for the $AlCl_3$-H_2O binary system as a function of molality of $AlCl_3$ at 25°C. (b) Experimental (symbols) and predicted (lines) halite and $AlCl_3.6H_2O$ (s) solubilities in NaCl-$AlCl_3$-H_2O system at 25°C. The solid symbol represents the experimental composition of invariant point, determined by [29].

3.2. NaCl-FeCl₃-H₂O system

The interaction parameters for the binary Fe(III)-Cl system are determined by numerous authors [21,31-35]. André et al. [35], presented a large review of concentration range of application of the existing sets of interaction parameters. It was demonstrated that the existing sets are not able to reproduce the behavior of Fe(III) solids in extremely high molality supersaturated region in binary Fe-Cl-H₂O, and in the ternary H-Fe-Cl-H₂O system. Consequently, André et al. [35] proposed the estimation of a new set of parameters for the binary $FeCl_3$-H_2O system using all available experimental activity data given in [27,36,37]. Following Tanaka et al. [32] and [14-17,19,21], a four-parameter approach (β^0, β^1, β^2, and C^φ) is applied for this binary, without considering any complex species in solution. The resulting parameterization gives a good agreement with water activity values up to 16 mol.kg^{-1}, widely over the solubility of $FeCl_3$, $6H_2O(s)$ (m(sat) ($FeCl_3$, $6H_2O(s)$) = 6.2 mol.kg^{-1}). Therefore, in construction of mixing Na-Fe(III)-Cl-H₂O model we used our previously evaluated $FeCl_3$-H_2O binary parameters from [35]. The solubility product (K°sp) value for $FeCl_3$, $6H_2O(s)$ is taken from Thermoddem database [38] and it is very close to those determinated by [21].

Rumyantsev et al. [37] and [21] developed a model for ternary system Na-Fe(III)-Cl-H₂O system. The activity model of [37] used their own low molality isopiestic measurements data to evaluate mixing parameters. The mixing solid-liquid equilibrium model of [21] have been developed on the basis on the solubility data only. The author evaluated the following values for mixing parameters: θ(Na,Fe(III) = -0.07, and ψ(Na,Fe(III),Cl) = -0.004. Here we tested how the mixing parameterization proposed by [5, 21], fits the experimental water activity data in mixed solutions. As we show on next Figure (2a) the agreement between experiments and calculation is good: total sigma (σ) value for 97 water activity data points is less than 0.02. As a next step, we used Christov's parameters to predict the solubilities of halite and $FeCl_3.6H_2O_{(s)}$ in mixed NaCl-FeCl₃-H₂O system. Experimental data from Hinrichsen and Sachsen [39] have been used (Figure 2b). To achieve the best agreement between model predictions and experiments ψ(Na,Fe(III),Cl) parameterization of Christov (2004)21 is modified, and in our new equilibrium model a value of 0.003 is accepted. The modeling results and available

experimental data are given on Fig. 2b. The predicted solubilities at 25°C of our new mixing model, are in a very good agreement with experimental data at 25ºC, and in good agreement with solubilities determinated by Atbir et al. [40] at 30°C.
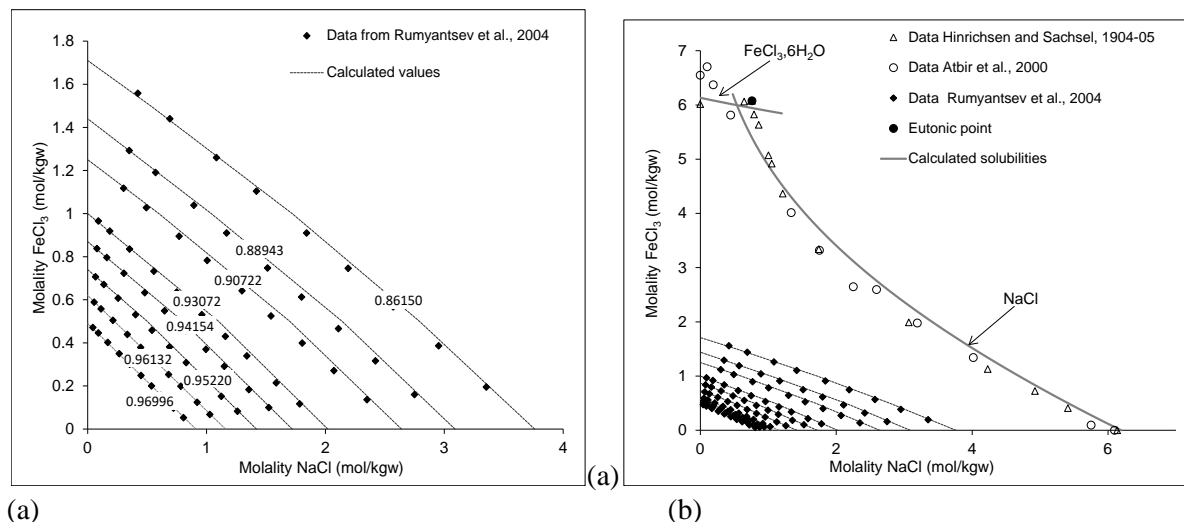

(a)   (b)

Fig. 2. (a) Experimental water activity (a_w) data (solid diamond symbols) and calculated isoactivites (dashed lines) in NaCl-FeCl$_3$-H$_2$O system at 25°C. (b) Experimental (25°C and 30°C: open symbols) and predicted (25°C : solid lines) halite and FeCl$_3$.6H$_2$O (s) solubilities in NaCl-FeCl$_3$-H$_2$O system. The solid circle represents the experimental composition of invariant point, determined by [39].

3.3. NaCl-CrCl$_3$-H$_2$O system

The osmotic coefficients data for CrCl$_3$-H$_2$O system at 25 ºC are available only up to m(max) = 1.4 mol.kg^{-1}, which is much below molality of saturation (m(sat)) of CrCl$_3$.6H$_2$O(s) (equals to 4.50 mol.kg^{-1}) (see [5,17,41]. In a previous study [41] evaluate binary parameters for CrCl$_3$-H$_2$O system at 25 ºC, using all available osmotic coefficients data for unsaturated solutions, and the data point at saturation, given in [27]. These parameters are directly used to develop a solid-liquid equilibrium model for Na-K-Cr-Cl-H$_2$O system at 25 ºC [41]. The binary parameters determinate by in [41] are tested using our calculation PHREEQC code. These parameters give a very good agreement between experimental φ data and model predictions (see Fig. 3a). The parameters of Christov [17] also give very reasonable φ predictions up to m(sat) of CrCl$_3$.6H$_2$O (s). According to the model the shape of the φ vs. molality curve is similar to those for AlCl$_3$-H$_2$O system with a continuous and monotonous increase of φ values with increasing the molality (Figure 3a). Therefore, binary parameters and solubility product for CrCl$_3$.6H$_2$O(s) determinate in [41] are selected without any modification in construction of mixing NaCl- CrCl$_3$-H$_2$O model.

To evaluate mixing parameters θ(Na,Cr) (equals to -0.07), and ψ(Na,Cr,Cl) (equals to 0.01) Christov [17,41], used his own experimental solubility data for NaCl- CrCl$_3$-H$_2$O system. In our new mixed model we keep the same value for θ(Na,Cr) parameter. The value for ψ(Na,Cr,Cl) parameter is very slightly changed to 0.02. On Fig. 3b we compare predicted and experimental solubilities in NaCl-CrCl$_3$-H$_2$O system. A very good agreement have been obtained.
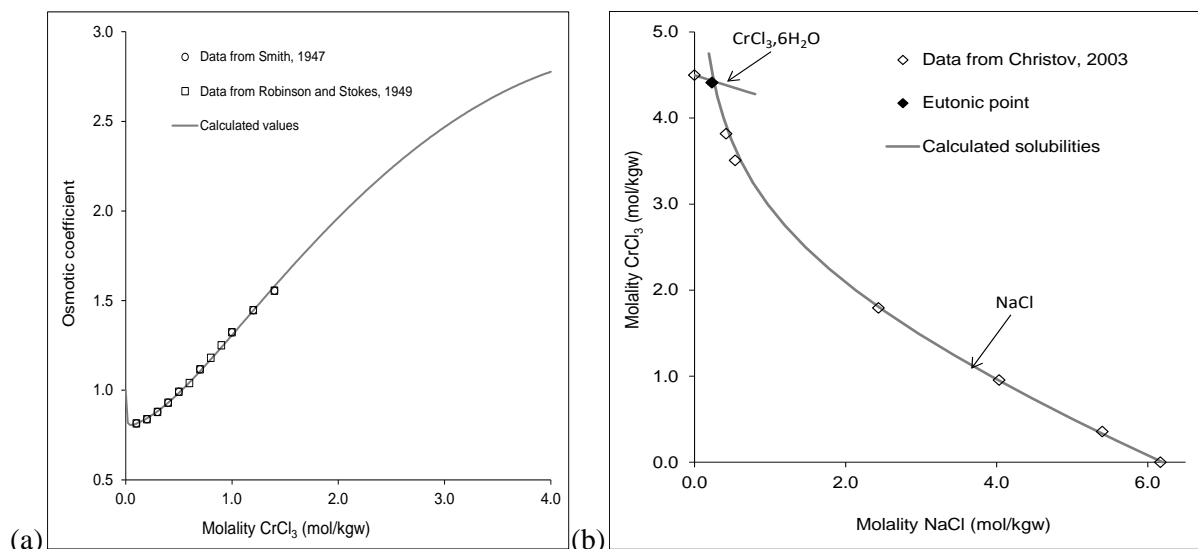
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Fig. 3. (a) Calculated (lines) and experimental (symbols) osmotic coefficients for the $CrCl_3$-H_2O binary system as a function of total molality of $CrCl_3$ at 25°C. (b) Experimental (symbols) and predicted (lines) halite and $CrCl_3.6H_2O$ (s) solubilities in NaCl-$CrCl_3$-H_2O system at 25°C. The solid symbol represents the experimental composition of invariant point, determined by [41].

3.4. $AlCl_3$- $FeCl_3$-$CrCl_3$-H_2O system

We could not find activity data (e.m.f., osmotic, water activity) data in the ternary sub-systems and in the quaternary $AlCl_3$- $FeCl_3$-$CrCl_3$-H_2O system. Solubility data for $AlCl_3$- $CrCl_3$-H_2O and $FeCl_3$-$CrCl_3$-H_2O systems are also not available in the literature for this quaternary system. The solubility data of Malquori [42] for $AlCl_3$- $FeCl_3$-H_2O system are the only data found in literature. According to these data the system is of simple eutonic type with crystalization of $AlCl_3.6H_2O$(s) and $FeCl_3.6H_2O$(s). Solubility data of [42] are used to evaluate mixing θ(Al,Fe), and ψ(Al,Fe,Cl) parameters. In this parameterization we keep the same values of binary $AlCl_3$-H_2O, and $FeCl_3$-H_2O parameters and of solubility product values of precipitates, and accepting a zero value for θ(Al,Fe) parameter. The results are presented on figure 4a. The predicted solubilities, and the predicted composition of invariant point are in good agreement with experiments of [42]. For $AlCl_3$- $CrCl_3$-H_2O and $FeCl_3$-$CrCl_3$-H_2O systems for which data are not available, we calculate phase diagrams, accepting eutonic type of phase diagrams, and using the same zero value for θ parameter as in $AlCl_3$- $FeCl_3$-H_2O model. The calculated diagrams are presented on fig. 4b and 4c.
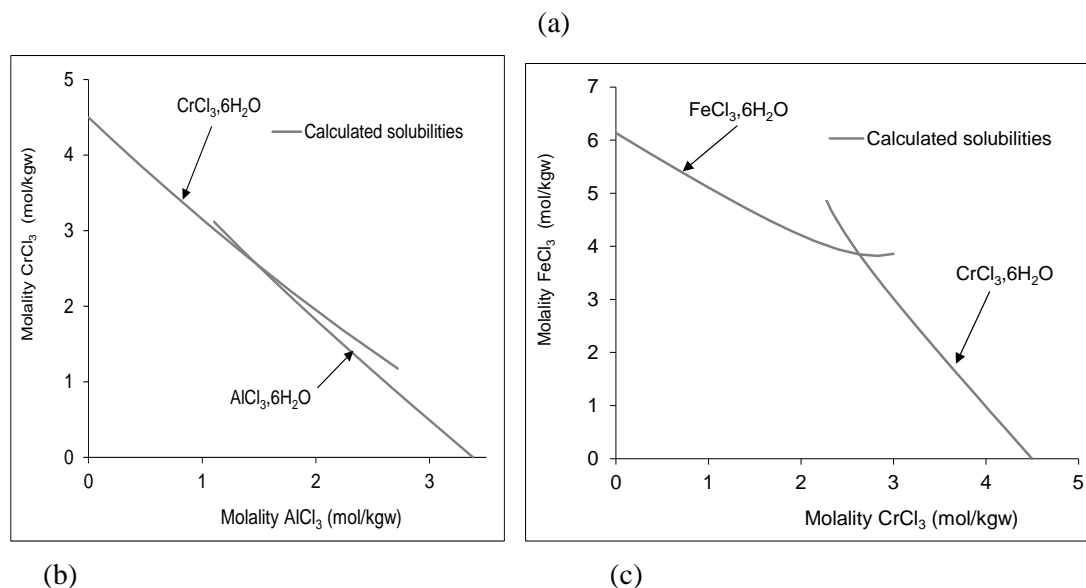
(a)

(b) (c)
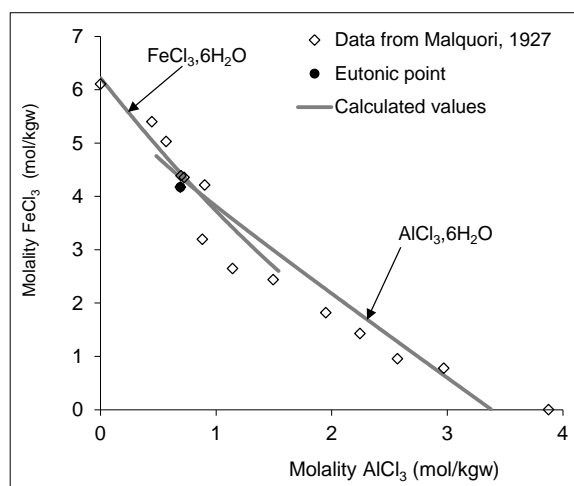
Fig. 4. Experimental (symbols on (a)) and predicted (lines) AlCl$_3$.6H$_2$O (s), CrCl$_3$.6H$_2$O (s) and FeCl$_3$.6H$_2$O (s) solubilities in AlCl$_3$-FeCl$_3$-H$_2$O (4a), AlCl$_3$-CrCl$_3$-H$_2$O (4b), and CrCl$_3$-FeCl$_3$-H$_2$O (4c) systems at 25°C. The solid symbol on fig. (4a) represents the experimental composition of invariant point, determined by [42]

4. Summary and Restrictions

The equilibrium model presented in this article calculates solubilities and solution activities in the Na-Al(III)-Cr(III)-Fe(III)-Cl-H$_2$O system at 25°C and to high solution concentration within experimental uncertainty. Following an approach in our previous modeeling studies on M(III) systems [10,14-17,21,35], in this work we accept that complex Al(III), Cr(III), and Fe(III) aqueous species do not exist in solutions. Binary and mixing solution parameters are evaluated using activity (when available) and solubility data. We test the model by comparing model predictions with experimental data (activity data for unsaturated solutions and solubility data in ternary systems).

Since the model has been parameterized for all the constituent binary and ternary systems in the quinary sytem under study, it can in principle, be applied to all compositions in the Na-Al(III)-Cr(III)-Fe(III)-Cl-H$_2$O system. However, there are several restrictions of the model due to: (1) lack of high molality activity data for binary CrCl$_3$-H$_2$O solutions, and with one exceptions (NaCl-FeCl$_3$-H$_2$O) for the ternary unsaturated solutions; (2) lack of solubility data for ternary sub-systems AlCl$_3$-CrCl$_3$-H$_2$O, and FeCl$_3$-CrCl$_3$-H$_2$O. New experimental data will be required to validate the model predictions. The model presented here represents a strong base to develop a comprehensive model that descriebe acurately the behavior of oxide (susch as Fe$_2$O$_3$(s), Al$_2$O$_3$(s)), hydroxide (s.a. Al(OH)$_3$(s), Fe(OH)3(s), Cr(OH)$_3$(s), FeOOH(s), AlOOH(s)), and sulfate (s.a. alums, and chromium alums) minerals in acidic natural fluid system of the type H-Na-K-NH$_4$-Mg-Ca-Al-Cr-Fe^{2+}-Fe^{3+}-Cl-SO$_4$-H$_2$O.

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