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A thermodynamic model for solution behavior and solid-liquid equilibrium in Na-K-Mg-Ca-Al(III)-Fe(III)-Cr(III)-Cl-H2O system from low to very high concentration at 25°C

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ABSTRACT: In this study we evaluated new mixing (θ and ψ) Pitzer parameters, and developed models for solution behavior and solid liquid equilibria for the following mixed systems: 1) KCl-AlCl3-H2O, 2) KCl-FeCl3-H2O, 3) KCl-CrCl3-H2O, 4) MgCl2-AlCl3-H2O, 5) MgCl2-FeCl3-H2O, 6) MgCl2-CrCl3-H2O, 7) CaCl2-AlCl3-H2O, 8) CaCl2-FeCl3-H2O, and 9) CaCl2-CrCl3-H2O at 25°C. The solubility modeling approach, implemented to the Pitzer specific interaction equations is employed. The values of the binary parameters for the binary sub-systems needed here to parameterize models for mixed systems are taken from our previous studies. Mixing solution parameters are evaluated in this study using activity (when available) and solubility data. Following an approach in our previous modeling studies on M(III) chloride and sulfate systems, in this work we accept that complex Al(III), Cr(III), and Fe(III) aqueous species do not exist in solutions. We test the new models by comparing model predictions with experimental data (activity data for unsaturated solutions and solubility data in ternary systems). The agreement between model predictions and experimental data is very good. Combining present parameterization, with our M(III) models developed previously we fully complete our at 25°C model for the 8th component system Na-K-Mg-Ca-Al(III)-Cr(III)-Fe(III)-Cl-H2O. The resulting model calculates solubilities and solution activities to high solution concentration within experimental uncertainty. Limitations of the model due to data insufficiencies are discussed. The resulting parameterization was developed for the Pitzer formalism based PHREEQC database.

Keywords: Geochemistry of Aluminum (Al(III)), Chromium(Cr(III)) and Iron (Fe(III)), Pitzer approach; Computer Chemical and Geochemical modeling; Solution and solute activity; Stable and metastable solid-liquid equilibria; Extended brine system model; Water-rock interactions; Physical Chemistry and Chemical Thermodynamics;

1. Introduction

The construction of thermodynamic models for accurate description of the geochemical behavior of aluminium, chromium and iron in highly saline solutions represents a big challenge, because of their wide applicability in different industrial and geosciences domains. These include exploitation of geothermal brines from deep reservoirs and geothermal energy production, CO2 storage in saline geochemical reservoirs, development of nuclear waste storage strategies, extraction of valuable mineral resources from saline fluids, desalination of sea waters, and many others. All these industrial and geosciences 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 here approach is its ability to predict correctly the chemical behavior of complex natural systems at various conditions, i.e. composition, temperature and pressure changes, and from extremely low to extremely high 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 concentrated saline solutions, a specific and robust approach is needed, which includes all possible solution species and interactions in solutions, as well as all experimentally identified equilibrium solids. The specific interaction approach for describing properties of 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 temperature \cite{Harvie2006,Christov2005}, as well as at wide range of temperatures from 0°C to 300°C \cite{Greenberg2003,Christov2005,Moller2014}, and from extremely low \cite{Christov2005,Moller2014}, to very high concentration of solutions \cite{Lach2016,Andre2016,Christov2019}. However, the existing Pitzer’s databases have different limitations, mostly because of limited number of implemented solution species and precipitating solids, and temperature and concentration restrictions of parameterization. This is why a permanent updating work must be done in order to increase the applicability of developed models, 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\textsuperscript{3+} \cite{Christov2005,Moller2014}3+\textsuperscript{3+}, chromium (Cr\textsuperscript{3+}) \cite{Andre2016,Christov2019}, Fe\textsuperscript{3+} \cite{Christov2005,Moller2014}, and Iron (as Fe\textsuperscript{2+} [30]), and Fe\textsuperscript{3+} \cite{Christov2005,Moller2014} 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 sea-type chloride solids, and M(III)Cl\textsubscript{3} (M = Al, Fe, Cr) minerals solubility in the following mixed systems: 1) KCl-AlCl\textsubscript{3}-H\textsubscript{2}O, 2) KCl-FeCl\textsubscript{3}-H\textsubscript{2}O, 3) KCl-CrCl\textsubscript{3}-H\textsubscript{2}O, 4) MgCl\textsubscript{2}-AlCl\textsubscript{3}-H\textsubscript{2}O, 5) MgCl\textsubscript{2}-FeCl\textsubscript{3}-H\textsubscript{2}O, 6) MgCl\textsubscript{2}-CrCl\textsubscript{3}-H\textsubscript{2}O, 7) CaCl\textsubscript{2}-AlCl\textsubscript{3}-H\textsubscript{2}O, 8) CaCl\textsubscript{2}-FeCl\textsubscript{3}-H\textsubscript{2}O, and 9) CaCl\textsubscript{2}-CrCl\textsubscript{3}-H\textsubscript{2}O at 25°C. Combining present parameterization, with our M(III) binary and mixed models developed previously \cite{Lach2016,Andre2016,Christov2005,Moller2014}, we fully complete our model for the 8\textsuperscript{th} component system Na-K-Mg-Ca-Al(III)-Cr(III)-Fe(III)-Cl\textsubscript{3}-H\textsubscript{2}O. 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, s.a. aluminium, 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 (Al(III)-Cr(III)-Fe(III)) and to use some analogies between these different systems, when experimental data are missing, in order to estimate new interaction parameters. The model for 8-component system is fully parameterized, i.e. model parameters for all binary and ternary sub-systems, and all experimentally identified precipitating minerals are introduced in the comprehensive model for complex system under study.

2. Model Parameterization

The 8\textsuperscript{th} component system Na-K-Mg-Ca-Al(III)-Cr(III)-Fe(III)-Cl\textsubscript{3}-H\textsubscript{2}O have been investigated according to the following scheme (Christov, 2000, 2005, 2009; Lassin et al., 2015): i) evaluation of not-concentration restricted ($\beta^{\theta}$, $\beta^I$, $\beta^2$ and $C^0$) solution parameters for all 7 chloride binary sub-systems systems (NaCl-H\textsubscript{2}O, KCl-H\textsubscript{2}O, MgCl\textsubscript{2}-H\textsubscript{2}O, CaCl\textsubscript{2}-H\textsubscript{2}O, AlCl\textsubscript{3}-H\textsubscript{2}O, FeCl\textsubscript{3}-H\textsubscript{2}O, and CrCl\textsubscript{3}-H\textsubscript{2}O); ii) determination of the chemical potential of solids (as thermodynamic solubility product, $K_{sp}$) precipitating from saturated binary solutions; iii) determination of mixing solution parameters for ternary sub-systems, i.e. $\theta$ for each unlike cation-cation pair, and $\varphi$ for each triple ion interaction where the ions are all not of the same sign; and iv) determination of the chemical potential of solids (low hydrate salts and double salts), precipitating from saturated ternary solutions, in addition to minerals which precipitate in binary sub-systems. It should be noted here that the model presented here does not includes the formation of aequous complexes (such as FeCl\textsubscript{3}aq)). This model expands the solid-liquid equilibria Na-Al(III)-Cr(III)-Fe(III)-Cl\textsubscript{3}-H\textsubscript{2}O model of Andre et al. [17] by validation of binary interaction parameters, and evaluation of new mixing interaction parameters for potassium, magnesium and calcium-, and M(III) - chloride systems, and (2) the chemical potentials of 2 double salts precipitating from saturated ternary solutions.

Models for binary systems

Since the calculation of the composition of saturated mixed solutions is one of the main purposes of the simulation, the applicability of the binary parameters to binary solutions of high molalities up to saturation (or supersaturation in case of FeCl\textsubscript{3}-H\textsubscript{2}O) with the lowest value of the standard deviation (\sigma) of the osmotic coefficients is a very important criterion for the choice of the binary parameters. In this study we used binary parameters for M(III)Cl\textsubscript{3}-H\textsubscript{2}O systems, and chemical potentials of hexahydrates M(III)Cl\textsubscript{3}.6H\textsubscript{2}O(s) determined in previous studies of Christov: for AlCl\textsubscript{3}-H\textsubscript{2}O and AlCl\textsubscript{3}.6H\textsubscript{2}O(s) from [20], for FeCl\textsubscript{3}-H\textsubscript{2}O and FeCl\textsubscript{3}.6H\textsubscript{2}O(s) from [30], and for CrCl\textsubscript{3}-H\textsubscript{2}O and CrCl\textsubscript{3}.6H\textsubscript{2}O(s) from [26]. Note that for AlCl\textsubscript{3}-H\textsubscript{2}O and
CrCl$_3$-$H_2$O systems Christov used a standard for 3-1 type electrolytes approach with 3 interaction parameters ($\beta^0$, $\beta^1$, and $\beta^2$) [1,2]. To describe correctly the activities for whole concentration range up to saturation in binary system FeCl$_3$-$H_2$O Christov [30] used extended version of Pitzer approach with 4 interaction parameters ($\beta^0$, $\beta^1$, $\beta^2$, and $\beta^3$) and by variation additionally of $\alpha_2$ term in fundamental Pitzer equations [4,28,29,31]. The applicability M(III)/Cl$_2$-$H_2$O parameters has been proved by development of solid-liquid equilibrium models for ternary and multicomponent systems of various type [5,17,20,25,26,30].

The values of the binary parameters for the systems KCl-$H_2$O, MgCl$_2$-$H_2$O, and CaCl$_2$-$H_2$O, and K$^+$ values of solids (K$^+_q$(KCl(s)), K$^+_q$(MgCl$_2$-$H_2$O(s), and K$^+_q$(CaCl$_2$-$H_2$O(s)) at $25^\circ$C needed here to parameterize models for mixed systems are re-calculated from T variation models of Greenberg and Moller [6], Christov [9,32], and Christov and Moller [13], respectively. They are valid up to saturation or almost to saturation of the binary solutions, and their applicability has been proved by development of T-variation solid-liquid equilibrium models for binary, ternary and multicomponent systems of various types [s.a. HCl-MgCl$_2$-CaCl$_2$-$H_2$O model [9,32]].

Models for ternary systems

To complete the model for the 8th component system Na-K-Mg-Ca-Al(III)-Cr(III)-Fe(III)-Cl-$H_2$O within this study we evaluate new mixing parameters as follow:

- $\theta$(K,Al), and $\psi$(K,Al,Cl) for ternary system KCl-AlCl$_3$-$H_2$O;
- $\theta$(K,Fe), and $\psi$(K,Fe,Cl) for ternary system KCl-FeCl$_3$-$H_2$O;
- $\theta$(K,Cr), and $\psi$(K,Cr,Cl) for ternary system KCl-CrCl$_3$-$H_2$O;
- $\theta$(Mg,Al), and $\psi$(Mg,Al,Cl) for ternary system MgCl$_2$-AlCl$_3$-$H_2$O;
- $\theta$(Mg,Fe), and $\psi$(Mg,Fe,Cl) for ternary system MgCl$_2$-FeCl$_3$-$H_2$O;
- $\theta$(Mg,Cr), and $\psi$(Mg,Cr,Cl) for ternary system MgCl$_2$-CrCl$_3$-$H_2$O;
- $\theta$(Ca,Al), and $\psi$(Ca,Al,Cl) for ternary system CaCl$_2$-AlCl$_3$-$H_2$O;
- $\theta$(Ca,Fe), and $\psi$(Ca,Fe,Cl) for ternary system CaCl$_2$-FeCl$_3$-$H_2$O;
- $\theta$(Ca,Cr), and $\psi$(Ca,Cr,Cl) for ternary system CaCl$_2$-CrCl$_3$-$H_2$O.

The solution models for mixed KCl-FeCl$_3$-$H_2$O, and KCl-CrCl$_3$-$H_2$O systems are also used to determine solubility product (K$^+_q$) of double salts 2KClFeCl$_3$-$H_2$O and 2KClCrCl$_3$-$H_2$O. In evaluation of mixing $\theta$ and $\psi$ parameters we use solubility data and solid liquid equilibrium models for binary systems described above without any adjustments. To determine mixing parameters we use all available activity and solubility data. The solubility data are taken mostly from compilations of Linke [33], for Al systems from Gmelin’s Handbuch [34], and some new original publications.

Christov et al. [24] developed a temperature variable ((0 to 100) $^\circ$C) model for H-Na-K-Al-Cl-$H_2$O system. The T-variation model for K-Al-Cl-$H_2$O sub-system have been constructed using only solubility data in this ternary. The model used constant with temeprature $\theta$(K,Al) parameter (equals to 0.41955), and T-variation $\psi$(K,Al,Cl) parameter. It should be noted that the accepted $\theta$(K,Al) value in Christov et al. [24] is much higher, compare to other $\theta$(K,M(III)) values for K$^+$M$^{3+}$ common anion chloride and sulfate systems (see Table 3 in [5]). In a series of papers Christov, and Christov and co-authors developed a solid-liquid equilibrium model, which includes all M(III)-tertiary subsystems within K-Mg-Al-Cl-$SO_4$-$H_2$O [20], Na-K-NH$_4$-Al-Cr-$SO_4$-$H_2$O [21-23], Na-K-Mg-Fe(III)-Cl-$SO_4$-$H_2$O [30], and Na-Al(III)-Fe(III)-Cr(III)-Cl-$H_2$O [17] systems. The authors found that for all considered ternary (1-1)+(3-1) chloride and (1-2)+(3-2) sulfate mixtures a $\theta$(M(I),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 [5, 20-23, 30]. The same value ($\theta$(Na,M(III)) = -0.07) is also accepted in our recent models for NaCl-AlCl$_3$-$H_2$O, NaCl-CrCl$_3$-$H_2$O, and NaCl-FeCl$_3$-$H_2$O systems [17]. Therefore, in this study we develop a new chloride (1-1)+(3-1) models for KCl-AlCl$_3$-$H_2$O (Fig. 1a), KCl-CrCl$_3$-$H_2$O (Fig. 1b), and KCl-FeCl$_3$-$H_2$O (Fig. 2) accepting $\theta$(K,M(III)) value equals to (-0.07). Then, the $\psi$(K,M(III),Cl) parameter values are adjusted to fit experimental data.

Rumyantsev et al. [35] determined activity data for low molality mixed ferrous chloride systems KCl-FeCl$_3$-$H_2$O, MgCl$_2$-FeCl$_3$-$H_2$O, and CaCl$_2$-FeCl$_3$-$H_2$O on the basis of isopiestic measurements. Using their own activity data the authors also created a solution model for the above mixed ferrous chloride solutions, without considering solid phases precipitation. In this study we test the applicability of the reported by Rumyantsev et al. [35] mixing parameters to plot the phase diagrams for KCl-FeCl$_3$-$H_2$O, MgCl$_2$-FeCl$_3$-$H_2$O, and CaCl$_2$-FeCl$_3$-$H_2$O systems. It was found that the reported $\theta$ and $\psi$ parameters [35] fit very well the activity data, but cannot be used for solubility calculations. Therefore, in this study to parameterize the model for KCl-FeCl$_3$-$H_2$O system we use activity data from Rumyantsev et al. [35] plus all available solubility data (see Fig. 2 below). For MgCl$_2$-FeCl$_3$-$H_2$O and CaCl$_2$-FeCl$_3$-$H_2$O systems there are not available solubility data. For these systems we found that zero values for mixing parameters fit very well experimental activity data [35], and provide very reasonable solubility predictions. Note that a zero value for $\theta$(Mg,Al) parameter is also
evaluated by Christov [20] for magnesium-aluminium chloride and sulphate mixed systems. According to conclusions made in Christov [5] a zero values for mixing parameters suppose that mixed systems follow the rule of Zdanovskii. Therefore in this study the developed new models for M(II)-M(III)Cl$_2$-H$_2$O {M(II) = Mg, Ca} used a zero values for θ and ψ parameters.

In this study we evaluated new mixing θ and ψ Pitzer parameters, and developed models for solution behavior and solid liquid equilibria for the following mixed systems: 1) KCl-AlCl$_3$-H$_2$O, 2) KCl-FeCl$_3$-H$_2$O, 3) KCl-CrCl$_3$-H$_2$O, 4) MgCl$_2$-AlCl$_3$-H$_2$O, 5) MgCl$_2$-FeCl$_3$-H$_2$O, 6) MgCl$_2$-CrCl$_3$-H$_2$O, 7) CaCl$_2$-AlCl$_3$-H$_2$O, 8) CaCl$_2$-FeCl$_3$-H$_2$O, and 9) CaCl$_2$-CrCl$_3$-H$_2$O at 25°C. Mixing solution parameters are evaluated in this study using activity (when available) and solubility data. Following an approach in our previous modeling studies on M(III) chloride and sulfate systems [16,17,20-26] in this work we accept that complex Al(III), Cr(III), and Fe(III) aqueous species (s.a. FeCl$_3$aq) do not exist in solutions. On next Figures (1 to 6) we test the new models by comparing model predictions with experimental data: activity data for unsaturated solutions and solubility data in ternary systems.

Fig. 1(a,b). Experimental (symbols) and predicted (lines) KCl(s), AlCl$_3$.6H$_2$O(s), CrCl$_3$.6H$_2$O(s) and 2KCl.CrCl$_3$.H$_2$O(s) solubilities in KCl-AlCl$_3$.H$_2$O(a), and KCl-CrCl$_3$.H$_2$O (b) systems at 25°C. The solid
symbols represent the experimental composition of invariant point. See the text into the figures and reference list for experimental data source.

The agreement between model predictions and experimental activity and solubility data is very good. For systems for which solubility data are not available (MgCl$_2$-FeCl$_3$-H$_2$O (Fig. 3c), CaCl$_2$-FeCl$_3$-H$_2$O (Fig. 6b), CaCl$_2$-CrCl$_3$-H$_2$O (Fig. 5b)) the model predicts very reasonable solubility isotherms, which are similar to those for other three (2-1)+(3-1) chloride mixtures for which solubility data are reported (MgCl$_2$-AlCl$_3$-H$_2$O (Fig.3a), CaCl$_2$-AlCl$_3$-H$_2$O (Fig.5a), MgCl$_2$-CrCl$_3$-H$_2$O (Fig. 4)). Combining present parameterization, with our Na-M(III) models developed previously [17] we fully complete our at 25°C model for the 8th component system Na-K-Mg-Ca-Al(III)-Cr(III)-Fe(III)-Cl-H$_2$O. The resulting model calculates solution activities in binary [5,16,17,20,26,30] and ternary (Fig. 2a, 3b, 6a) M(III) solutions and solubilities in mixed systems to very high solution concentration, and within experimental uncertainty.

![Graph a) Data from Rumyantsev et al., 2004](image)

![Graph b) Data from Malquori, 1928](image)
Figure 2(a,b). Experimental water activity ($a_w$) data (solid diamond symbols) and calculated isoactivities (dashed lines) in KCl-FeCl$_3$-H$_2$O system at 25°C (a). Experimental (25°C and 30°C: open symbols) and predicted (25°C: solid lines) KCl(s), FeCl$_3$,6H$_2$O(s), and 2KCl$\cdot$FeCl$_3$,H$_2$O(s) solubilities in KCl-FeCl$_3$-H$_2$O system (b). The solid circles represent the experimental composition of invariant point, determined by Atbir et al. [39]. See the text into the figures and reference list for experimental data source.

Figure 3(a,b,c). Experimental ((a): open symbols) and predicted (solid lines) MgCl$_2$,6H$_2$O(s), AlCl$_3$,6H$_2$O(s), and FeCl$_3$,6H$_2$O solubilities in MgCl$_2$-AlCl$_3$-H$_2$O(a) and MgCl$_2$-FeCl$_3$-H$_2$O (c) systems. Experimental water
activity (a) data (solid diamond symbols) and calculated isoactivites (dashed lines) in MgCl$_2$-FeCl$_3$-H$_2$O system at 25°C (b and c). See the text into the figures and reference list for experimental data source.

Figure 4. Experimental (open symbols, Christov [5]) and predicted (solid lines) MgCl$_2$·6H$_2$O(s), and CrCl$_3$·6H$_2$O(s) solubilities in MgCl$_2$-CrCl$_3$-H$_2$O system. The solid symbol represents the experimental composition of invariant point [5].

Figure 5(a,b). Experimental (open symbols only on (a)) and predicted (solid lines) CaCl$_2$·6H$_2$O(s), AlCl$_3$·6H$_2$O(s), and CrCl$_3$·6H$_2$O(s) solubilities in CaCl$_2$-AlCl$_3$-H$_2$O(a) and CaCl$_2$-CrCl$_3$-H$_2$O (b) systems. See the text into the figures and reference list for experimental data source.
Figure 6 (a,b). Experimental water activity (a$_w$) data (solid diamond symbols) and calculated isoactivity (dashed lines) in CaCl$_2$-FeCl$_3$-H$_2$O system at 25°C (a). (b) Predicted (25°C: solid lines) CaCl$_2$.6H$_2$O(s) and FeCl$_3$.6H$_2$O(s) solubilities in CaCl$_2$-FeCl$_3$-H$_2$O system. See the text into the figures and reference list for experimental data source.

3. Summary and Restrictions

In this study we evaluated new mixing θ and ψ Pitzer parameters, and developed models for solution behavior and solid liquid equilibria for the following mixed systems: 1) KCl-AlCl$_3$-H$_2$O, 2) KCl-FeCl$_3$-H$_2$O, 3) KCl-CrCl$_3$-H$_2$O, 4) MgCl$_2$-AlCl$_3$-H$_2$O, 5) MgCl$_2$-FeCl$_3$-H$_2$O, 6) MgCl$_2$-CrCl$_3$-H$_2$O, 7) CaCl$_2$-AlCl$_3$-H$_2$O, 8) CaCl$_2$-FeCl$_3$-H$_2$O, and 9) CaCl$_2$-CrCl$_3$-H$_2$O at 25°C. The values of the binary parameters for the binary subsystems needed here to parameterize models for mixed systems are taken from our previous studies [7,9,13,20,26,30,32]. They are valid up to saturation of the binary solutions, and their applicability has been proved by development of solid-liquid equilibrium models for ternary and multicomponent systems of various types [13,9,17,32]. Mixing solution parameters are evaluated in this study using activity (when available) and solubility data. Following an approach in our previous modeling studies on M(III) chloride and sulfate systems [16,17,20-24,26], in this work we accept that complex Al(III), Cr(III), and Fe(III) aqueous species do not exist in solutions. We test the new models by comparing model predictions with experimental data (activity data for unsaturated solutions and solubility data in ternary systems). The agreement between model predictions and available experimental data is very good. Combining present parameterization, with our M(III) models developed previously we fully complete our at 25°C model for the 8th component system Na-K-Mg-Ca-Al(III)-Cr(III)-Fe(III)-Cl-H$_2$O. The resulting model calculates solubilities and solution activities to high solution concentration within experimental uncertainty. Since the model has been parameterized for all the constituent binary and ternary systems in the 8th component system under study, it can in principle, be applied to all compositions in the Na-K-Mg-Ca-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 CrCl$_3$.H$_2$O binary solutions, and with exception of FeCl$_3$.mixtures, for all other ternary unsaturated solutions; (2) lack of solubility data for ternary sub-systems AlCl$_3$-CrCl$_3$-H$_2$O, FeCl$_3$-CrCl$_3$-H$_2$O [17], MgCl$_2$-FeCl$_3$.H$_2$O, and CaCl$_2$-FeCl$_3$.H$_2$O CaCl$_2$-CrCl$_3$-H$_2$O [this study]. 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 describe accurately the
behavior of oxide (such as Fe$_2$O$_3$), Al$_2$O$_3$), hydroxide (s.a. Al(OH)$_3$), Fe(OH)$_3$, Cr(OH)$_3$, FeOOH, AlOOH), and sulfate (s.a. alums, tamagurite type salts, basic aluminium sulfate (BAS) minerals in acidic natural fluid system of the type H-Na-K-NH$_4$-Mg-Ca-Al$^{3+}$-Fe$^{2+}$-Fe$^{3+}$-Cl-SO$_4$-$H_2$O.

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