Experimental Determination of Solubilities of Tri-calcium Di-
Citrate Tetrahydrate $[\text{Ca}_3[\text{C}_3\text{H}_5\text{O(COO)}_3]_2\cdot\text{H}_2\text{O}]$, Earlandite, in
NaCl and MgCl$_2$ Solutions to High Ionic Strengths and Its Pitzer
Model: Applications to Nuclear Waste Isolation and Other Low
Temperature Environments

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ABSTRACT

In this study, solubility measurements on tri-calcium di-citrate tetrahydrate \([\text{Ca}_3\text{[Citrate]}_2\cdot4\text{H}_2\text{O}]\) as a function of ionic strength are conducted in NaCl solutions up to \(I = 5.0 \text{ mol}\cdot\text{kg}^{-1}\) and in MgCl\(_2\) solutions up to \(I = 7.5 \text{ mol}\cdot\text{kg}^{-1}\), at room temperature (22.5 ± 0.5°C). The solubility constant \((\log K_{sp})\) for \([\text{Ca}_3\text{[Citrate]}_2\cdot4\text{H}_2\text{O}]\) and formation constant \((\log \beta^0)\) for \([\text{Ca}_3\text{H}_5\text{O}\text{(COO)}_3]^-\),

\[
\begin{align*}
\text{Ca}_3\text{[Citrate]}_2\cdot4\text{H}_2\text{O} (\text{earlandite}) &= 3\text{Ca}^{2+} + 2[\text{C}_3\text{H}_5\text{O}\text{(COO)}_3]^{3-} + 4\text{H}_2\text{O} \quad (1) \\
\text{Ca}^{2+} + [\text{C}_3\text{H}_5\text{O}\text{(COO)}_3]^{3-} &= \text{Ca}[\text{C}_3\text{H}_5\text{O}\text{(COO)}_3]^- \quad (2)
\end{align*}
\]

are determined as \(-18.11 \pm 0.05\) and \(4.97 \pm 0.05\), respectively, based on the Pitzer model with a set of Pitzer parameters describing the specific interactions in NaCl and MgCl\(_2\) media.

The solubility measurements and thermodynamic modeling indicate that \([\text{Ca}_3\text{[Citrate]}_2\cdot4\text{H}_2\text{O}]\) could become a solubility-controlling phase for citrate in geological repositories for nuclear waste when the inventories of citrate reach the saturation concentrations for \([\text{Ca}_3\text{[Citrate]}_2\cdot4\text{H}_2\text{O}]\).
1. INTRODUCTION

Citric acid (chemical formula, $\text{C}_6\text{H}_8\text{O}_7$, or structural formula, $\text{CH}_2\text{COOH} - \text{C(OH)COOH-CH}_2\text{COOH}$, and its dissociated forms such as $[\text{C}_3\text{H}_5\text{O(COO)}_3]^{3-}$, abbreviated as “Citrate” hereafter) is present in nuclear waste streams (Brush and Xiong, 2009), as citrate is used in decontamination processes in the nuclear field (Hummel et al., 2005). Therefore, it has a significant effect on the Performance Assessment (PA) for the geological repositories for nuclear waste because of its ability to form relatively strong aqueous complexes with actinides, especially actinides in the $+\text{III}$ oxidation state, potentially increasing solubilities of actinides. The strength of citrate aqueous complexes with actinides is only second to those of EDTA with actinides. More importantly, citrate has usually a higher inventory than EDTA, resulting in potentially higher concentrations. As an example, the 2009 citrate inventory in the form of $\text{NaH}_2\text{Citrate}$ and citric acid for the Waste Isolation Pilot Plant (WIPP), a U.S. DOE geological repository for defense-related transuranic (TRU) waste, was $8.23 \times 10^3$ kg for the 2009 Compliance Recertification Application Performance Assessment Baseline Calculations (CRA-2009 PABC) (Brush and Xiong, 2009), and the calculated citrate concentration in brines for CRA-2009 was $2.38 \times 10^{-3}$ mol$\cdot$dm$^{-3}$ (Brush and Xiong, 2009), higher than EDTA concentration (Brush and Xiong, 2009).

In addition, citrate is naturally present in other low temperature environments, and therefore it plays an important role in mobilization of metals in low temperature environments such as metallurgical slags (e.g., Ettler et al., 2004). Earlandite was found in the Weddell Sea, Antarctic (Bannister and Hey, 1936; Rex et al., 1970). The formation of earlandite in nature suggests that it is a stable phase
in natural environments, indicating that it has relatively low solubilities. This means that earlandite could be a solubility-controlling phase for citrate in low temperature environments. However, the solubility of earlandite as a function of ionic strength is not well known in media that are important to geochemical processes. Such knowledge is required for geochemical modeling of natural waters which may vary from dilute surface and groundwater to highly concentrated brines saturated. Therefore, the objective of this work is to determine solubilities of earlandite as a function of ionic strength to 5.0 mol•kg\(^{-1}\) in a NaCl medium, and to 7.5 mol•kg\(^{-1}\) in MgCl\(_2\) medium, as NaCl and MgCl\(_2\) are the most common and important components in natural aqueous systems, and they are dominant components in the WIPP Generic Weep Brine (GWB) and Energy Research and Development Administration Well 6 (ERDA-6) (Xiong and Lord, 2008). Based on the measured solubilities, a Pitzer model was developed here for solubilities of earlandite, and the interactions of citrate with NaCl and MgCl\(_2\) media. The model would enable researchers to estimate with a degree of high precision regarding solubilities of earlandite in various environments over a wide range of ionic strengths.

2. EXPERIMENTAL SECTION

In these solubility experiments, about 2 grams of the starting material—ACS reagent grade tri-calcium di-citrate tetrahydrate (Ca\(_3\)[Citrate]\(_2\)•4H\(_2\)O, earlandite, CAS 5785-44-4) from ACROS ORGANICS was weighed out and placed into 150 mL plastic bottles. Then, 100 mL of supporting electrolyte solution were added to those bottles. Once filled, the lids of the bottles were sealed with parafilm.
The supporting electrolytes are a series of NaCl solutions ranging from 0.010 mol•kg\(^{-1}\) to 5.0 mol•kg\(^{-1}\), and MgCl\(_2\) solutions ranging from 0.01 mol•kg\(^{-1}\) to 2.5 mol•kg\(^{-1}\). The supporting electrolyte solutions were prepared from degassed deionized (DI) water. The degassed DI water was prepared by following a procedure similar to that used by Wood et al. (2002) to remove dissolved CO\(_2\). The undersaturation experiments are conducted at laboratory room temperature (22.5 ± 0.5°C).

The pH readings were measured with an Orion-Ross combination pH glass electrode, coupled with an Orion Research EA 940 pH meter that was calibrated with three pH buffers (pH 4, pH 7, and pH 10). In solutions with an ionic strength higher than 0.10 mol•kg\(^{-1}\), hydrogen-ion concentrations on molar scale (pcH) were determined from pH readings by using correction factors for NaCl and MgCl\(_2\) solutions determined by Rai et al. (1995) and Hansen (2001), respectively. Based on the equation in Xiong et al. (2010), pcHs are converted to hydrogen-ion concentrations on the molal scale (pmH) (see details in footnotes for Tables 1 and 2).

Solution samples were periodically withdrawn from experimental runs. Before solution samples were taken, pH readings of experimental runs were measured. The sample size was usually 3 mL. After a solution sample was withdrawn from an experiment and filtered with a 0.2 μm syringe filter, the filtered solution was then weighed, acidified with 0.5 mL of concentrated TraceMetal\textsuperscript{®} grade HNO\(_3\) from Fisher Scientific, and finally diluted to a volume of 10 mL with DI water. If subsequent dilutions were needed, aliquots were taken from the first dilution samples for the second dilution, and aliquots of the second dilution were then taken for further dilution.
Calcium concentrations of solutions were analyzed with a Perkin Elmer dual-view inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer DV 3300). Calibration blanks and standards were precisely matched with experimental matrices. The linear correlation coefficients of calibration curves in all measurements were better than 0.9995. The analytical precision for ICP-AES is better than 1.00% in terms of the relative standard deviation (RSD) based on replicate analyses. Stoichiometric dissolution of earlandite was confirmed by analyzing for citrate concentrations with a DIONEX ion chromatograph (IC) (DIONEX IC 3000) for selected samples. Uncertainties are estimated using a method described in one of our previous publications (i.e., Nemer et al., 2010).
3. EXPERIMENTAL RESULTS, AND THERMODYNAMIC MODELING

3.1 Experimental Results

Experimental results for solubilities in NaCl and MgCl$_2$ solutions are tabulated in Tables 1 and 2, respectively. In Figure 1, solubilities of earlandite as a function of experimental time in NaCl solutions are displayed. From Figure 1, it is clear that steady-state concentrations in NaCl solutions are achieved in the second sampling, which was taken at 375 days (Table 1). Solubilities of earlandite as a function of experimental time in MgCl$_2$ solutions are displayed in Figure 2. It is clear from Figure 2 that steady-state concentrations in MgCl$_2$ solutions are achieved in the first sampling, which was taken at 385 days (Table 2). It is assumed that steady-state concentrations represent equilibrium concentrations, as the duration of experiments in this work, up to 1,067 days, is significantly longer than previous studies under similar conditions. For instance, in the experiments of Vavrusova and Skibsted (2016), they mentioned that equilibrium was established in several hours in their study.

In Figure 3, concentrations of calcium as a function of molalities of NaCl are displayed. Figure 3 indicates that concentrations of calcium in equilibrium with earlandite have a dependence on concentrations of NaCl. The calcium concentrations first increase with NaCl molality.

Similarly, concentrations of calcium as a function of ionic strength in MgCl$_2$ solutions are displayed in Figure 4. Figure 4 suggests that concentrations of calcium in equilibrium with earlandite have a dependence on concentrations of MgCl$_2$ with rising solubilities with increasing MgCl$_2$ concentrations up to 1.0 mol•kg$^{-1}$. Above 1.0
mol\cdot kg^{-1} regarding molality of MgCl₂, the dependence of solubility on ionic strength become weaker, indicating a weaker, negative dependence on ionic strength.

3.2 Thermodynamic Modeling

In the following, the experimental data described above are used to derive the thermodynamic parameters. The dissolution of earlandite can be expressed as,

\[
\text{Ca}_3[\text{C}_3\text{H}_5\text{O(COO)}_3]_2\cdot 4\text{H}_2\text{O} \text{ (earlandite)} = 3\text{Ca}^{2+} + 2[\text{C}_3\text{H}_5\text{O(COO)}_3]^{3-} + 4\text{H}_2\text{O} \quad (1)
\]

At the same time, the formation of CaCitrate⁻ complex can be expressed as,

\[
\text{Ca}^{2+} + [\text{C}_3\text{H}_5\text{O(COO)}_3]^{3-} = \text{Ca}[\text{C}_3\text{H}_5\text{O(COO)}_3]^- \quad (2)
\]

Using experimental data produced in this study, the solubility constant of earlandite related to Reaction (1) and formation constant related to Reaction (2) along with a set of Pitzer parameters are obtained (Table 3), based on thermodynamic modeling with the Pitzer equations. The auxiliary parameters are listed in Table 3. The computer code, EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011), is used as the modeling platform, which was also used in previous modeling work for obtaining thermodynamic properties including the Pitzer parameters (e.g., Xiong et al., 2013, 2017; Xiong, 2013, 2015). The database containing all parameters necessary including thermodynamic properties for the modeling, is the fm1 database (data0.fm1) (Xiong, 2011). In the fm1
database, the interaction parameters for major ions are from Harvie et al. (1984), and the interaction parameters for organic ligands are from Choppin et al. (2001).

In the model fitting, the experimental data were first used to generate EQ3/6 input files. Then, a script such as a Python script was generated to call the targeted parameters, and call EQ3/6. The minimization subroutine in the script automatically compares total sum of squared residuals between experimental values [i.e., total calcium concentrations, \( \Sigma \text{Ca(II)/mol\cdot kg}^{-1} \)] and model-predicted values produced by each set of adjusted parameters in each iteration. The iteration is completed when the total sum of squared residuals reaches a minimum.

In Table 3, the dissolution constant for earlandite, the formation constant for \( \text{CaCitrate}^- \), and a set of Pitzer parameters describing the specific interactions of citrate species in NaCl and MgCl\(_2\) media are listed. These Pitzer parameters are similar to those found in the literature for the similar interactions in terms of magnitude. For instance, the \( \beta^{(0)} \) for \( \text{Mg}^{2+}--\text{CaCitrate}^- \) interaction, a 2:1 interaction, is 0.3760 (Table 3), which is similar to the \( \beta^{(0)} \) of 0.35235 for \( \text{Mg}^{2+}--\text{Cl}^- \) interaction (Harvie et al., 1984), also a 2:1 interaction. It is also similar to the \( \beta^{(0)} \) of 0.32 for \( \text{Na}^+-\text{H}_2\text{SiO}_4^{2-} \) interaction (Hershey and Millero, 1986), also a 1:2 interaction.

It is worth noting that the formation constant for \( \text{CaCitrate}^- \) obtained in this study is in excellent agreement with the literature values. In this work, the derived \( \log \beta_1^0 \) is 4.97. The \( \log \beta_1^0 \) experimentally evaluated by Davies and Hoyle (1953) 4.90. This agreement between the value determined in this study and those in the literature provide the additional support for the model presented here.
In the NEA review, $\log \beta_1^0$ for CaCitrate$^-$ has a value of $4.80 \pm 0.03$ (Hummel et al., 2005), evaluated with the SIT model. It is worth noting that the value evaluated in the NEA review is based on experimental data in low ionic strength range, i.e., predominantly at 0.1 mol•kg$^{-1}$. The NEA review series also mentioned that when the Pitzer and SIT models apply to the same data set for a reaction involving highly charged species such as NpO$_2$(CO$_3$)$_3^{35-}$, to calculate activity coefficients, the $\log K^o$ can differ by ~0.5 logarithmic units (Guillaumont et al., 2003). Therefore, it is expected that the $\log \beta_1^0$ evaluated in this work using the Pitzer model based on a data set over a wide range of ionic strengths would slightly differ from the value in the NEA review with the SIT model based on a data set in low ionic strength range predominantly at 0.1 mol•kg$^{-3}$.

The $\log K^0_{sp}$ presented in the NEA review was $-17.9 \pm 0.1$ (Hummel et al., 2005), using the SIT model for evaluation, based on the data limited to $I_m \leq 0.5$ mol•kg$^{-1}$ from Ciavatta et al. (2001). The $\log K^0_{sp}$ obtained in this study is $-18.11 \pm 0.05$, agreeing with the NEA value within the quoted uncertainties.

It should be noted that the $\beta^{(1)}$'s in Table 3 were not calculated. Instead, they are pre-set to the average values for the respective interactions, following the paradigm of Choppin et al. (2001). In Choppin et al. (2001), they calculated and recommended a set of average values of $\beta^{(1)}$'s for various interactions (e.g., 1:1, 1:2/2:1, 1:3/3:1, etc., interactions), based on the $\beta^{(1)}$ values for respective interactions from literature.

In the following, solubilities of earlandite in a wide range of ionic strengths predicted by the model are compared with experimental data. The solubilities of earlandite as a function of ionic strength in a NaCl medium predicted by the model...
developed in this study are represented by the solid curve in Figure 3. From Figure 3, it is clear that the model developed in this study can accurately describe solubilities of earlandite over a wide range of ionic strengths. There are few experimental studies on solubility of earlandite.

Notice that the model-predicted values are in excellent agreement with the model-independent solubility data of earlandite in water from Apelblat (1993), Vavrusova and Skibsted (2016).

It is worth noting that the solubility behavior of earlandite in NaCl solutions is different from that of Ca\textsubscript{2}EDTA\textbullet7H\textsubscript{2}O(s) in NaCl solutions (Xiong et al., 2017).

Regarding the solubility behavior of Ca\textsubscript{2}EDTA\textbullet7H\textsubscript{2}O(s) in NaCl solutions, the calcium concentrations first increase with NaCl molality in the range of 0.01 mol\textbullet kg\textsuperscript{-1} to 1.0 mol\textbullet kg\textsuperscript{-1} (Xiong et al., 2017). Above 1.0 mol\textbullet kg\textsuperscript{-1}, the calcium concentrations decrease with increasing concentrations of NaCl (Xiong et al., 2017). In contrast, the calcium concentrations in equilibrium with earlandite in NaCl solutions monotonically increase with molality of NaCl. This is due to the strong interactions between Na\textsuperscript{+} and Citrate\textsuperscript{3–} (Gácsi et al., 2016), as indicated by the negative values of $\beta^{(0)}$ and $C^{\phi}$ for Na\textsuperscript{+}—Ca[C\textsubscript{3}H\textsubscript{5}O(COO)\textsubscript{3}]\textsuperscript{2–} (Table 3).

Similarly, the solubilities of earlandite as a function of ionic strength in an MgCl\textsubscript{2} medium predicted by the model developed in this study are represented by the solid curve in Figure 4. It is clear from Figure 4 that the model developed in this study can satisfactorily reproduce solubilities of earlandite in MgCl\textsubscript{2} solutions over a wide range of ionic strengths. In the very high ionic strength range, the model predicts a slightly stronger negative dependence on ionic strength in comparison with the experimental
results. In addition, in contrast with the trend in a NaCl medium, the solubility of earlandite in a MgCl₂ medium does not change significantly with ionic strength at \( I_m \geq 3 \) mol•kg⁻¹.

The above thermodynamic modeling indicates that earlandite may be a solubility-limiting phase for citric aqueous concentrations dominated by Na-Mg-Cl in geological repositories when inventories of citrate increase to a level reaching the solubility limit of citrate.

4. CONCLUSIONS

Long-term solubility measurements up to 1,067 days and to high ionic strengths for earlandite in NaCl and MgCl₂ solutions produced at Sandia National Laboratories Carlsbad Facility are presented in this work. A Pitzer model is developed based on these solubility measurements. This model would provide accurate descriptions about the interaction of citrate with NaCl, and satisfactory descriptions about the interaction of citrate with MgCl₂, under various conditions with applications to many fields such as nuclear waste management and environmental remediation of heavy metal contamination.

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Table 1. Experimental results concerning solubility of earlandite, Ca$_3$[Citrate]$_2$$\cdot$4H$_2$O(s), in NaCl solutions produced at SNL at 22.5 ± 0.5 °C.

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* Values of pmH reported are calculated by using the correction factors ($A_M$) from Rai et al. (1995) for pH readings, and conversion factors ($\Theta$) from molarity to molality, $\text{pmH} = \text{pH}_{\text{ob}} + A_M - \log \Theta$ (Xiong et al., 2010). The conversion factors are calculated from densities for NaCl solutions, which are from Söhnel and Novotný (1985).
Table 2. Experimental results concerning solubility of earlandite, Ca₃[Citrate]₂•4H₂O(s),
in MgCl₂ solutions produced at SNL at 22.5 ± 0.5 °C.

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<td>pH</td>
<td>pmH</td>
<td>Conversion Factor</td>
</tr>
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<td>----------------</td>
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<tr>
<td>ACROS-ELDT-2.0 Mg-2</td>
<td>2.0</td>
<td>758</td>
<td>5.25</td>
<td>5.06E-02</td>
</tr>
<tr>
<td>ACROS-ELDT-2.5 Mg-1</td>
<td>2.5</td>
<td>758</td>
<td>5.14</td>
<td>4.85E-02</td>
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<tr>
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<td>0.010</td>
<td>813</td>
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<td>8.07E-03</td>
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<td>ACROS-ELDT-0.1 Mg-2</td>
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<td>4.96E-02</td>
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<td>2.5</td>
<td>813</td>
<td>4.79</td>
<td>4.73E-02</td>
</tr>
</tbody>
</table>

*Values of pmH reported are calculated by using the correction factors \(A_M\) from Hansen (2001) for pH readings, and conversion factors \(\Theta\) from molarity to molality, \(pmH = pH_{ob} + A_M - \log \Theta\) (Xiong et al., 2010). The conversion factors are from the EQ3 output files with the respective MgCl\(_2\) concentrations.
Table 3. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters in the Na\(^+\)—Mg\(^{2+}\)—Ca\(^{2+}\)—Cl\(^−\)—[C\(_3\)H\(_5\)O(COO)]\(_3\)\(^{3−}\) (or Citrate\(^{3−}\)) system

<table>
<thead>
<tr>
<th>Species, (i)</th>
<th>Species, (j)</th>
<th>(β^{(0)})</th>
<th>(β^{(1)})</th>
<th>(C^#)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>Ca[C(_3)H(_5)O(COO)](_3)(^{3−})</td>
<td>-0.1310</td>
<td>0.29 (^A)</td>
<td>-0.006818</td>
<td>This work</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>Mg[C(_3)H(_5)O(COO)](_3)(^{3−})</td>
<td>1.0915</td>
<td>1.74 (^A)</td>
<td>0</td>
<td>This work</td>
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<td>Mg(^{2+})</td>
<td>Ca[C(_3)H(_5)O(COO)](_3)(^{3−})</td>
<td>0.3760</td>
<td>1.74 (^A)</td>
<td>0</td>
<td>This work</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>[C(_3)H(_5)O(COO)](_3)(^{3−})</td>
<td>0.9330</td>
<td>4.4 (^B)</td>
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</table>

Pitzer Mixing Interaction Parameters

<table>
<thead>
<tr>
<th>Species (i)</th>
<th>Species (j)</th>
<th>Species (k)</th>
<th>(θ_{ij})</th>
<th>(ψ_{ijk})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>Ca(^{2+})</td>
<td>ClO(_4)(^−)</td>
<td>0.07</td>
<td>0.1574</td>
<td>(θ_{ij}) from data0.fm1; (ψ_{ijk}) from this work</td>
</tr>
</tbody>
</table>

Equilibrium Constants for Dissolution Reaction of Earlandite and Formation Reaction for Ca[C\(_3\)H\(_5\)O(COO)]\(_3\)\(^{3−}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log (K_{sp}) and log (β_l) at 25 (^o)C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(_3)[C(_3)H(_5)O(COO)](_3)(_2)•4H(_2)O (earlandite) = 3Ca(^{2+}) + 2[C(_3)H(_5)O(COO)](_3)(^{5−}) + 4H(_2)O</td>
<td>-18.1061</td>
<td>This work</td>
</tr>
<tr>
<td>Ca(^{2+}) + [C(_3)H(_5)O(COO)](_3)(^{3−}) = Ca[C(_3)H(_5)O(COO)](_3)(^{3−})</td>
<td>4.9730</td>
<td>This work</td>
</tr>
</tbody>
</table>

\(^A\) Values are set according to AP-154, Revision 2 (Xiong, 2013b).
\(^B\) The value for \(β^{(1)}\) is set to 4.4 based on the analog to that for the Mg\(^{2+}\)—NpO\(_2\)(CO\(_3\))\(_2\)\(^{3−}\) interaction from FM1.DATAM0, which originated from Al Mahamid et al. (1998).
Figure Captions

Figure 1. A plot showing experimental total calcium concentrations in equilibrium with earlandite, Ca$_3$(Citrate)$_2$$•$4H$_2$O(s), in NaCl solutions as a function of experimental time produced in this study.

Figure 2. A plot showing experimental total calcium concentrations in equilibrium with earlandite, Ca$_3$(Citrate)$_2$$•$4H$_2$O(s), in MgCl$_2$ solutions as a function of experimental time produced in this study.

Figure 3. A plot showing experimental total calcium concentrations in equilibrium with earlandite, Ca$_3$(Citrate)$_2$$•$4H$_2$O(s), produced in this study as a function of molalities of NaCl, in comparison with the predicted values based on the model developed in this work.

Figure 4. A plot showing experimental total calcium concentrations in equilibrium with earlandite, Ca$_3$(Citrate)$_2$$•$4H$_2$O(s), produced in this study as a function of ionic strengths in MgCl$_2$ solutions, in comparison with the predicted values based on the model developed in this work.
Figure 1.
Figure 2.
Solubility of Earlandite as Total Calcium Concentration ($\sum$Ca, mol∙kg⁻¹) vs. Ionic Strength of Supporting Electrolyte on Molality Scale ($m_{NaCl}$)

Figure 3.

Ciavatta et al. (2001)
Figure 4. Solubility of Earlandite as Total Calcium Concentration (Ω_Ca, mol/kg⁻¹) versus Ionic Strength of Supporting Electrolyte on Molality Scale (in MgCl₂ Solutions)

- 203 days, Experimental
- 385 days, Experimental
- 458 days, Experimental
- 660 days, Experimental
- 709 days, Experimental
- 758 days, Experimental
- 813 days, Experimental
- 961 days, Experimental
- Predicted by Model Developed in This Study