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Solubility of $FeC_2O_4 \cdot 2H_2O$ in $MgCl_2$ and NaCl Solutions[1]

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Introduction

- **Oxalate**
  - Present in the waste
  - Capable of solubilizing actinides via aqueous complexation
- **Iron (Fe)**
  - Present in the waste and containers
  - Buffers reduction potential in the repository via anoxic corrosion
  - Forms insoluble minerals with oxalate, such as, $FeC_2O_4 \cdot 2H_2O$

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Objectives

- To determine the solubility of $FeC_2O_4 \cdot 2H_2O$ in $MgCl_2$ and NaCl solutions and the relevant Pitzer ion-interaction parameters.

Material and Methods

- Iron(II) oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$, 99.999 % metal basis, Alfa Aesar)
- Reactors (serum bottles, 50 or 120 mL) were prepared in the glovebox (P_{O_2} less than 10 ppm, 26 ± 1.5 °C)
  - $FeC_2O_4 \cdot 2H_2O$ in $MgCl_2$ and NaCl solutions of various concentrations
  - Known volume of deoxygenated, deionized water was mixed with preweighed salts in the glovebox
  - For most conditions, more than two replicates prepared

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Material and Methods

- Fe(II) and Fe_T: ferrozine method coupled with UV-VIS spectrophotometer
- ICP-AES for Mg and Na
- IC for oxalate and Cl
- pH: glass combination electrode calibrated using commercial pH buffers
- XRD: characterization of solid

Speciation model for Fe^{2+}

	logK
$FeOH^{+} + H^{+} \Leftrightarrow Fe^{2+} + H_2O$:	9.31
$FeC_2O_4(aq) \Leftrightarrow Fe^{2+} + C_2O_4^{-2}$:	-3.79
$Fe(C_2O_4)_2^{-2} \Leftrightarrow Fe^{2+} + 2C_2O_4^{-2}$:	-5.90
$FeC_2O_4{\cdot}2H_2O(s) \Leftrightarrow Fe^{2+} + C_2O_4^{-2} + 2H_2O$:	-6.68
$MgOH^{+} + H^{+} \Leftrightarrow Mg^{2+} + H_2O$:	11.81
$MgC_2O_4(aq) \Leftrightarrow Mg^{2+} + C_2O_4^{-2}$:	-3.79

Activity correction made using the Pitzer formulations

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Fitting Procedure

$$S = \sum \left(\log Q_{\exp} - \log Q_{calc} \right)^2$$

- log Q_{exp} = log $m_{Fe}{}^{2+}$ + log $m_{Ox}{}^{2-}$
- log Q_{calc} determined by running EQ3
- Minimize S as a function of log K, Pitzer parameters

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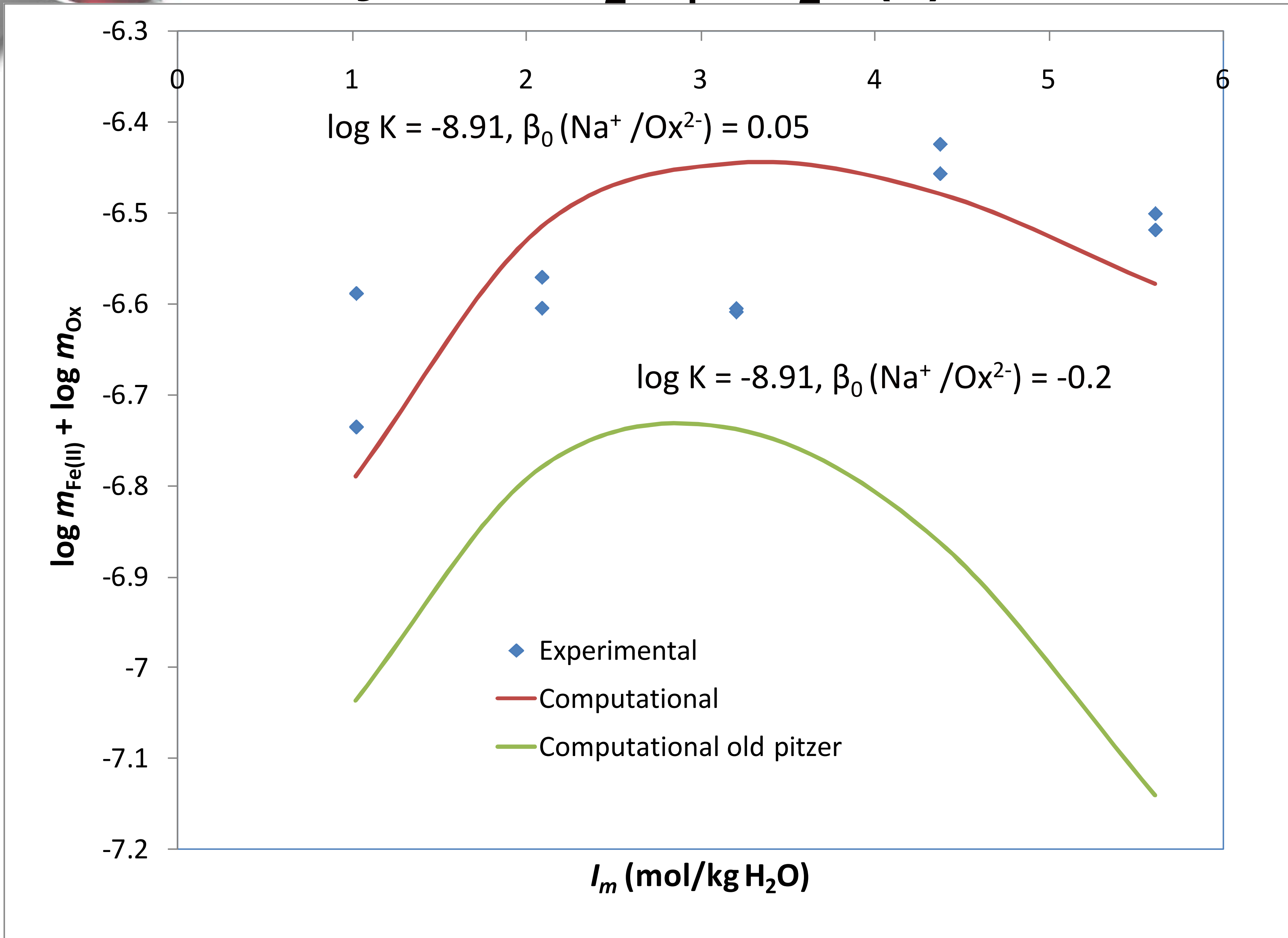
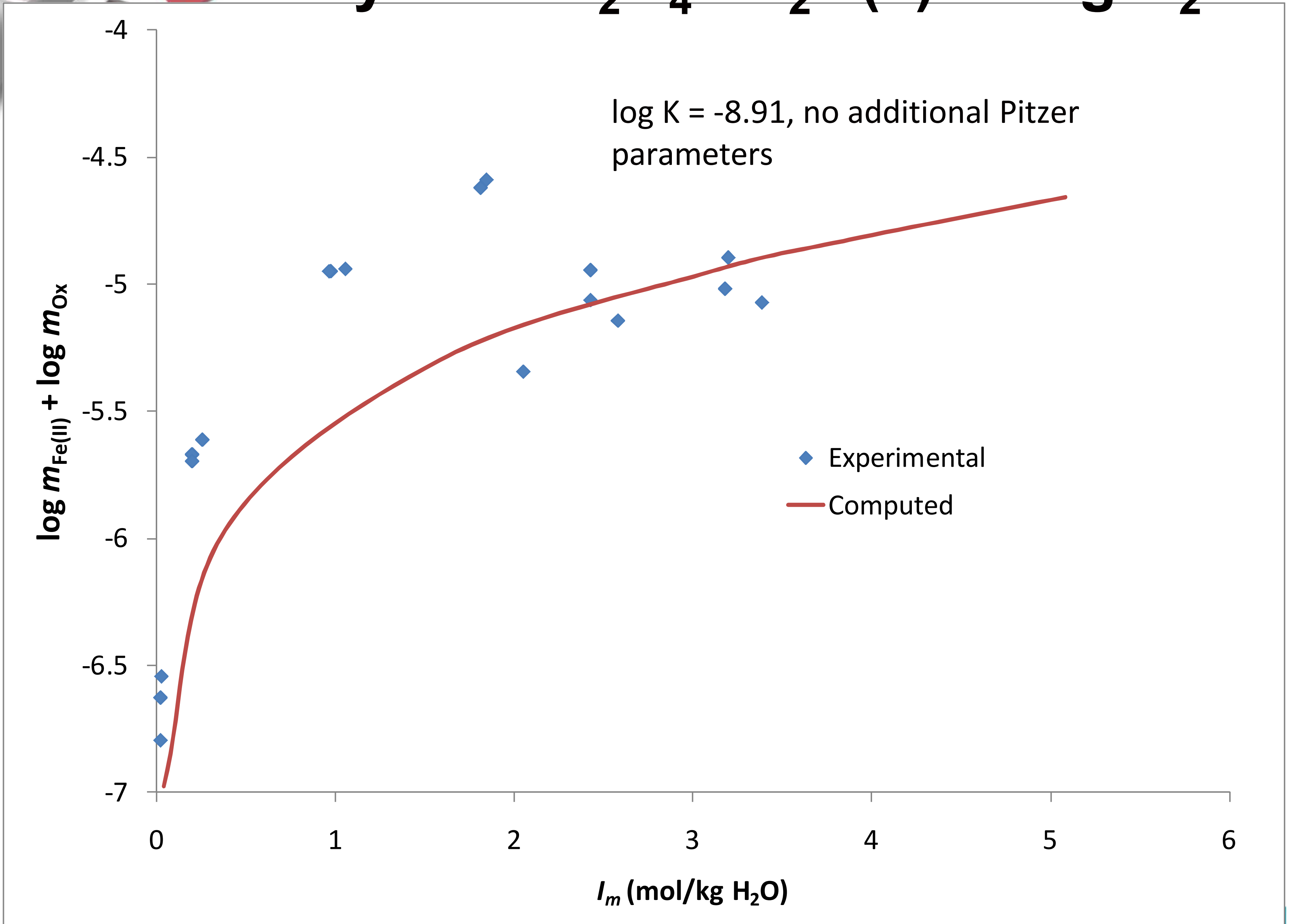
Solubility of $FeC_2O_4 \cdot 2H_2O(s)$ in NaCl



Solubility of $FeC_2O_4 \cdot 2H_2O(s)$ in $MgCl_2$



Conclusions

- **Preliminary modeling results indicated that use of lower solubility constant and adjusted Pitzer parameter resulted in better fit.**
  - **log K = -8.91**
  - **$\beta_0(Na^+/C_2O_4^{-2})$ = 0.05 for the experiment in NaCl solutions**
- **Future study includes the investigation of magnesium oxalate precipitation.**

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