Supporting Information

to

Oxygenation of Fe(II) in the Presence of Citrate in Aqueous Solutions at pH 6.0 – 8.0 and 25 °C: Interpretation from an Fe(II)/Citrate Speciation Perspective

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S-1. Extrapolation of the Stability Constant from $I = 1$ (in both NaCl and NaClO$_4$ Medium) to $I = 0$ using the Specific Ion Interaction Theory

For a general case of a complex formation reaction

$$nM + pL + rH_2O = M_nL_p(OH)_r + rH^+ \quad S-1$$

the formation constant of $M_nL_p(OH)_r$, $\beta_{npr}$, determined in a media of an ionic strength $I_m$, is related to the corresponding value at zero ionic strength, $\beta^0_{npr}$ by

$$\log \beta_{npr} = \log \beta^0_{npr} + n \log \gamma_M + p \log \gamma_L + r \log a_{H_2O} - \log \gamma_{npr} - r \log \gamma_H \quad S-2$$

where $\gamma_i$ and $a_{H_2O}$ are the activity coefficients of species $i$ and water in the media respectively. The general formula for the estimation of the activity coefficient $\gamma_i$ is given by

$$\ln \gamma_i = \ln \gamma_{DH} + \sum_j B_{ij}[S_j] + \sum_j \sum_k C_{ijk}[S_j][S_k] + ... \quad S-3$$

where the first term on the right hand side of eq S-3 ($\gamma_{DH}$) is simply the Debye-Hückel activity coefficient. The second virial coefficients ($B_{ij}$) account for specific interactions among pairs of ions while the third virial coefficients ($C_{ijk}$) account for specific interactions among three ions and so on. $[S_j]$ denotes the molar concentration of species $S_j$.

In this study, use is made of the method developed by Grenthe and Wanner$^2$ which has been accepted by IUPAC for the extrapolation of the stability constant from $I = 1$ to $I = 0$. In this method, estimation of the activity coefficient (eq S-3) stops with the second virial coefficients ($B_{ij}$) which, as indicated by Morel and Hering$^1$, could provide good agreement with experimental data up to ionic strength of about 4 M. The activity coefficient $\gamma_i$, expressed in base-10 logarithm, is given by

$$\log \gamma_i = -z_i^2D + \sum_j e_{(i,j,t_o)}[S_j] \quad S-4$$
where $z_i$ is the charge of specie $i$, $\varepsilon_{(i,j,I_m)}$ denotes for the specific ion interaction coefficient (SIT parameter) between species $i$ and $j$ in a media with an ionic strength $I_m$ (i.e., the second virial coefficients $B_{ij}$ in eq S-3) and $D$ is the Debye-Hückel term. At 25 °C, $D$ is given by \(^2\)

$$D = -\frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad \text{S-5}$$

If the concentration of electrolytes (1:1 salt NX) is much greater than the concentrations of M, L, H$^+$ and their complexes (i.e., $I_m \approx [N]=[X]$), only [N] and [X] need to be taken into account for the estimation of the second term in eq S-4. That is,

$$\log \gamma_M = -\frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} z_M^2 + \varepsilon_{(M,X,I_m)} I_m \quad \text{S-6}$$

$$\log \gamma_L = -\frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} z_L^2 + \varepsilon_{(L,N,I_m)} I_m \quad \text{S-7}$$

$$\log \gamma_{npr} = -\frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} z_{npr}^2 + \varepsilon_{(npr,I_m)} I_m \quad \text{S-8}$$

In addition, because the pH is defined as $-\log\{H^+\}$ in this study, the term that represents for H$^+$ activity ($\gamma_{H^+}$) in eq S-2 will not be considered. Thus, by substituting eqs S-6, S-7, S-8 to eq S-2 and assuming $\alpha_{H_2O} \approx 1$ (when water is used in large excess with respect to the reactants \(^2\)), the value of $\log^* \beta_{npr}$ can be determined.

In this study, due to the lack of SIT parameters for Fe$^{2+}$, the SIT data for Co$^{2+}$ \(^3,4\) is used for the extrapolation of the stability constant of various ferrous species from $I = 1$ in both NaCl and NaClO$_4$ medium to $I = 0$. If the interactions among solutes other than chemical reactions are mainly due to their electrical charge (considered as point charges), not their chemical nature then we would expect both Fe$^{2+}$ and Co$^{2+}$ have similar activity coefficients in the same medium (as they both have similar ionic radius and surface
charge). In addition, even though the specific ion interaction model is approximate, the set of values derived from this model is internally consistent. Therefore, the above assignment is considered to be reasonable. Summary of the SIT parameters used for the extrapolation of the stability constant of various Fe(II)-citrate complexes is given in Table S-1. Values of the stability constants (both original & extrapolated values) are given in Table S-2.

Table S-1. SIT Parameters Used for the Extrapolation of the Stability Constant of Fe(II)-Citrate Species from $I = 1$ (in both NaCl and NaClO₄ Medium) to $I = 0$

<table>
<thead>
<tr>
<th>Species $i$</th>
<th>SIT parameter, $\varepsilon_{i,i_{ref}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>NaClO₄</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.12 ± 0.01</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.16 ± 0.02</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>cit³⁻</td>
<td>-0.07 ± 0.04</td>
<td>-0.07 ± 0.04</td>
</tr>
<tr>
<td>FeHcit⁰</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fecit⁻</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>FeHcit²⁻</td>
<td>-0.3 ± 0.03</td>
<td>-0.3 ± 0.03</td>
</tr>
<tr>
<td>Fecit²⁺</td>
<td>-0.45 ± 0.03</td>
<td>-0.45 ± 0.03</td>
</tr>
<tr>
<td>Fe(OH)cit²⁻</td>
<td>-0.6 ± 0.03</td>
<td>-0.6 ± 0.03</td>
</tr>
</tbody>
</table>

(1) Ciavatta³ and (2) Pettit et al.⁴
Table S-2. Stability Constant, $\beta_{appr}$ of Fe(II)-Citrate Species from the Literature and the Extrapolated Values to $I = 0$ (this work)

<table>
<thead>
<tr>
<th>Medium</th>
<th>$\log\beta_{110}$</th>
<th>$\log\beta_{111}$</th>
<th>$\log\beta_{112}$</th>
<th>$\log\beta_{11-1}$</th>
<th>$\log\beta_{120}$</th>
<th>$\log\beta_{121}$</th>
<th>$\log\beta_{12-1}$</th>
<th>$\log\beta_{22-2}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M NaClO$_4$ (25 °C)</td>
<td>3.08</td>
<td>8.20</td>
<td>-0.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ham et al.$^3$</td>
</tr>
<tr>
<td>$I = 0$</td>
<td>5.24</td>
<td>10.58</td>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M NaClO$_4$ (20 °C)</td>
<td>4.40</td>
<td>8.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Timberlake $^6$</td>
</tr>
<tr>
<td>$I = 0$</td>
<td>5.72</td>
<td>9.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M KNO$_3$ (25 °C)</td>
<td>4.80</td>
<td>8.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Field et al. $^7$</td>
</tr>
<tr>
<td>$I = 0$</td>
<td>6.12</td>
<td>10.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I = 0$ (90 °C)</td>
<td>6.13</td>
<td>10.2</td>
<td>13.6</td>
<td>-0.86</td>
<td>7.80</td>
<td></td>
<td></td>
<td></td>
<td>Duffield et al. $^8$</td>
</tr>
<tr>
<td>0.15 M KNO$_3$ (37 °C)</td>
<td>4.56</td>
<td>8.72</td>
<td>11.0</td>
<td>11.9</td>
<td>-5.4</td>
<td></td>
<td></td>
<td></td>
<td>Amico et al. $^9$</td>
</tr>
<tr>
<td>$I = 0$</td>
<td>6.04</td>
<td>10.34</td>
<td>12.48</td>
<td>13.5</td>
<td>-4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 M NaCl (25 °C)</td>
<td>3.33</td>
<td>7.48</td>
<td>6.27</td>
<td>10.6</td>
<td>-0.86</td>
<td></td>
<td></td>
<td></td>
<td>Konigsberger et al. $^{10}$</td>
</tr>
<tr>
<td>$I = 0$</td>
<td>5.68</td>
<td>10.04</td>
<td>7.00</td>
<td>12.9</td>
<td>-2.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a \beta_{appr} = \frac{[M_nL_pH_r]}{[M]^n[L]^p[H]^r}$ from complexation reaction of the type $nM^+ + pL + rH = M_nL_pH_r$.

$^b$ Formation constant corrected using specific ion interaction theory (SIT) after Grenthe and Wanner. $^2$

$^c$ Formation constants corrected using Davies equation after Morel and Hering. $^1$

It should be noted that at low ionic strength, the term Debye-Hückel dominates the general formula of the activity coefficient. Therefore the extrapolated formation constants should be similar under such conditions whether the second virial coefficients (i.e., SIT method) or the third virial coefficients (i.e., Pitzer method) are incorporated in the formula or none of them (i.e., Debye-Hückel and Davies methods).
S-2. Justification of the Assumption that the Oxidation of Fe(II) is First-Order Kinetics with Respect to both Total [Fe(II)] and [O₂] (eq 1)

In the presence of millimolar concentrations of citrate, most Fe(II) is likely bound to citrate ions and the oxidation of Fe(II) therefore governed by the oxidation of organically complexed Fe(II) (denoted as Fe^{II\text{cit}}). The overall oxidation scheme, in analogy to the oxidation of inorganic Fe(II), thus can be described by reactions S-9 to S-12 below.

\[
\text{Fe}^{II\text{cit}} + O_2 \xrightarrow{k_1} \text{Fe}^{III\text{cit}} + O_2^- \quad \text{S-9}
\]

\[
\text{Fe}^{II\text{cit}} + O_2^- \xrightarrow{k_2} \text{Fe}^{III\text{cit}} + H_2O_2 \quad \text{S-10}
\]

\[
\text{Fe}^{II\text{cit}} + H_2O_2 \xrightarrow{k_3} \text{Fe}^{III\text{cit}} + OH^- + OH^- \quad \text{S-11}
\]

\[
\text{Fe}^{III\text{cit}} + O_2^- \xrightarrow{k_4} \text{Fe}^{II\text{cit}} + O_2 \quad \text{S-12}
\]

Note that the precipitation reaction of inorganic Fe(III) is excluded in the oxidation mechanism because most iron species are present in complexed forms. The disproportionation reaction of O₂⁻ is also excluded because it is unlikely to be important in the overall oxidation of Fe(II) \(^{11}\).

Applying rate law for reactions S-9 to S-12

\[
\frac{d[Fe(II)]_r}{dt} = \frac{d[Fe^{II\text{cit}}]}{dt} = -\{k_1[O_2] + k_2[O_2^-] + k_3[H_2O_2]\}[Fe^{II\text{cit}}] + k_4[O_2^-][Fe^{III\text{cit}}] \quad \text{S-13}
\]

Because superoxide reacts rapidly with organically complexed iron and the oxygenation of Fe^{II\text{cit}} is rather slow \(^{11,12}\), [O₂⁻] may reach to a steady state ([O₂⁻] ss) immediately. In addition, if the reactions S-9 and S-10 are assumed to control the overall oxidation of Fe(II) initially, condition of steady state concentration of [O₂⁻] would lead to an approximation

\[
k_2[O_2^-] \approx k_2[O_2^-]_{ss} \approx k_1[O_2] \quad \text{S-14}
\]

and
\[ k_4[O_2^-] \approx k_4[O_2^-]_{ss} \approx \frac{k_4}{k_2} \{k_1[O_2]\} \]  

S-15

On the other hand, the rate law expression for the change of \([H_2O_2]\) with time is given by

\[ \frac{d[H_2O_2]}{dt} = \left\{k_2[O_2^-] - k_3[H_2O_2]\right\}[Fe^{II}cit] \]  

S-16

Model simulation indicates that \(H_2O_2\) is always present at a concentration less than submicromolar under the experimental condition conducted in this study. Given our interest in the \(Fe(II)\)-citrate at concentrations above the sub-micromolar, it is reasonable to assume that \([Fe^{II}cit] >> [H_2O_2]\) during the course of experiments. Eq S-16 thus reduces to pseudo first-order and \([H_2O_2]\) is given by

\[ [H_2O_2] = \frac{k_2[O_2^-]}{k_3} \left\{1 - \exp(-k_3[Fe^{II}cit]t)\right\} \]  

S-17

Because the term \(\exp(-k_3[Fe^{II}cit]t)\) rapidly reduces to zero at the experimental time scale, a steady state concentration of hydrogen peroxide \([H_2O_2]_{ss}\) is immediately reached and estimated to be

\[ [H_2O_2]_{ss} = \frac{k_2[O_2^-]}{k_3} \]  

S-18

Therefore,

\[ k_3[H_2O_2] \approx k_3[H_2O_2]_{ss} \approx k_2[O_2^-] \approx k_1[O_2] \]  

S-19

Substituting eqs S-14, S-15 and S-19 into eq S-13 gives

\[ \frac{d[Fe(II)]_{II}}{dt} \approx -k_1[O_2] \left\{3[Fe^{II}cit] - \frac{k_4}{k_2}[Fe^{III}cit]\right\} \]  

S-20

If the reaction kinetics of both \(Fe(II)\)-citrate and \(Fe(III)\)-citrate with \(O_2^-\) are controlled by the rate of water exchange at the metal complex’s coordination sphere (in analogy to
the reaction between inorganic iron and \( \text{O}_2^{-13} \) and the kinetics of water loss of Fe(III)-citrate is slower than the kinetics of water loss of Fe(II)-citrate (simply due to charge effect) then it is possible to assume that \( k_4 < k_2 \). Therefore the back reduction of Fe(III)-citrate by superoxide that is included in eq S-20 may not be significant, particularly in the early stages of oxidation of Fe(II) where \([\text{Fe}^{II}\text{cit}] > [\text{Fe}^{III}\text{cit}]\). For this reason,

\[
\frac{d[\text{Fe}^{II}]}{dt} \approx -3k_i[\text{O}_2][\text{Fe}^{II}\text{cit}] \approx -3k_i[\text{O}_2][\text{Fe}(II)]_r
\]  

and the assumption that the oxidation of Fe(II) is first-order kinetics with respect to both total \([\text{Fe}(II)]\) and \([\text{O}_2]\) implicit in eq 1 is validated.

S-3. Testing of the Validity of the Kinetic Analysis Methodology

In this study, the absorbance of Fe\(^{II}\)FZ\(_3\) measured colorimetrically at 562 nm has been demonstrated to be equivalent to total Fe(II) (i.e., sum of the concentration of both inorganic Fe(II) and organically complexed Fe(II)). The validity of the experimental approach depends significantly on the mechanism by which FZ reacts with Fe(II) species (both organic and inorganic species). In previous studies \(^{14,15}\), it has been assumed that FZ reacts with organically complexed Fe(II) via a disjunctive pathway and that the dissociation of organically complexed Fe(II) is slow compared to the timescale of investigation. Under such conditions, the measured absorbance at 562 nm (of the Fe\(^{II}\)FZ\(_3\) complex) is therefore representative of the concentration of inorganic Fe(II) species only. This conclusion is however only appropriate when the contact time (incubation time) between FZ and the solution containing Fe(II) and organic ligand is short and the concentration of FZ used is small. Under such conditions, the exchange kinetics between FZ and Fe(II)-organic complexes is slow. At high concentration of FZ and long incubation time as used in this study, the measured absorbance of Fe\(^{II}\)FZ\(_3\) is found to be equivalent to the total Fe(II) concentration (i.e., the sum of the concentrations of both inorganic and organically complexed Fe(II)). Addition of 5 mM FZ to a mixture of 5 \(\mu\)M Fe(II) and 50 mM citrate (under anoxic conditions) gives an instant rise in absorbance which is similar to the absorbance that is measured in the absence of citrate. The rapid procurement of Fe(II)-citrate by FZ \(^{11}\) also supports the conclusion that under the
conditions of the studies undertaken here, FZ can acquire Fe(II) from Fe(II)-citrate complexes.

The possibility exists that if inorganic Fe(II) is reduced significantly by FZ complexation, then we might see dissociation of Fe(III) organic complexes and ongoing production of Fe(II) in order to re-establish the thermodynamically expected ratio of inorganic Fe(II) and Fe(III). In order to examine this possibility, a solution containing 5 μM Fe(II) and 50 mM citrate was left to oxidize for one hour. Over this period of time, oxidation of Fe(II) is assumed to reach completion and the end-products is assumed to be mostly Fe(III)-citrate. Concentrated FZ was then added to the solution and no reaction was clearly observed. This control experiment demonstrates that reduction of Fe(III) and its complexes by FZ is very unlikely under our experimental conditions. This is also in agreement with Pullin and Cabaniss\textsuperscript{14} who found no indication of FZ induced reduction of Fe(III) from either Fe(III) colloidal or organically complexed forms at pH 6.0 or pH 8.0.

S-4. Fe(II)/Citrate Speciation Based on Literature Constants

![Graph showing Fe(II)/Citrate Speciation based on Literature Constants](image-url)
Figure S-1. Speciation of Fe(II) in the presence of 5 mM citrate in buffered solutions (2 mM NaHCO₃, 0.1 M NaCl and 10 mM buffer MES/HEPES) based on the Timberlake model. [Fe]₀ = 5 μM. Data were calculated using MINEQL+. Other Fe(II) species are not shown because they both are present at low concentrations and have negligible effect on the overall oxidation of Fe(II).

Figure S-2. Speciation of Fe(II) in the presence of 5 mM citrate in buffered solutions (2 mM NaHCO₃, 0.1 M NaCl and 10 mM buffer MES/HEPES) based on the Amico et al. model. [Fe]₀ = 5 μM. Data were calculated using MINEQL+. Inorganic Fe(II) species are not shown because they both are present at low concentrations and have negligible effect on the overall oxidation rate of Fe(II).

S-5. References


