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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The kinetics of Fe(II) oxidation in the presence of various citrate concentrations have been investigated in aqueous solutions over the pH range 6.0−8.0 using colorimetry and speciation modeling. Oxidation of Fe(II) was interpreted and quantitatively modeled in terms of oxidation of various Fe(II)−citrate species. Using the model, it is possible to predict whether the presence of citrate would dominate the Fe(II) oxidation and thus enhance/retard the oxidation rate of Fe(II) and vice versa. The study also supports the presence of other Fe(II)−citrate species rather than just the monomeric species at circumneutral pH. At low pH and in a system where complexation of Fe(II) by citrate is dominant, oxidation of Fe(II) is controlled by the oxidation of both $Fecit^-$ and $Fecit_2^{4-}$. As the pH increases, the oxidation of $Fe(OH)cit_2^{5-}$ becomes increasingly important and dominates the oxidation of Fe(II) at pH 8.0. Rate constants for the oxidation of all five suggested Fe(II)−citrate species have been estimated and may be used to predict the rate of Fe(II) oxidation at any combination of pH and citrate concentration.

1. Introduction

Citric acid is ubiquitous in nature (5% by weight of lemon juice and 0.3% by weight of teeth and bone), is found in soil and plant exudates and is produced by microorganisms, especially fungi.[1,2] In plants, citric acid serves to depolymerize and solubilize ferric oxy-hydroxide in the vicinity of the roots and transports soluble Fe(III) to leaves.[3] In animals including humans, citrate is present in blood plasma at about 0.1 mM and is believed to be mostly associated with non-transferrin-bound iron.[4] Although it is not formed by bacteria, citrate may act as an exogenous siderophore, which can sequester Fe(III) that can subsequently be utilized by bacteria to satisfy their iron requirements. Indeed, *E. coli* was found to possess a transport system specific for ferric citrate.[5] Because of its strong affinity for metals, citric acid is also widely used in foods and beverages (as an anti-oxidant) and in a number of other industrial applications.

Despite the crucial role of citrate to iron metabolism in living organisms, the chemistry of iron−citrate is still poorly understood. The discrepancy among independent studies is reflected primarily in the disagreement between the suggested major iron−citrate species present with respect to both their stoichiometry and formation constants (Table 1). Because Fe(II) and Fe(II)−citrate can oxidize quite rapidly in the presence of ambient oxygen at physiological pH,[6,7] it is possible that many of the studies of the Fe(II)/citrate system have been complicated by the presence of varying proportions of inorganic Fe(II) and Fe(III) species as well as Fe(II)−citrate and Fe(III)−citrate. In addition, rapid formation of iron oxyhydroxide,[8,9] particularly at high Fe(II):citrate molar ratios, could cause light scattering and thus greatly obfuscate the study of the iron−citrate system in aqueous solutions at high pH.
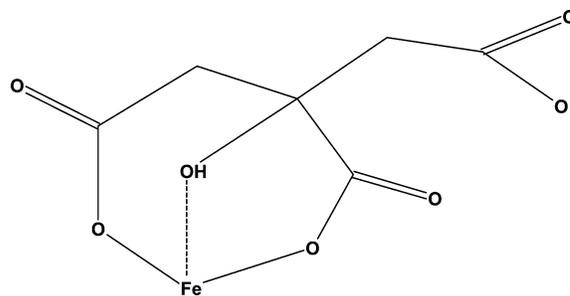

Figure 1. Proposed structure of $Fecit^-$.

Until the early 1970s, most Fe(II)/citrate models[10−12] assumed the presence of monomeric Fe(II)−citrate complexes (Table 1). This is a reasonable assumption because these early studies were carried out at low pH (pH < 5). In addition, X-ray structural studies of an Fe(II)−citrate complex crystallized from an alkaline solution[13] also revealed a monomeric form of Fe(II)−citrate complex in which the protonated hydroxyl group, the central carboxyl group and one terminal carboxyl group (of a citrate molecule), was coordinated to a single Fe(II) ion (Figure 1).

^{13}C NMR studies of the paramagnetic 1:1 Fe(II):citrate in alkaline solution at pH 7.6[14] however suggested that there may be several forms of the Fe(II)−citrate complex that are present. This finding was later supported by a number of studies[15−17] in which both monomeric and polymeric Fe(II)−citrate complexes have been considered. However, significant differences in the major Fe(II)−citrate species in the various models proposed are apparent (Table 1).

Adding to the uncertain coordination chemistry of Fe(II)/citrate[2] is the discrepancy among literature studies of the effect of citrate on the rate of Fe(II) oxidation. Early studies[18,19] reported an increase in the oxidation rate of Fe(II) in the presence of citrate at around neutral pH. On the other hand, Krishnamurti and Huang[20] and, more recently Rose and Waite,[21]

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TABLE 1: Literature Formation Constant, β_{npr},[a] of Fe(II)−Citrate Species at $I = 0$

log β_{110}	log β_{111}	log β_{112}	log β_{11-1}	log β_{120}	log β_{121}	log β_{12-1}	log β_{22-2}	ref[b]
5.24	10.58		0.91					1[c,e]
5.72	9.77							2[d,f]
6.12	10.06							3[d,e]
6.13	10.2	13.6	−0.86	7.80				4[g]
6.04	10.34	12.48			13.5		−4.2	5[d,h]
5.68	10.04			7.00	12.9	−2.18		6[c,e]

[a] $\beta_{npr} = [M_nL_pH_r]/[M]^n[L]^p[H]^r$ from reaction of the type $nM + pL + rH = M_nL_pH_r$. [b] (1) Ham et al.,[10] (2) Timberlake,[11] (3) Field et al.,[12] (4) Duffield et al.,[16] (5) Amico et al.,[15] and (6) Konigsberger et al.[17] [c] Formation constant corrected from $I = 1$ to $I = 0$ using specific ion interaction theory (SIT) after Grenthe and Wanner.[36] [d] Formation constants corrected from $I = 0.1$ and 0.15 to $I = 0$ using Davies equation. [e] At 25 °C. [f] At 20 °C. [g] At 90 °C. [h] At 37 °C.

found that citrate reduces the rate of oxidation of Fe(II). This incongruity can only be explained by detailed consideration of the particular experimental conditions and the associated iron species present.

In this study, the kinetics of Fe(II) oxidation in the presence of various citrate concentrations and at different pH are investigated in light of recently developed Fe(II)/citrate models. Because citrate fully deprotonates at neutral pH (except for the proton on the hydroxyl group), it reacts rapidly with Fe(II). At low Fe(II):citrate molar ratios, Fe(II) and citrate can be assumed to be at equilibrium prior to the oxygenation of the complexes and thus the overall oxidation of Fe(II) can be described in terms of oxidation of various individual Fe(II) species. Literature Fe-(II)/citrate models have been examined and the most appropriate model is selected on the basis of its ability to describe the experimental data. Oxidation rate constants of different Fe(II)−citrate species are estimated on the basis of the selected Fe(II)/citrate model. Using the model, discrepancies between previous studies of Fe(II) oxidation in the presence of citrate are examined.

2. Experimental Section

2.1. Terms and Definitions. Citric acid has three readily dissociable protons associated with its three carboxylic groups (pK_1 3.13, pK_2 4.76, pK_3 6.50[2]), and as a result, citric acid is traditionally denoted as H$_3$cit in most studies.[10−12,16,17] However, when citrate ions are coordinated to Fe(II) in neutral or alkaline solutions, the hydroxyl group may also be ionized (p$K_4 \sim 11$). Therefore, in recent studies,[2,22] citric acid has been considered as having four protonation sites (H$_4$cit) and the citrate ion denoted as cit^{4-}. Because we are interested in the Fe(II)/citrate system at circumneutral pH (pH 6.0−8.0) in the present study, citric acid is considered as having three dissociable protons and denoted as H$_3$cit. The citrate ion is denoted as cit^{3-}.

The terms "Fecit$^-$"and "Fe^{II}cit$^-$" (when both ferrous citrate and ferric citrate complexes are considered) refer to a specific 1:1 stoichiometry complex formed between Fe(2+) and cit (3−). Correspondingly, the terms "Fecit^0"and "Fe^{III}cit^0" refer to a specific 1:1 stoichiometry complex formed between Fe-(3+) and cit(3−). The term "Fe(II)−citrate" will be used to refer to any complex formed between Fe(II) and citrate ions including possibly Fecit$^-$, FeHcit^0, Fecit$_2^{4-}$, FeHcit$_2^{3-}$, Fe(OH)cit$_2^{5-}$ and Fe$_2$(OH)$_2$cit$_2^{4-}$. Correspondingly, the term "Fe(III)−citrate" refers to any complex formed between Fe(III) and citrate ions.

2.2. Kinetic Analysis. 2.2.1. Prediction of Pseudo First-Order Rate Constants of Fe(II) Oxidation in the Presence of Citrate. In the presence of high concentrations, of citrate, the oxidation of Fe(II) at any given pH, in analogy to its inorganic

oxygenation, is assumed to follow first-order kinetics with respect to both total [Fe(II)] and [O$_2$], i.e.

$$\frac{d[Fe(II)]_T}{dt} = -k^{app}[Fe(II)]_T[O_2] \qquad (1)$$

where [Fe(II)]$_T$ denotes total Fe(II) concentration (including both organic and inorganic Fe(II) complexes) and k^{app} is the apparent oxidation rate constant with units of M^{-1} s^{-1}. Justification of the assumption implicit in eq 1 is given in the Supporting Information.

At conditions where ambient oxygen concentration ([O$_2$]$_0$ = 2.61×10^{-4} M) is in excess of [Fe(II)]$_T$ (5 μM), eq 1 reduces to a pseudo-first-order and can be integrated to

$$[Fe(II)]_{T,t} = [Fe(II)]_{T,0} \exp(-k^{app}[O_2]_0 t) \qquad (2)$$

Hence a plot of $\ln\{[Fe(II)]_{T,t}/[Fe(II)]_{T,0}\}$ versus $\{-[O_2]_0 t\}$ should be a straight line with slope k^{app}. [Fe(II)]$_{T,t}$ is measured in these studies using the ferrozine method (see the experimental procedure below).

Inspection of the experimental data at various pH and citrate concentrations also shows an exponential decay of the total [Fe-(II)] over time, which further supports the assumption of pseudo first-order kinetics of Fe(II) oxidation in the presence of high concentrations of citrate.

2.2.2. Prediction of Oxygenation Rate Constant of Various Fe(II)−Citrate Species. If the oxidation of Fe(II) is described in terms of a number of parallel reactions involving the various Fe(II) species then the overall apparent rate constant (k^{app}) is the weighted sum of rate constants of any individual reaction;[23] i.e.

$$k^{app} = \sum_i k_{Fe(II)_i}\alpha_{Fe(II)_i} + \sum_j k_{Fe(II)L_j}\alpha_{Fe(II)L_j} \qquad (3)$$

where Fe(II)$_i$ represents inorganic Fe(II) species i, Fe(II)L$_j$ represents organic Fe(II) species j, k_i represents apparent oxidation rate constant of species i, and α_i is the molar fraction of species i in the total [Fe(II)].

To reduce the number of unknown parameters, we do not consider the oxidation of Fe(II) species by intermediate species including superoxide (O$_2^{\bullet-}$) and hydrogen peroxide (H$_2$O$_2$). The oxidation rate constant of species i and j in eq 3 instead should be considered as an apparent rate constant that accounts for the oxidation of this species by a number of different pathways.

The speciation of Fe(II) in the absence and presence of citrate was computed using the speciation package MINEQL$^+$.[24,25] Individual oxidation rate constants of various Fe(II)−citrate species (according to eq 3) were estimated using the least-squares method (in MATLAB).

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2.3. General Reagents. All solutions were prepared using 18 MΩ. cm Milli-Q water. All chemicals were analytical grade and purchased from Sigma-Aldrich (or as otherwise stated). All glassware was acid washed (using 5% w/v HNO_3) one week before use. Stock solutions were refrigerated (at 4 °C) in the dark when not in use.

Solutions at pH (p^aH) 6.0, 6.5, 7.0, 7.5, and 8.0 were prepared by adding appropriate concentrations of NaOH or HCl to solutions containing 10 mM buffer, 2 mM $NaHCO_3$, and 0.1 M NaCl. MES hydrate (2-(N-morpholino)ethanesulfonic acid hydrate, SigmaUltra) buffer was used for pH 6.0 and 6.5. HEPES (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid, SigmaUltra) buffer was used for pH 7.0, 7.5, and 8.0. Both MES and HEPES are noncomplexing agents[26] and do not participate in the various chemical reactions of iron species.[27]

All pH measurements were made using a Hanna HI9025 pH meter combined with a glass electrode and Ag/AgCl reference. The pH electrode was calibrated using NIST buffer solutions (pH 4.01, 7.01, and 10.01). During the course of experiments, no shift in pH was detectable to within ±0.02 pH units.

Temperature was maintained at 25 ± 0.6 °C at all times using a Thermoline recirculator and experiments were conducted in ambient light conditions at a room temperature setting of 25 °C.

Fe(II) stock solutions were prepared by dissolving ferrous ammonium sulfate hexahydrate ($Fe(NH_4SO_4)_2$·$6H_2O$) in 2 mM HCl. This level of acidity prevented Fe(II) oxidation over time scales of interest yet did not induce significant pH change when aliquots of the Fe(II) stock were added to sample solutions.

A ferrozine working solution of 0.1 M was prepared by dissolving 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p′-disulfonic acid, monosodium salt hydrate in buffer solutions and pH was adjusted accordingly. Ferrozine (FZ) was used as a color forming agent for determination of Fe(II) because it reacts extremely rapidly with Fe(II)[28,29] to form a stable purple complex at neutral pH with maximum absorbance at 562 nm and molar absorptivity of $\epsilon_{562} = 30\,000$ M^{-1} cm^{-1}.[30,31] In addition, FZ does not bind Fe(III) to any significant extent[32] and is commercially available.

Citrate working solutions (of 5, 10, 25, 50, and 100 mM) were prepared by dissolving disodium hydrogen citrate sesquihydrate ($C_6H_6Na_2O_7$·$1.5H_2O$) in buffer solutions and the pH of the solutions was adjusted accordingly.

2.4. Experimental Procedures. Fe(II) stock was added to solutions containing known concentrations of citrate and the reaction time was recorded by a stopwatch. In each subsequent period of time, 3.6 mL of solution was quickly pipetted into a 1.0 cm path length cuvette (6Q) that already contained 0.18 mL of 0.1 M ferrozine. Rapid complexation of Fe(II) and its complexes by concentrated ferrozine prevents both Fe(II) and Fe(II)−citrate being further oxidized. Experimental evidence confirms that 5 mM FZ in the reactor was sufficient to successfully out-compete the oxidation of both Fe(II) and Fe-(II)−citrate complexes for Fe(II). The resulting $Fe^{II}FZ_3$ complex was measured colorimetrically at 562 nm using a Cary 50 Bio UV−visible spectrophotometer. It is important to note that the absorbance of $Fe^{II}FZ_3$ measured in this study 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)) (see Supporting Information). Because the experiments were conducted over the circumneutral pH range 6.0−8.0, reduction of Fe(III) and its complexes by FZ is insignificant.[33]
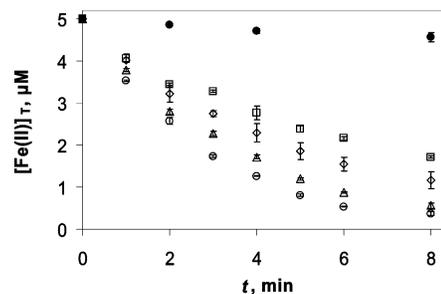

Figure 2. Oxidation of Fe(II) in the absence and presence of citrate at pH 7.0 and initial $[Fe(II)]_0 = 5$ μM. Symbols represent the experimental data in the presence of (●) no citrate, (□) 5 mM citrate, (◇) 10 mM citrate, (△) 50 mM citrate, and (○) 100 mM citrate. Error bars are standard errors for triplicate measurements.

Control solutions containing FZ (with no iron) were added in the reference cell to account for variations in lamp output during the experiments and the small background absorbance of the medium.

Calibration curves were developed at all pHs for 1, 2, 3, 4, 5, and 6 μM of Fe(II) in the presence of excess (5 mM) FZ with high r^2 values (>0.98).

3. Results

3.1. Fe(II) Oxidation in the Absence of Citrate. In the absence of citrate, the rate of oxidation of Fe(II) is slow at low pH, with the half-life of Fe(II) on the order of hours at pH 7.0 (Figure 2 and Table 2). However at pH 8.0, Fe(II) is rapidly oxidized with a half-life of only a few minutes (Figure 3 and Table 2). The increase in the oxidation kinetics of Fe(II) as the pH increases is due to the changes in inorganic Fe(II) speciation, particularly due to increase in the concentrations of highly reactive species such as $Fe(OH)_2^0$, $Fe(CO_3)_2^{2-}$, and $Fe(CO_3)(OH)^-$.[27,34]

3.2. Fe(II) Oxidation in the Presence of Citrate. In the presence of citrate, the rate of oxidation of Fe(II) increases markedly, particularly at low pH. Addition of 10 mM of citrate reduces the half-life of Fe(II) in the solution to the order of minutes at pH 7.0 (Figure 2 and Table 2). A similar effect was observed at pH lower than 7.0 but less effect of citrate was observed at pH 8.0 (Figure 3 and Table 2). Increase in the concentration of citrate also enhances the rate of Fe(II) oxidation at all pHs examined (Figure 2 and Figure 3). A summary of the apparent oxidation rate constants of Fe(II) (k^{app}, eq 1) in the absence and presence of various citrate concentrations at different pHs is given in Table 2.

As noted in the Introduction, enhancement of Fe(II) oxidation kinetics in the presence of citrate has been documented previously.[18,19] Nonetheless, Krishnamurti and Hoang[20] reported a decrease in the rate constant of Fe(II) oxidation with an increase in the citrate/Fe(II) molar ratio from 0 to 0.1 at pH 6.0 in 0.01 M ferrous perchlorate system. Rose and Waite[21] also observed a reduction in the rate of oxidation of Fe(II) in the presence of citrate in seawater. As will be illustrated below, this apparent discrepancy can be explained by the differences in the composition of Fe(II)−citrate species that are present in each of the systems considered.

4. Discussion

4.1. Modeling the Kinetics of Fe(II) Oxidation in the Presence of Citrate. **4.1.1. Selection of Fe(II)−Citrate Speciation Model.** To elucidate the effect of pH and citrate concentration on the kinetics of Fe(II) oxidation, it is important to determine the major Fe(II)−citrate species that are present

TABLE 2: Apparent Oxidation Rate Constants of Fe(II) (k^{app}, M^{-1} s^{-1}) in the Presence of Different Citrate Concentrations over the pH Range 6.0−8.0, [Fe(II)]$_0$ = 5 μM [Standard Errors Given for Triplicate Experiments]

[citrate], mM	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
0	$(2.1 \pm 0.1) \times 10^{-3}$	$(2.5 \pm 0.1) \times 10^{-2}$	0.5 ± 0.0	1.8 ± 0.1	18.1 ± 0.4
5	8.3 ± 1.8	9.2 ± 1.6	7.2 ± 1.1	9.0 ± 0.1	22.1 ± 1.4
10	10.5 ± 0.1	10.2 ± 0.6	10.6 ± 1.0	11.7 ± 0.1	23.3 ± 2.0
25	13.3 ± 0.1	14.1 ± 0.1	16.2 ± 0.6	16.9 ± 0.2	27.6 ± 0.2
50	15.3 ± 0.2	17.7 ± 0.1	17.7 ± 0.4	21.2 ± 0.8	30.6 ± 1.2
100	16.2 ± 0.6	19.8 ± 0.6	21.2 ± 0.7	25.2 ± 1.3	35.2 ± 0.1

in the system and their oxidation rate constants. However, as mentioned above, serious differences exist between studies with regard to the suggested major Fe(II)−citrate species present, their stoichiometry and their formation constants (Table 1). Our oxidation data nevertheless provides useful information for the selection of the most appropriate Fe(II)/citrate model at neutral and alkaline conditions.

If only monomeric Fe(II)−citrate species (i.e., FeHcit^0, Fecit$^-$, and Fe(OH)cit^{2-}) are included in the Fe(II)/citrate model, as suggested previously,[10−12] then the oxidation of Fe(II) is expected to remain constant in the presence of 5, 10, 25, 50, and 100 mM of citrate because Fecit$^-$ is the only complex that dominates at neutral and alkaline solutions (Figure S-1). As the oxidation rate of Fe(II) is enhanced in the presence of citrate, reactive inorganic Fe(II) species including Fe(OH)$_2$^{0}, Fe(CO$_3$)$_2$$^{2-}$, and Fe(CO$_3$)(OH)$^-$, which are present at much lower concentrations than is the case in the absence of citrate, are no longer considered to be important.

On the other hand, if the Fe(II)/citrate model proposed by Amico et al.[15] is used (Table 1) then the increase in the oxidation rate of Fe(II) when either pH or citrate concentration increases would suggest that Fe$_2$(OH)$_2$cit$_2$$^{4-}$ may solely control the oxidation of Fe(II) over the entire pH considered (Figure S-2). However, if this is the case then we would expect an almost 10-fold difference in the oxidation rate constant of Fe(II) between pH 7.5 and pH 8.0 because the concentration of Fe$_2$(OH)$_2$cit$_2$$^{4-}$ increases by almost 10-fold over this pH range (Figure S-2). The difference in rates observed however is significantly less than 10-fold (Table 2).

The Fe(II)/citrate model proposed by Duffield et al.[16] (Table 1) is not considered here because their studies were undertaken at high temperature (90 °C) and the constants derived are unlikely to be appropriate to the 25 °C conditions of our investigations.

In this study, use is made of the Fe(II)/citrate model developed by Konigsberger et al.[17] In this model, both monocitrate and dicitrate Fe(II) complexes are present at significant concentrations over a range of pH and citrate concentrations (Figure 4). Formation constants of Fe(II)−citrate species in this model are also in reasonable agreement with those reported in previous
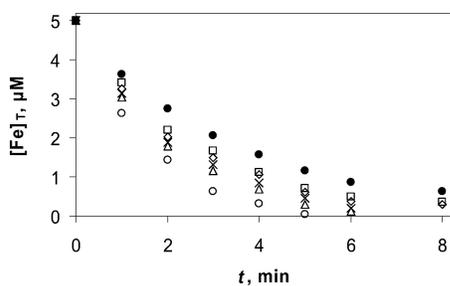
studies conducted at low pH. In addition, recent X-ray studies on the Fe(III)−citrate system[22,35] found that a dicitrate Fe(III) species is the dominant Fe(III) complex over a range of pH at low Fe(III):citrate molar ratios (1:20). This finding supports the likelihood of a dicitrate Fe(II) complex being present in our Fe(II)/citrate system at circumneutral pH.

4.1.2. Model Results and Kinetics Analysis. A list of all possible equilibrium reactions that may be considered relevant in the Fe(II)/citrate system is given in Table 3. Formation constants of Fe(II)−citrate species are taken from Konigsberger et al.[17] and extrapolated to zero ionic strength using specific ion interaction theory.[36] Details of the extrapolation are given in the Supporting Information. Because almost all Fe(II) is precomplexed by citrate, inorganic Fe(III) (as a product of oxidation of inorganic Fe(II)) is not significant in our system and therefore will not be included in Table 3.

To quantify the kinetics of oxidation of Fe(II) in the presence of different citrate concentrations, the overall oxidation rate constants of Fe(II) linearized from eq 2 were fitted to a model as described in eq 3. Oxidation rate constants of all five Fe-(II)−citrate complexes (i.e., Fecit$^-$, FeHcit^0, Fecit$_2$$^{4-}$, FeHcit$_2$$^{3-}$, and Fe(OH)cit$_2$$^{5-}$) were considered as part of the fitting exercise and were derived as follows.

In the presence of milimolar concentrations of citrate, oxidation of inorganic Fe(II) species is negligible because all reactive species such as Fe(CO$_3$)(OH)$^-$, Fe(CO$_3$)$_2$$^{2-}$, and Fe-(OH)$_2$^{0} are present at very low concentrations (at almost 2 orders of magnitude less than is the case in the absence of citrate). Therefore, the inorganic component can be ignored and eq 3 reduces to

$$k^{app} = k_{Fecit^-}\alpha_{Fecit^-} + k_{FeHcit^0}\alpha_{FeHcit^0} + \\ k_{Fecit_2^{4-}}\alpha_{Fecit_2^{4-}} + k_{FeHcit_2^{3-}}\alpha_{FeHcit_2^{3-}} + \\ k_{Fe(OH)cit_2^{5-}}\alpha_{Fe(OH)cit_2^{5-}} \quad (4)$$

It may not be possible to estimate the oxidation rate constant of FeHcit^0 based on the model and eq 4 because it is present at very low concentrations. In addition, the concentration of FeHcit^0 decreases as the pH and citrate concentration increase,
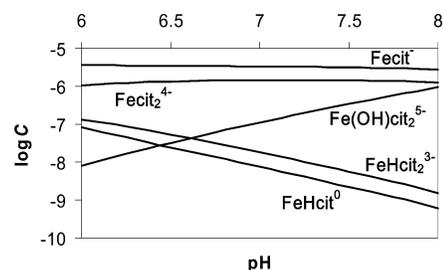

Figure 3. Oxidation of Fe(II) in the absence and presence of citrate at pH 8.0 and initial [Fe(II)]$_0$ = 5 μM. Symbols represent the experimental data in the presence of (●) no citrate, (□) 5 mM citrate, (◇) 10 mM citrate, (×) 25 mM citrate, (△) 50 mM citrate, and (○) 100 mM citrate. Error bars are omitted for clarity.

Figure 4. Speciation of Fe(II) in the presence of 5 mM citrate in buffered solutions (2 mM NaHCO$_3$, 0.1 M NaCl and 10 mM buffer MES/HEPES) based on the Konigsberger et al.[17] model. [Fe]$_T$ = 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).

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TABLE 3: Stability Constants for Formation of Fe(II) Complexes Considered in the Speciation Model

no.	species	log K, $I = 0$, 25 °C	ref[a]
1	$H^+ + OH^- = H_2O$	14.0	1
2	$H^+ + CO_3^{2-} = HCO_3^-$	10.3	1
3	$2H^+ + CO_3^{2-} = H_2CO_3^*$	16.7	1
4	$H^+ + cit^{3-} = Hcit^{2-}$	6.40	2
5	$2H^+ + cit^{3-} = H_2cit^-$	11.2	2
6	$3H^+ + cit^{3-} = H_3cit^0$	14.3	2
7	$NH_3 + H^+ = NH_4^+$	9.24	2
8	$H^+ + SO_4^{2-} = HSO_4^-$	1.99	2
9	$Fe^{2+} + H_2O = FeOH^+ + H^+$	−9.51	2
10	$Fe^{2+} + 2H_2O = Fe(OH)_2^0 + 2H^+$	−20.6	2
11	$Fe^{2+} + CO_3^{2-} = FeCO_3^0$	5.69	3
12	$Fe^{2+} + H^+ + CO_3^{2-} = FeHCO_3^+$	11.8	4
13	$Fe^{2+} + 2CO_3^{2-} = Fe(CO_3)_2^{2-}$	7.45	3
14	$Fe^{2+} + CO_3^{2-} + H_2O = Fe(OH)CO_3^- + H^+$	−4.03	3
15	$Fe^{2+} + Cl^- = FeCl^+$	0.30	3
16	$Fe^{2+} + SO_4^{2-} = FeSO_4^0$	2.42	3
17	$Fe^{2+} + cit^{3-} = Fecit^-$	5.68	5[b]
18	$Fe^{2+} + H^+ + cit^{3-} = FeHcit^0$	10.0	5[b]
19	$Fe^{2+} + 2cit^{3-} = Fecit_2^{4-}$	7.00	5[b]
20	$Fe^{2+} + H^+ + 2cit^{3-} = FeHcit_2^{3-}$	12.9	5[b]
21	$Fe^{2+} + H_2O + 2cit^{3-} = Fe(OH)cit_2^{5-} + H^+$	−2.18	5[b]
22	$Na^+ + CO_3^{2-} = NaCO_3^-$	1.27	3
23	$Na^+ + H^+ + CO_3^- = NaHCO_3$	10.1	3
24	$Na^+ + SO_4^{2-} = NaSO_4^-$	1.06	3
25	$Na^+ + cit^{3-} = Nacit^{2-}$	1.03	6
26	$Na^+ + H^+ + cit^{3-} = NaHcit^-$	6.45	6
27	$2Na^+ + cit^{3-} = Na_2cit^-$	1.5	6
28	$NH_4^+ + SO_4^{2-} = NH_4SO_4^-$	1.03	6

[a] (1) Millero et al.;[46] (2) Morel and Hering;[40] (3) King;[27] (4) Millero and Hawke;[47] (5) Konigsberger et al.;[17] (6) Schecher and McAvoy.[25] [b] Extrapolated to zero ionic strength using specific ion interaction theory (SIT).[36]

which suggests that its oxidation may not be important in the overall oxidation of Fe(II). An upper value for k_{FeHcit^0} however is estimated on the basis of an empirical equation developed by Tratnyek and Hoigne[37] (see section below).

The rate constants for all Fe(II)−citrate species (except for FeHcit^0) were estimated from linearization (according to eq 4) using the least-squares method (with 4 variables obtained from fitting 25 data points in MATLAB).

Results of the model fits and experimental data of the overall oxidation rate constant of Fe(II) described as the weighted sum of individual rate constants of various Fe(II)−citrate species (eq 4) are shown in Figure 5. The estimated individual rate constants of the five Fe(II)−citrate complexes are given in Table 4. In general, the model describes reasonably well the kinetics of oxidation of Fe(II) in the presence of various citrate concentrations and over a range of circumneutral pH. There are, however, some outliers in Figure 5 that the model is not able to describe. At 5 mM citrate and at pH 8.0, the model underestimates the oxidation rate constant of Fe(II). Slightly overestimation of the oxidation rate constant of Fe(II) at pH 7.5 is also observed at all citrate concentrations considered (Figure 5). Discussion of model uncertainties and possible source of errors are given in the Analytical Considerations section below.

According to the kinetics model, at low concentrations of citrate and low pH, the kinetics of oxidation of Fe(II) is primarily controlled by the oxidation of two major species, Fecit$^-$ and Fecit$_2^{4-}$ (Figure 6A). As the pH increases, the oxidation of Fe(OH)cit$_2^{5-}$ becomes increasingly important at any citrate concentration examined (Figure 6B). The oxidation of FeHcit^0 is predicted to be slow and therefore of negligible impact on the overall oxidation rate of Fe(II). The oxidation of FeHcit$_2^{3-}$
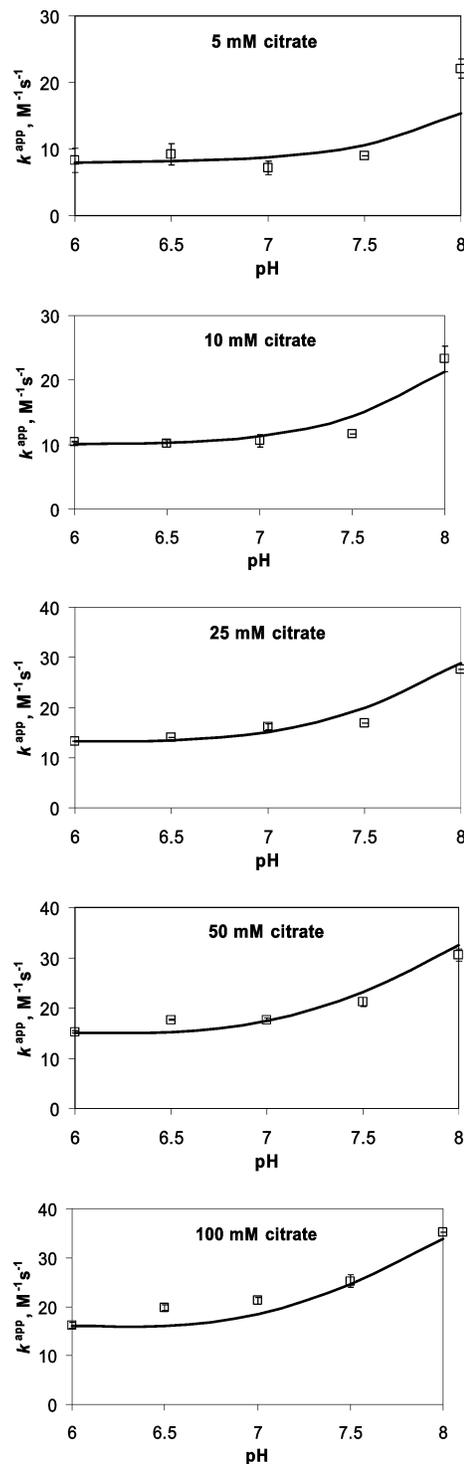

Figure 5. Modeled fits and experimental data of the apparent oxidation rate constant as the weighted sum of oxidation rate constants of individual Fe(II) species, $[Fe(II)]_0 = 5 \mu M$.

TABLE 4: Estimated Apparent Oxidation Rate Constants of Fe(II)−Citrate Species with O$_2$ at 25 °C

no.	species	k^{app} ($M^{-1}s^{-1}$)
1	Fecit$^-$	5.0
2	FeHcit^0	<5.0
3	Fecit$_2^{4-}$	16.3
4	FeHcit$_2^{3-}$	35.7
5	Fe(OH)cit$_2^{5-}$	46.5

is only important at low pH (pH 6.0 and 6.5) because its concentration decreases significantly at high pH (Figure 6).

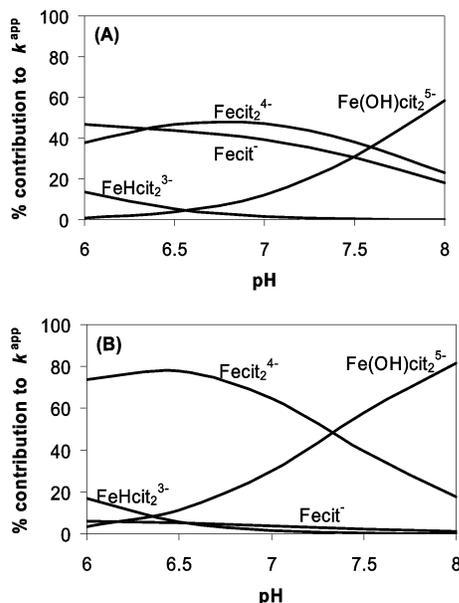**Figure 6.** Fractional contribution (%) of various Fe(II)−citrate complexes in the overall oxidation of Fe(II), $[Fe(II)]_0 = 5\ \mu M$. (A) in the presence of 5 mM citrate and (B) in the presence of 50 mM citrate. Oxidation of FeHcit^0 is negligible in both cases.

In contrast to the oxidation of inorganic Fe(II) species where the rate constant varies significantly between species,[27] the oxidation of Fe(II)−citrate complexes is generally slow and the rate constant varies by no more than an order of magnitude (Table 4). The low oxidation rate constants are found for monocitrate species with $k_{FeHcit^0} < 5.0\ M^{-1}\ s^{-1}$ and $k_{Fecit^-} = 5.0\ M^{-1}\ s^{-1}$. Dicitrate species on the other hand exhibit slightly higher oxidation rate constants with $k_{Fecit_2^{4-}} = 16.3\ M^{-1}\ s^{-1}$, $k_{FeHcit_2^{3-}} = 35.7\ M^{-1}\ s^{-1}$, and $k_{Fe(OH)cit_2^{5-}} = 46.5\ M^{-1}\ s^{-1}$ (Table 4).

4.2. Justification of the Derived Kinetic Constants Based on Linear Free Energy Relationships. The oxidation rate constants of Fe(II)−citrate complexes may be independently predicted using Marcus theory.[38] According to Wehrli,[39] oxygenation of Fe(II), including Fe(II) complexes, almost certainly proceeds via an outer-sphere electron-transfer mechanism, in which O_2 initially forms a precursor complex with the Fe(II), followed by electron transfer and dissociation of the successor complex without any change in the primary hydration sphere of the metal molecule. Such outer-sphere mechanisms would be expected to obey a linear free energy relation (LFER), and as such, Marcus theory[38] can be applied to estimate rate constants based on the free energy change of reactants.[40,41]

In addition, Tratnyek and Hoigne[37] developed an equation for direct calculation of the second-order rate constant based on the theory of Marcus,[38] which was successfully applied by King and Farlow[42] for the estimation of inorganic Fe(II) oxidation by H_2O_2 (presumably obeying the outer-sphere electron-transfer mechanism) and Rose and Waite[21] for the estimation of organic Fe(II) oxidation by O_2. That is,

$$k_{ox} = \frac{k_d}{1 + \dfrac{k_d}{K_d Z} \exp\left[\dfrac{\dfrac{\lambda}{4}\left(1 + \dfrac{\Delta G^\circ}{\lambda}\right)^2}{RT}\right]} \quad (5)$$

where $k_d = 10^{10}\ M^{-1}\ s^{-1}$ is the diffusion control limit, the combined term $k_d/K_d Z$ is assigned to a value of 0.1 (K_d is the equilibrium constant for the precursor complex and Z is the universal collision frequency factor).

The adjustable parameter λ is related to the energy required to reorganize the transition state and was determined to be 103 kJ/mol for inorganic Fe(II) complexes[42] and 135 kJ/mol for organic Fe(II) complexes.[21] In this study, for the purpose of crude estimation of the oxidation rate constants of Fe(II)−citrate species by O_2, λ is assigned to be 103 kJ/mol given that the energy required for the transition state re-organization of these simple organic Fe(II) complexes is likely to be similar to that of inorganic Fe(II) complexes.

At standard state concentrations (1.0 M), standard free energy change (ΔG^0) for $Fe^{II}L$ oxidation to $Fe^{III}L$ (L can be either inorganic anion or organic ligand) via one electron reduction of oxygen to superoxide is given by

$$\Delta G^0 = -F(E^0_{O_2 \to O_2^-} - E^0_{Fe^{III}L \to Fe^{II}L}) \quad (6)$$

where $E^0_{O_2 \to O_2^-} = -0.16$ V.[42]

On the other hand, the reduction potential $E^0_{Fe^{III}L \to Fe^{II}L}$ is estimated by applying the Nernst equation[40] as follows:

$$Fe^{3+} + e^- = Fe^{2+} \quad E^0_{Fe^{3+} \to Fe^{2+}} \quad \Delta G^0 = -FE^0_{Fe^{3+} \to Fe^{2+}} \quad (7)$$

$$Fe^{2+} + L = Fe^{II}L \quad K_{Fe^{II}L}$$
$$\Delta G^0 = -2.303RT \log_{10} K_{Fe^{II}L} \quad (8)$$

$$Fe^{III}L = Fe^{3+} + L \quad 1/K_{Fe^{III}L}$$
$$\Delta G^0 = +2.303RT \log_{10} K_{Fe^{III}L} \quad (9)$$

$$Fe^{III}L + e^- = Fe^{II}L \quad E^0_{Fe^{III}L \to Fe^{II}L}$$
$$\Delta G^0 = -FE^0_{Fe^{III}L \to Fe^{II}L} \quad (10)$$

Therefore,

$$-FE^0_{Fe^{III}L \to Fe^{II}L} = -FE^0_{Fe^{3+} \to Fe^{2+}} + 2.303RT \log_{10}\left(\frac{K_{Fe^{III}L}}{K_{Fe^{II}L}}\right) \quad (11)$$

or

$$E^0_{Fe^{III}L \to Fe^{II}L} = E^0_{Fe^{3+} \to Fe^{2+}} - 0.059 \log_{10}\left(\frac{K_{Fe^{III}L}}{K_{Fe^{II}L}}\right) \quad (12)$$

where $E^0_{Fe^{3+} \to Fe^{2+}} = 0.77$ V is the standard reduction potential of Fe^{3+} [40] and K_i is the stability constant of the complex i.

For the estimation of rate constant of Fecit$^-$ oxidation by O_2, substituting $\log_{10}[K_{Fe^{III}cit^0}/K_{Fe^{II}cit^-}] = 7.3$[17] to eq 12 gives

$$E^0_{Fe^{III}cit^0 \to Fe^{II}cit^-} = 0.77 - 0.059 \times 7.3 = 0.34 \quad (13)$$

Substituting eq 13 to eq 6 gives the standard free energy change $(\Delta G^0$, kJ mol$^{-1})$ for $Fe^{II}cit^-$ oxidation (to $Fe^{III}cit^0$) via one electron reduction of oxygen to superoxide,

$$\Delta G^0 = -F(E^0_{O_2 \to O_2^-} - E^0_{Fe^{III}cit^0 \to Fe^{II}cit^-}) =$$
$$-\frac{96490 \times (-0.16 - 0.34)}{1000} = 48.2 \quad (14)$$

Substituting eq 14 to eq 5 gives $k_{Fecit^-} = 18.9\ M^{-1}\ s^{-1}$.

This value is higher than our estimated values of 5.0 M^{-1} s^{-1} (Table 4). However, the energy required for complex reorganization (λ) of Fecit$^-$ should be higher than that for

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inorganic Fe(II) complexes (which are typically smaller molecules). The estimated rate constant of 18.9 M^{-1} s^{-1} therefore should be treated as an upper value for the oxidation rate constant of Fecit$^-$.

A similar approach can be applied for the estimation of the oxidation rate constant of FeHcit^0. Because FeHcit^0 is present at a negligible concentration, its oxidation rate constant is not well-established in our kinetic model. However, by comparing $\log[K_{Fe^{III}cit^0}/K_{Fe^{II}cit^-}] > \log[K_{Fe^{III}Hcit^+}/K_{Fe^{II}Hcit^0}][12]$ and assuming $\lambda_{Fe^{II}Hcit^0} > \lambda_{Fe^{II}cit^-}$, the oxidation rate of FeHcit^0 is expected (from Marcus theory) to be slower than the oxidation rate of Fecit$^-$.

For other Fe(II)−citrate complexes such as Fecit$_2^{4-}$, FeHcit$_2^{3-}$ and Fe(OH)cit$_2^{5-}$, even though the values of $\log[K_{Fe^{III}L}/K_{Fe^{II}L}]$ for those species (if the corresponding Fe(III)−citrate complexes exist) are likely higher compared to that of Fecit$^-$, the energy required for complex reorganization of these dicitrate complexes is expected to be higher (because they are larger molecules than Fecit$^-$). The oxidation rates of these complexes therefore would not be expected to be particularly high. This is also reflected in our model estimates of rate constants for the dicitrate Fe(II) species (Table 4).

The low rate constants estimated for oxidation of Fe(II)−citrate complexes such as Fecit$^-$ is consistent both with other reports and with expectation. Thus, Rose and Waite[21] reported a value of 2.6 M^{-1} s^{-1} for the oxidation rate constant of Fe-(II)−citrate. In comparison, both our own studies[43] and Santana-Casiano et al.[34] report a much higher rate constant for the oxidation of the mono complex Fesal^0 (of ∼ 1.0×10^4 M^{-1} s^{-1}). Because $\log[K_{Fe^{III}sal^+}/K_{Fe^{II}sal^0}] \gg \log[K_{Fe^{III}cit^0}/K_{Fe^{II}cit^-}]$,[40] it is expected that Fesal^0 will oxidize much faster than Fecit$^-$ according to Marcus theory.

4.3. Revisiting Literature Discrepancies in Light of the Current Oxidation Model. As mentioned above, our oxidation/speciation model of the Fe(II)/citrate system could help to explain why, in some systems, the presence of citrate could slow down the oxidation of Fe(II)[20,21] and, in the other cases, enhance the oxidation of Fe(II).[18,19]

In the Rose and Waite study,[21] although citrate was used in excess of Fe(II), bicarbonate complexation of Fe(II) (∼2.3 mM NaHCO$_3$ in seawater) still out-competes the complexation of Fe(II) by citrate (1 mM citrate) (also see Table 3 for formation constants of Fe(II) with carbonate and citrate ions). Oxidation of Fe(II) therefore is still controlled by oxidation of inorganic Fe(II) species. As demonstrated elsewhere,[27,34] the most reactive inorganic Fe(II) species that contributes largely to the overall inorganic oxidation of Fe(II) are Fe(CO$_3$)$_2^{2-}$, Fe(OH)$_2^0$, and Fe(OH)CO$_3^-$. In seawater and in the absence of citrate, the percentage of these species present under the conditions used by Rose and Waite[21] are 7.04×10^{-2}%, 5.21×10^{-4}%, and 2.25%, respectively. In the presence of citrate (at a molar ratio 8 nM Fe(II):1 mM citrate), the concentration of these species slightly reduces to 7.02×10^{-2}%, 4.98×10^{-4}%, and 2.20%, respectively. Although the reduction in concentrations of these highly reactive species are not significant compared to the decrease in the observed apparent rate constant reported in presence of citrate by Rose and Waite,[21] the speciation/oxidation model does help to explain that citrate does not enhance the oxidation of Fe(II) in their system. Furthermore, our measurements of Fe(II) oxidation in the presence of citrate using the chemiluminescence method[43] clearly indicated that citrate significantly reduced the chemiluminescence produced by the luminol oxidation product. Oxidation data using the chemiluminescence method therefore would need to be calibrated in the presence of citrate. This suggests that measured Fe(II) concentration may have been overestimated in the Rose and Waite[21] study. Thus, the lack of initial data points (before the steady flow condition in the FeLume system is reached) and the overestimation of measured Fe(II) concentrations in the presence of citrate coupled with the time zero Fe(II) concentration (which is independent of the calibration method) may lead to the misinterpretation of the oxidation rate. In addition, the oxidation of Fe(II) is rapid in seawater and observed to be strictly pseudo first order only during the initial 1−2 min of oxidation.[21]

It should also be noted that, under a circumstance where citrate complexation of Fe(II) is significant and the speciation is dominated by Fecit$^-$ and/or Fecit$_2^{4-}$ (see Pham[43]), then oxidation of Fe(II) at high pH (e.g., pH 8.0) may be slower in the presence of citrate. This is simply because both Fecit$^-$ and Fecit$_2^{4-}$ oxidize more slowly than the inorganic Fe(II) at high pH (Tables 2 and 4).

Krishnamurti and Hoang[20] also reported a decrease in the oxidation rate of Fe(II) in the presence of citrate. Because citrate was used at a much lower concentration than that of Fe(II), the presence of citrate would not be expected to alter the speciation of Fe(II) and is therefore unlikely to influence the kinetics of Fe(II) oxidation initially. However, strong complexation of Fe-(III) by citrate may retard the formation of iron oxyhydroxide, particularly in the later stage of the Fe(II) oxidation, as reported in Krishnamurti and Hoang.[20] An impediment of iron oxyhydroxide formation in turn may reduce the rate of autocatalytic oxidation of Fe(II), which could be important in the overall oxidation of Fe(II).[44,45]

On the other hand, in the systems where the concentration of citrate is high (submillimolar) and the concentration of bicarbonate is negligible (for example, in equilibrium with ambient air), as in the studies described by Theis and Singer[19] and Harris and Aisen,[18] most Fe(II) is complexed by citrate. In these cases, the oxidation of Fe(II) should be controlled by the oxidation of Fe(II)−citrate species and therefore would be expected to occur, at least at near neutral and acidic pHs, at a faster rate than corresponding inorganic systems. Caution however must be exercised in drawing conclusions concerning effects at pH 8.0 because inorganic oxidation of Fe(II) (at this pH) is faster than oxidation of the monomeric complex Fecit$^-$ (Table 4) but slower than that of Fe(OH)cit$_2^{5-}$. It is therefore important to determine the major Fe(II) species in the system before any prediction can be made.

4.4. Analytical Considerations. Although the Fe(II)/citrate kinetic model presented here provides a reasonable description of the effect of pH and citrate concentrations on the oxidation rate of Fe(II), the validity of estimated oxidation rate constants of individual Fe(II)−citrate species still relies greatly on a number of assumptions, particularly with regard to selection of the particular species present and their associated thermodynamic constants. Despite the conclusion that the Fe(II)/citrate model taken from Konigsberger et al.[17] is the most appropriate model to describe the effect of citrate and pH on the oxidation of Fe(II), it is not possible to guarantee that the assignment of major Fe(II)−citrate species proposed to be present is correct nor that their formation constants are accurate and uniquely defined. In addition, extrapolation of formation constants of Fe-(II)−citrate species from $I = 1$, as examined in Kongisberger et al.,[17] to zero ionic strength based on the specific interaction theory (SIT) has been oversimplified due to the lack of knowledge of several Fe(II)−citrate SIT parameters in NaCl medium (see Supporting Information).

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It is also assumed in this study that the overall oxidation rate of Fe(II) is first order with respect to both [Fe(II)]$_T$ and [O$_2$] (eq 1). This assumption only appears to be reasonable at times lower than the half-time ($t_{1/2}$) of Fe(II) oxidation. Estimated apparent rate constants from linearization (eq 2) and consequent oxidation rate constant of individual Fe(II) species predicted in the speciation model (Table 4) therefore should be treated as approximate values. Greater attention in future should be given to the possible impact of formation of superoxide and hydrogen peroxide, particularly in the later stages of the oxidation process where peroxide concentrations might be expected to become significant.

Poor prediction of the model at high pH (pH 7.5 and pH 8.0) and at high citrate concentration (100 mM) may suggest the presence of other (possibly polymeric) Fe(II)−citrate species and/or significant effects of other oxidation pathways.

5. Conclusion

In this study, the oxidation of Fe(II) in the presence of various citrate concentrations and over a range of circumneutral pH (pH 6.0−8.0) has been interpreted (and modeled quantitatively) from an Fe(II)/citrate speciation perspective. Using the model, it is possible to predict whether the presence of citrate would dominate the Fe(II) speciation and thus enhance the oxidation rate of Fe(II) and vice versa.

The study also supports the presence of other Fe(II)−citrate species in neutral and alkaline solutions other than just the two monomeric species Fecit$^-$ and FeHcit^0. It is also proposed that at low pH in a system where complexation of Fe(II) by citrate is dominant, oxidation of Fe(II) is governed by both Fecit$^-$ and Fecit$_2^{4-}$. As the pH increases, the oxidation of Fe(OH)cit$_2^{5-}$ becomes increasingly important and dominates the oxidation of Fe(II) at pH 8.0. Rate constants for the oxidation of five Fe(II)−citrate species have been estimated and may be used to predict the rate of Fe(II) oxidation at any combination of pH and citrate concentration.

Although a model for the overall oxidation of Fe(II) has been developed in terms of oxidation of its important individual species with the starting species concentrations determined using a specific Fe(II)/citrate speciation model, it does not guarantee that the selected speciation model could be accurately generalized to any environmental conditions. The large discrepancy among previous Fe(II)−citrate studies would suggest that more work is needed to validate the presence of major Fe(II)−citrate species, their stoichiometry, and their formation constants. Improvement of rate constants of individual Fe(II)−citrate species is also necessary to achieve an accurate estimation of the overall oxidation rate constant of Fe(II) in various environmental conditions. In addition, further attention to the impact of superoxide on the reduction of Fe(III)−citrate species and oxidation of Fe(II)−citrate species is needed, as is the possibility that hydrogen peroxide-mediated oxidation of Fe(II)-species becomes important in the later stages of the oxidation process.

Supporting Information Available: 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 and tables of SIT parameters and stability constants. S-2: Justification of the assumption that the oxidation of Fe(II) is first-order kinetics with respect to both total [Fe(II)] and [O$_2$] (eq 1). S-3. Testing of the validity of the kinetic analysis methodology. S-4. Figures of literature Fe(II)/citrate speciation models. This material is available free of charge via the Internet at http://pubs.acs.org.

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