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The effect of organic compounds in the oxidation kinetics of Fe(II)

J. Magdalena Santana-Casiano [a,*], Melchor González-Dávila [a], Ma. Jesús Rodríguez [a], Frank J. Millero [b]

[a] *Departamento de Química, Facultad de Ciencias del Mar, Universidad de Las Palmas de Gran Canaria, Las Palmas de Gran Canaria 35017, Spain*

[b] *Rosenstiel School of Marine and Atmospheric Science, University of Miami, Coral Gables, FL, USA*

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Abstract

The oxidation of Fe(II) has been studied in the presence of the natural organic compounds alanine, glutamic acid, cysteine, and two synthetic aminocarboxilates [(ethylenedioxi)diethylenedinitrilo]tetra-acetic acid (EGTA) and (ethylenedinitro)tetra-acetic acid (EDTA), as a function of pH_t (6–8), ionic strength (0.2–1 m) and temperature (5–35°C), in NaCl solutions, at different Fe(II)–organic compound ratios. Alanine and glutamic acid did not affect the oxidation kinetics of Fe(II). For these compounds, a second order pH dependence is obeyed over the pH range studied, where $\log k_{obs} = -16.29(0.16) + 2.09(0.02)pH$ and $\log k_{obs} = -15.26(1.3) + 1.94(0.18)pH$, for the alanine and glutamic acid, respectively. EGTA formed a strong ferrous complex that inhibited the oxidation of Fe(II) and EDTA increased the oxidation of ferrous iron forming a Fe(III)–EDTA complex that showed photoreduction in the presence of light, regenerating Fe(II). In the pH range from 6 to 8.2, the process was not affected by pH. The dependence with ionic strength was described by the equation $\log k = 15.351 + 0.565I^{1/2} - 1.388I$. Cysteine modified this behavior as a function of the Fe(II)–cysteine ratios. A Fe(III)–cysteine complex is formed through a one-electron transfer process that involved the thiol group and resulted in the reduction of Fe(III) back to Fe(II), and the oxidation of cysteine to cystine. The Fe(OH)L complex formation and reduction was affected by pH and cysteine concentration. A kinetic model that describes the behavior observed has been developed.

Keywords: Fe(II); oxidation; amino acids; EGTA; EDTA

1. Introduction

Iron is an element of great biological and geochemical importance. Iron plays an essential role in photosynthesis and it has been suggested to be a potential factor in limiting phytoplankton production in high-nutrient, low-chlorophyll areas of the oceans (Martin and Fitzwater, 1988; Martin and Gordon, 1988). The transformation of Fe(III) in water occurs in many geochemical environments: at the oxic/anoxic boundary in marine and freshwater basins; at the oxycline, which exists in sediments; at the sediment–water interfaces; and in surface seawaters by

* Corresponding author. Tel.: +34-928-45-44-48; fax: +34-928-45-29-22.

E-mail address: magda@cicei.ulpgc.es (J.M. Santana-Casiano).

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photochemical processes. The Fe(III) in marine aerosols and rainwater can be reduced to Fe(II) by photochemical processes and by its reaction with sulfite (Millero et al., 1995a). Ferric oxide/hydroxide formation caused by the changes of the redox potentials in water, such as the spring and fall turnover in lakes systems (Davison et al., 1982), has an impact on the distribution of trace metals and organic compounds through adsorption and coprecipitation. In addition, the Fe(III)-oxide particles in surface water attenuate light, affecting photosynthesis. However, the iron oceanic chemistry, such as inorganic speciation and organic complexes, is very complex and not yet fully understood. The kinetics of oxidation of Fe(II) have been studied in fresh water (Stumm and Lee, 1961; Ghosh, 1974; Tamura et al., 1976; Sung and Morgan, 1980; Davison and Seed, 1983) and in seawater (Kester et al., 1975; Murray and Gill, 1978; Roekens and Van Grieken, 1983; Waite and Morel, 1984; Millero, 1989; Millero and Izaguirre, 1988; Millero et al., 1987a,b). Dissolved Fe can exist in two different oxidation states in seawater, Fe(II) and Fe(III). Fe(III) is the thermodynamically stable form in oxygenated waters. However, in surface waters, there are several processes that reduce Fe(III) leading to measurable steady concentrations of Fe(II). This inorganic Fe(II) is oxidized back to Fe(III) with a half-life time of a few minutes (Millero et al., 1987b). The inorganic Fe(III) speciation is dominated by their hydrolysis products (with $Fe(OH)_2^+$, and possibly, $Fe(OH)_3$, as the dominant inorganic species in seawater). The oxidation of Fe(II) is strongly affected by the formation of inorganic complexes in natural waters, $FeCO_3$, $FeOH^+$, $FeHCO_3^+$ (King et al., 1995; Millero et al., 1995b).

King (1998) developed a mixed specific interaction–ion-pairing model for Fe(II) speciation and oxidation by molecular oxygen as a function of pH and media composition. The model is in accordance with the experimental results and determines that ferrous carbonate complexes [$FeCO_3$, $Fe(CO_3)^{2-}$ and $Fe(CO_3)OH^-$] dominate the speciation of Fe(II) in natural waters containing greater than 1 mM carbonate alkalinity. This model provides a reference point to evaluate Fe(II) oxidation by O_2 in natural waters, where organic ligands and surfaces may accelerate or decelerate the rates.

Since Fe(II), as well as the other metals, can form strong organic complexes, one might expect organic ligands to also affect its oxidation (Kester et al., 1975; Millero, 1985; Millero et al., 1987b). Theis and Singer (1973, 1974) found that tannic acid, gallic acid and pyrogallol prevented the oxidation of Fe(II). Other organics, such as glutamic acid, tartaric acid and glutamine slowed down the oxidation. Citric acid, however, accelerated the oxidation; phenol and histidine had no observable effect on the oxidation reaction. Although these studies demonstrate that organic can inhibit, retard or accelerate the oxidation of Fe(II), these measurements were made in distilled water and low pH, 6.3, and not in the range of natural waters.

Emmenegger et al. (1998) studying Fe(II) oxidation in lake water found that the Fe(II) oxidation showed a marked acceleration at pH lower than 7.5, attributed to the presence of organic ligands. The effect of the presence of surfaces in the Fe(II) oxidation has been also reported (Tamura et al., 1976; Sung and Morgan 1980; Wehrli, 1990; Amirbahman et al., 1997; Emmenegger et al., 1998).

To elucidate the effect that organics can produce on the oxidation of Fe(II) with O_2, we have studied the effect that a number of organic compounds, like alanine, cysteine, glutamic acid, (ethylenedinitro)tetra-acetic acid (EDTA) and [(ethylenedioxi)diethylenedinitrilo]tetra-acetic acid (EGTA) have on the oxidation of Fe(II) in NaCl solutions as a function of pH, I, T, and different Fe(II)–amino acid ratios. Although thermodynamic calculations are useful in attempting to determine the most probable redox and complexed form of a metal in aqueous solutions, the speciation is normally controlled by the kinetics of redox reactions. The formation of ion-pairs or complexes can either accelerate or decrease the rates of oxidation and reduction of metals in natural waters (Millero, 1990; Millero et al., 1995a).

2. Experimental

2.1. Chemicals

Fe(II) stock solutions (0.05 M) were prepared using $FeCl_2 \cdot 4H_2O$ (Merck), acidified with HCl

(Millero et al., 1987b). Stock solutions (5 mM) of different organic compounds were prepared with deionized water. The organic compounds studied are DL-alanine, L-glutamic acid, L-cysteine, EGTA and EDTA (Sigma). The complexation constants for these ligands with Fe(II) and Fe(III) are listed in Table 1. The corresponding total inorganic (hydroxo and carbonate) iron and Fe–L complex concentrations coordinated by each ligand is also included (Fe(II):L of 1:100).

2.2. Oxygen concentration

All of the measurements were made in solutions saturated with air. The solution was saturated at 25°C by bubbling with air.

2.3. pH measurements

Since the oxidation of Fe(II) in aqueous solutions is strongly dependent upon the pH (Davison and Seed, 1983), the solutions were buffered with 0.009 m $NaHCO_3$. This buffer system can adequately control the pH to ± 0.01 during an experimental run (Millero et al., 1987a,b). Tris-(hydroxymethyl)aminomethane (TRIS)–NaCl buffers (Millero, 1986; Millero et al., 1987a,b, 1993) were used to calibrate the electrode system and calculate the pH of the solution. This buffer was prepared by adding 0.005 m TRIS and 0.005 m TRIS–hydrochloride to 0.7 m NaCl. In the studies of ionic strength, the concentration of NaCl was changed. The pH was measured on the total scale with an Orion pH meter using an Orion glass electrode and an Orion Calomel reference electrode. The outer sleeve of the reference electrode was filled with 0.7 m NaCl.

Table 1
Ionization and complexation constants for the different organic ligands, and Fe(II) and Fe(III) used in this work. Data are after Martell and Smith (1974) and corrected for ionic strength effects. With these data, the fraction of Fe(II) coordinated by each ligand at pH = 7.98, $I = 0.7$ and $T = 25$°C was estimated

Compound	$-\log K_a$	$\log K_{f,\,\mathrm{Fe(II)-L}}$	$\log K_{f,\,\mathrm{Fe(III)-L}}$	%Fe(II)–L
Alanine	9.64	3.58	10.2	7.5
Glutamic acid	9.56	3.53	12.0	7.4
Cysteine	8.13	–	–	–
EGTA	8.76	11.78	20.2	100
EDTA	6.09	14.25	24.9	100

2.4. Oxidation experiments

Fe(II) oxidation experiments were performed by adding 20-μM Fe(II) to the O_2-saturated 0.7-m NaCl solutions buffered with 0.009-m HCO_3^-. For the ligand effect experiments, organics were added to the NaCl solution before the iron addition. Reactions were studied in a 500-ml glass thermostatically controlled vessel. The temperature was controlled to 25 ± 0.02°C with a Selecta circulating bath. The top of the vessel had four openings, one for a glass frit to bubble air–CO_2 mixture through the solutions, two for the glass and reference electrodes, and one to insert a 10 cm^3 calibrated automatic repipette, from which the samples were taken. The solutions were stirred with a teflon-coated magnetic stirrer.

2.5. Fe(II) analysis

The Fe(II) concentrations were determined spectrophotometrically using the bathophenantroline technique (Sung and Morgan, 1980; Millero et al., 1987b). The absorbance was measured at 511 nm on a Hewlett Packard Spectrophotometer using a 10-cm pathlength cell.

2.6. Fe(III)–cysteine analysis

The Fe(III)–cysteine complex concentrations were determined spectrophotometrically at 492 nm (Jamenson et al., 1988a,b). In alkaline solutions, cysteine reacts with Fe(III) to form a pink complex, which rapidly disappears with the formation of Fe(II) and cystine.

3. Fe(II) kinetic background

Reactions 1–4 describe the mechanism of the oxidation of Fe(II) by O_2. Reactions 2 and 4 are

much faster than the rate-determining reactions 1 and 3 in natural waters.

$$\mathrm{Fe(II)} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{Fe(III)} + \mathrm{O_2^{\cdot -}} \quad (1)$$

$$\mathrm{Fe(II)} + \mathrm{O_2^{\cdot -}} \xrightarrow{k_2 2\mathrm{H}^+} \mathrm{Fe(III)} + \mathrm{H_2O_2} \quad (2)$$

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \xrightarrow{k_3} \mathrm{Fe(III)} + \mathrm{HO^{\cdot}} + \mathrm{OH^-} \quad (3)$$

$$\mathrm{Fe(II)} + \mathrm{HO^{\cdot}} \xrightarrow{k_4} \mathrm{Fe(III)} + \mathrm{OH^-} \quad (4)$$

When the Fe(II) concentration is at micromolar levels, this elevated Fe(II) concentration ensures that the steady-state concentrations of $O_2^{\cdot -}$, H_2O_2 and $OH^{\cdot}$ are reached rapidly in all the kinetic runs (King et al., 1995). From both the results obtained and the observed 4:1 stoichiometry, King et al. (1995) considered that the CO_3^{2-} radical must be implicated in the Fe(II) oxidation by $OH^{\cdot}$ by acting as an intermediate. They indicated that at 100 μM Fe(II), 99% of the $OH^{\cdot}$ reacts with CO_3^{2-} and less than 1% of the $OH^{\cdot}$ is reduced directly by Fe(II).

Although CO_3^{2-} shows a high complexation capacity for Fe(II), increasing the Fe(II) oxidation rate, carbonate buffer was used in our studies because we were interested in natural water systems that have carbonate. In order to keep its effect constant in all the studies, carbonate concentration was fixed at 9 mM.

The overall rate constant for the oxidation of Fe(II) is given by

$$\frac{\mathrm{d[Fe(II)]}}{\mathrm{d}t} = -k'[\mathrm{Fe(II)}][\mathrm{O_2}] \quad (5)$$

where k' is a complex function of pH and media composition. In the absence of a ligand and at a constant pH and pO_2, the time dependence of the ferrous iron concentration is the same as that for a simple first-order reaction (Millero et al., 1987a,b).

$$\frac{\mathrm{d[Fe(II)]}}{\mathrm{d}t} = -k_{\mathrm{app}}[\mathrm{Fe(II)}] \quad (6)$$

At micromolar Fe(II) concentrations, a 4:1 stoichiometry of oxidation by oxygen is expected. Thus, the reported rate constants are four times larger than the $\mathrm{Fe(II)} + \mathrm{O_2}$ rate. The presence of organic material in the medium modifies the values of these constants working at the same conditions due to the competitive effects produced between the redox and the complexing processes. A limitation of the kinetic model for Fe(II) oxidation is the uncertainty in the role that organic ligands play in the oxidation rates. The organic chromophore reacts with O_2 to form $O_2^{\cdot -}$, and then, H_2O_2 (Faust and Zepp, 1993).

In the presence of excess organic compounds for each pH, we can define an observed pseudo-first-order rate constant k_{oc} instead of k_{app}.

$$\frac{\mathrm{d[Fe(II)]}}{\mathrm{d}t} = -k_{\mathrm{oc}}[\mathrm{Fe(II)}] \quad (7)$$

The results of the Fe(II) oxidation experiments at different experimental conditions were treated as pseudo-first-order (Fig. 1). Due to the micromolar levels of Fe(II) used in our experiments, which produce steady-state levels of H_2O_2 (King et al., 1995), a linear dependence was found.

Emmenegger et al. (1998) and Voelker and Sulzberger (1996), in order to explain the deceleration found for the oxidation Fe(II) rates, developed a simple model that describes the oxidation of Fe(II) by O_2 in two parallel pathways that involves both

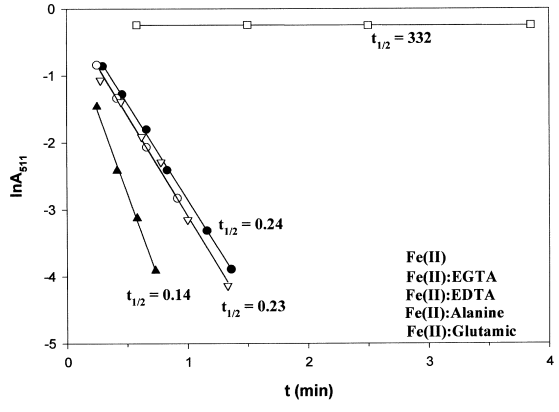

Fig. 1. Fe(II) oxidation shows pseudo-first-order kinetics in 0.7 m NaCl solutions (0.009 M HCO_3^-) in the presence of organic compounds (Fe(II):L 1:100) at pH 7.98, $t = 25$°C, $[\mathrm{Fe(II)}]_o = 20$ μM.

the inorganic Fe(II) species and Fe(II)–L complex. Defining α_i as the fraction of hydroxo and carbonate complexes, and α_L as the fraction of Fe(II)–L,

$$k_{oc} = \alpha_i k_i + \alpha_L k_L . \quad (8)$$

4. Results and discussion

Organic compounds can form complexes with both Fe(II) and Fe(III) as a function of the pH of the solution and ligand stabilization capacity of the organic compounds.

$$Fe(II) + O_2 \Leftrightarrow Fe(III) \quad (9)$$

$$FeL^+ \Leftrightarrow Fe(II) + L^- \quad (10)$$

$$FeL^{2+} \Leftrightarrow Fe(III) + L^- \quad (11)$$

The Fe complex formation will affect the oxidation rate due to the simple attenuation of the free Fe(II) concentration. The complex formation can also hinder the oxidation as a consequence of a rate-limiting release of Fe(II) from the complex (FeL^+). The complexed ferrous iron can be oxidized to form the corresponding ferric complex. This ferric complex can be unstable and be reduced by organic compounds regenerating Fe(II), which can participate in the cycle again. Moreover, the Fe(II) complex can enhance the oxidation rate to form the corresponding Fe(III) complex (Pankow and Morgan 1981; Liang et al., 1993).

Of the organic compounds identified in natural waters, amino acids are the major class with sizable complexation affinities for metals. The presence of both a carboxyl and an amino group gives all amino acids the ability to coordinate metals at two positions, and they are among the simplest chelating agents. The aquatic organisms produce complexing agents in their growth medium, whose affinity for metals range from that of simple amino acids up to that of strong artificial chelating agents such as EDTA (Morel, 1983).

In order to determine whether the organic term in Eq. 8 is significant, we examined the effect of the selected organic compounds on the apparent rate constant in oxygenated systems as a function of pH, ionic strength and temperature. Pseudo-first-order rate constants in the pH range from 6 to 8 ($I = 0.7$ m, $T = 25$°C), at different ionic strengths (pH = 7.98, $T = 25$°C) and temperature (pH = 7.98 and $I = 0.7$ m) are given in Tables 2–4. The rate constants in Table 3 have been corrected for variations of pOH and oxygen due to the salting out effects and the

Table 2
Coefficients for $\log k_{obs} = a + b$ pH for the oxidation of Fe(II) in 0.7 m NaCl and 0.009 M HCO_3^- solution in the presence of different organic compounds at 25°C. $[Fe(II)]_o = 20$ μM

Compounds	*A*	*b*
Fe(II)	−16.17 ± 0.47	2.05 ± 0.06
Fe(II)–Alanine 1:100	−16.29 ± 0.16	2.09 ± 0.02
Fe(II)–Glutamic acid 1:100	−15.26 ± 1.30	1.94 ± 0.18
Fe(II)–Cysteine 2:1	−17.43 ± 0.55	2.28 ± 0.07
Fe(II)–Cysteine 1:2	−11.22 ± 2.54	1.48 ± 0.33
Fe(II)–Cysteine 1:10	−12.87 ± 2.14	1.60 ± 0.30
Fe(II)–EDTA 1:100	−0.08 ± 0.06	0.08 ± 0.08

Table 3
Coefficients for $\log k = a + bI^{1/2} + cI$ for the oxidation of Fe(II) in NaCl and 0.009 M HCO_3^- solutions in the presence of different organic compounds at 25°C and 7.98 pH. [Fe(II)] = 20 μM. Rate constants have been corrected for pOH and oxygen variations due to salting out effect and variation of pK_W^* for the dissociation of water in different ionic strength media

Compounds	*a*	*b*	*c*
Fe(II)	15.78 ± 0.23	−1.36 ± 0.76	−0.04 ± 0.01
Fe(II)–Alanine	15.41 ± 0.49	−0.16 ± 0.04	−0.88 ± 0.10
Fe(II)–Glutamic acid	15.74 ± 0.19	−1.12 ± 0.57	−0.31 ± 0.39
Fe(II)–EDTA	15.35 ± 0.05	0.56 ± 0.16	−1.39 ± −0.12

Table 4
Coefficients for $\log k_{obs} = a + b(1/T)\cdot 10^3$ for the oxidation of Fe(II) in 0.7 m NaCl and 0.009 M HCO_3^- solution in the presence of different organic compounds at pH 7.98. [Fe(II)] = 20 μM

Compounds	*a*	$B\cdot 10^{-3}$	ΔH (kJ/mol)
Fe(II)	17.46 ± 2.8	−5.2 ± 0.8	99 ± 16
Fe(II)–Alanine	16.13 ± 0.43	−4.8 ± 0.1	92 ± 2
Fe(II)–Glutamic acid	13.96 ± 3.8	−4.2 ± 0.1	80 ± 21
Fe(II)–Cysteinel 1:2	18.00 ± 1.5	−5.3 ± 0.4	101 ± 9
Fe(II)–EDTA	10.52 ± 1.2	−2.9 ± 0.4	57 ± 7

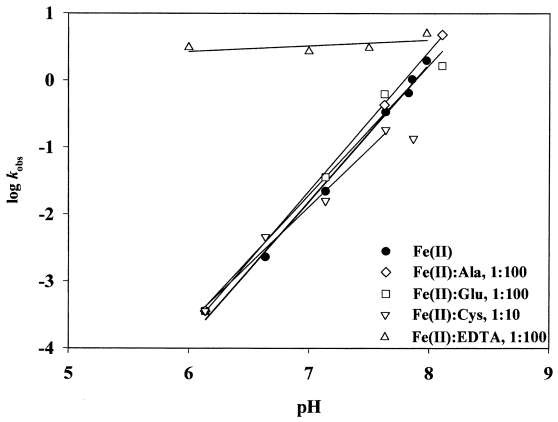

Fig. 2. Observed rate constants for the oxidation of Fe(II) in the presence of organic compounds in 0.7 m NaCl solution (0.009 M HCO_3^-) at 25°C as a function of pH_t. $[Fe(II)]_o = 20$ μM.

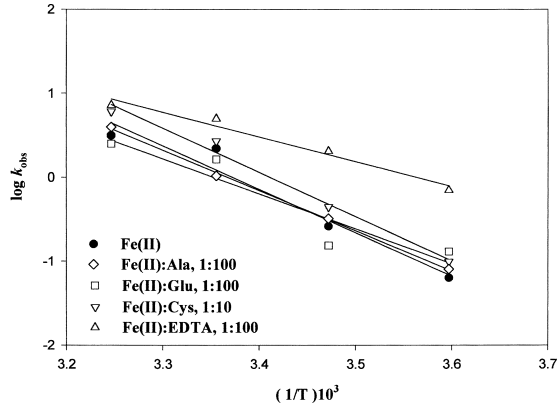

Fig. 4. Observed rate constants for the oxidation of Fe(II) in the presence of organic compounds, in 0.7 m NaCl solution (0.009 M HCO_3^-) as a function of temperature (T in (K)). $pH_t = 7.98$. $[Fe(II)]_o = 20$ μM.

variation of pK_w^* for the dissociation of water in different ionic strength media (Millero et al., 1987b).

4.1. Alanine and glutamic acid

Alanine is an aliphatic amino acid while glutamic acid belongs to the acidic group of amino acids. These compounds had a negligible effect on the rates for all the experimental conditions, as shown in Figs. 2–4. This behavior is similar to that found by Theis and Singer (1973) for vanillic acid, phenol, resorcinol and histidine in pure water. If we consider that only a small portion of the total Fe(II) is organically complexed (from 6% to 8%; Table 1) in these systems, then α_i should not change as a function of ligand concentration, and $k_{oc} = \alpha_i k_i$ (Tables 2–4).

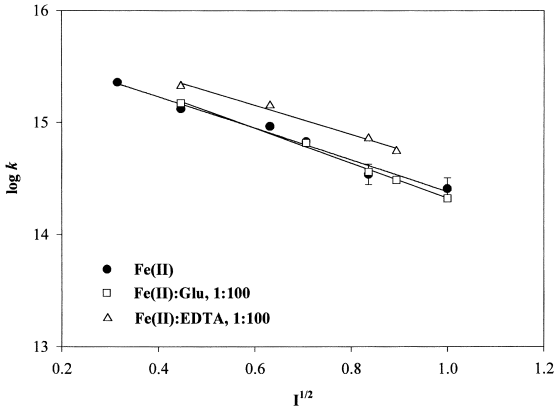

Fig. 3. Observed rate constants for the oxidation of Fe(II) in the presence of organic compounds in NaCl solution (0.009 M HCO_3^-) as a function of ionic strength. $pH_t = 7.98$, $t = 25$°C. $[Fe(II)]_o = 20$ μM. Rate constants have been corrected for pOH and oxygen variations due to salting out effect and variation of pK_w^* for the dissociation of water in different ionic strength media.

4.2. EGTA and EDTA

EGTA and EDTA are two synthetic chelators. These complexing agents are usually used to model the behavior of some natural organic complexes in seawater due to the complexity of the natural organic ligands. The concentration of these ligands was in excess with respect to the Fe(II) concentration, but lower than the HCO_3^- concentration.

EGTA completely inhibits the oxidation of Fe(II) (Fig. 5). The Fe(II)–EGTA complex is kinetically stable and makes it unavailable for oxygen attack. Theis and Singer (1974) reported a similar behavior for tannic acid. This stabilization of Fe(II) through complexation can only occur if the Fe(II)–organic complex is a major species (Voelker and Sulzberger, 1996).

The addition of EDTA accelerates that rates. The Fe(II)–EDTA complex initially formed is rapidly transformed to the Fe(III)–EDTA complex (Table 1). The production rate of the Fe(III)–EDTA complex is well above the oxidation consumption rates

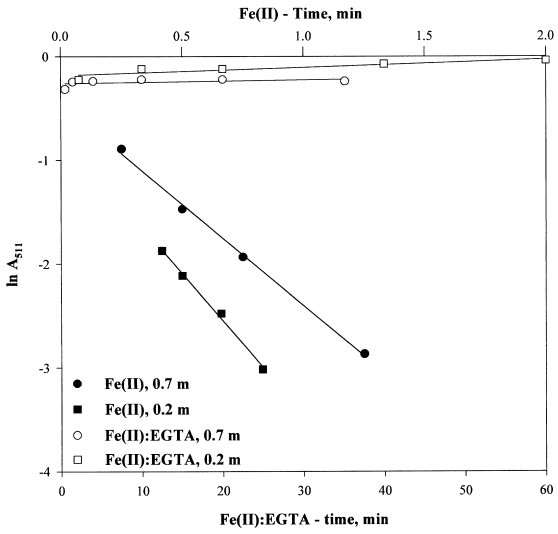

Fig. 5. Effect of ionic strength on the oxidation rate of Fe(II) in the presence of EGTA. $[Fe(II)]_o = 20$ μM, 0.009 M HCO_3^- was kept in all the studies, Fe(II):EGTA = 1:100, $t = 25$°C.

of Fe(II) by oxygen throughout the course of the reaction. Carboxylate ligands are known to accelerate the effective rate of the reaction by forming complexes with Fe(II). The Fenton reaction (Eq. 3) produces $OH^{\cdot}$, which can rapidly oxidize organic substances, as well as Fe(II). $OH^{\cdot}$ may abstract a hydrogen atom from the organic molecule and then, the oxygen will produce a peroxy radical (Eq. 14). In our study, EDTA is in excess, and an important fraction of the ligand is not complexed and could be affected by the presence of $OH^{\cdot}$ radical.

$$L - H + OH^{\cdot} \rightarrow L^{\cdot} + H_2O \quad (12)$$

$$L^{\cdot} + O_2 \rightarrow LO_2^{\cdot} \rightarrow L_{ox} + HO_2^{\cdot}/O_2^{\cdot -} \quad (13)$$

$$2HO_2^{\cdot}/O_2^{\cdot -} \rightarrow H_2O_2 + O_2 \quad (14)$$

The presence of additional $HO_2^{\cdot}/O_2^{\cdot -}$ in the solution can accelerate the Fe(II) oxidation. H_2O_2 reacts much faster with Fe(II)–polycarboxilate complexes than with inorganic Fe(II) (Voelker and Sulzberger, 1996). The different behavior shown by EGTA and EDTA may be due to the differences in the structure of the complexes.

In the pH range from 6 to 8.2, an increase in the oxidation kinetics of iron is observed that is not affected by change in pH (Fig. 2 and Table 2). At these values of pH, Fe(II) speciation is controlled by the organic ligand. At 25°C and pH 7.98, the effect of increasing NaCl concentration (Fig. 3) is given by the equation

$$\log k = 15.351 + 0.565 I^{1/2} - 1.388 I \quad (15)$$

which is not affected by the presence of EDTA. The enthalpy obtained for the process, $\Delta H = 57 \pm 7$ kJ mol^{-1}, is the lowest observed for the organic compounds studied (Fig. 4 and Table 4).

When a solution containing the Fe(III)–EDTA complex was added to the bathophenantroline to quench the reaction, the concentration of Fe(II) increased with time. This effect was only observed when the reaction vessel was placed under light. This increase in the Fe(II) concentration is due to the photodegradation of the Fe(III)–EDTA complex as has been observed by others (Anderson and Morel, 1982). A photochemically induced electron transfer from complexing organic ligands to oxidized metal occurs,

$$Fe(III) - L + h\nu \rightarrow Fe(II) + L^{\cdot} \quad (16)$$

and subsequently, the electron-deficient organic ligand and further reduces O_2 to $HO_2^{\cdot}/O_2^{\cdot}$ as in Eq. 13.

This photo-redox behavior has been found for other simple Fe(III)–carboxylate complexes in atmospheric and surface waters (Zuo and Holgné, 1992; Faust and Zepp, 1993; Voelker and Sulzberger, 1996; Voelker et al., 1997). This process is of interest in natural waters as a source and sink of reactive oxygen species ($HO_2/O_2^{\cdot -}$, hydrogen peroxide, and $HO^{\cdot}$) that can control the specification of iron.

Further measurements are planned to investigate the composition and H_2O_2 effects before a more detailed and rigorous mechanistic interpretation of this complicated process can be made.

4.3. Cysteine

The study of iron with cysteine is of great interest from a biological point of view. The ferric ion, for example, catalyzes the oxidation of cysteine, which may occur in living cells. Cysteine is a sulfhydril amino acid. Some studies of Fe(II)–cysteine have been carried out by different authors under anoxic

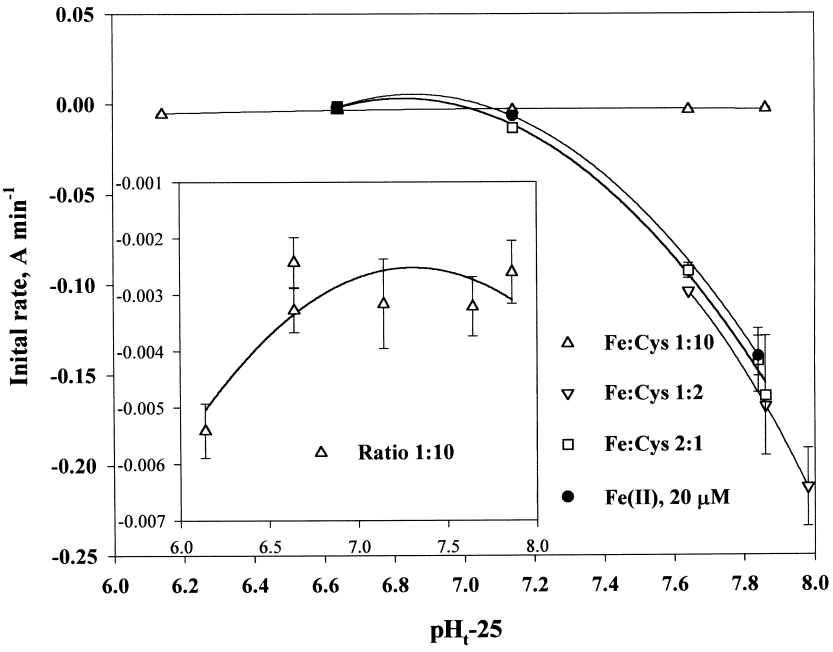

Fig. 6. Initial Fe(II) oxidation rates in the presence of different Fe(II):cysteine ratios in 0.7 m NaCl (0.009 M HCO_3^-), $t = 25$°C. $[Fe(II)]_o = 20$ μM.

conditions in both basic and acidic media (Baiocchi et al., 1983; Jamenson et al., 1988a,b; Sisley and Jordan, 1995; Amirbahman et al., 1997) always outside of the 6–8 pH range. We were able to study the Fe(II) oxidation in the presence of cysteine, only at Fe(II):cysteine ratios lower than 1:10 (Fig. 6). At this ratio, a decrease in the initial Fe(II) oxidation rate was observed at values of pH higher than 7.2 due to the continuous supply of Fe(II) coming from the reduction of the Fe(III)–cysteine complex. At higher ratios, a pink color appears in the solution, which disappears with time because the complex was not stable at this pH. Jamenson et al. (1988a,b) have indicated the formation of the monocysteine Fe(III) complex, Fe(OH)L in the pH range of 5–8. This complex formation takes place through a one-electron transfer process that involves the thiol group and results in the reduction of Fe(III) back to Fe(II) and the oxidation of cysteine to cystine as follows:

$$Fe(II) + O_2 + H^+ \rightarrow Fe(III) \quad (17)$$

$$2Fe(III) + 2\text{cysteine} \Leftrightarrow \text{cystine} + 2Fe(II) + 2H^+. \quad (18)$$

The pH dependence of the rates at Fe(II):cysteine ratios of 2:1, 1:2 and 1:10 (at pH lower than 7.2 for the 1:10 ratio) are shown in Table 2. Only when the concentration of Fe(II) is twice that for cysteine is a second order pH dependence observed (as in the absence of cysteine). When the cysteine is present at concentrations higher than those for Fe(II), the second-order pH dependence is not observed due to the formation of the organic complex. The observed slopes are 1.48 ± 0.33 and 1.60 ± 0.31 for 1:2 and 1:10 ratios, respectively. At higher Fe(II):cysteine ratios, the formation of Fe(II) is not observed. In this case, the Fe(OH)L complex formation and reduction is clearly affected by pH. Fig. 7 shows the results for the decomposition kinetics for the Fe(III)–cysteine complex at different cysteine concentrations in the pH range 6–8.

The shape of the kinetic curves in Fig. 7 suggests that an intermediate is formed. The first part of the kinetic curves represents the formation of the monocysteine Fe(III) complex, Fe(OH)L. This process is not only controlled by the kinetics of Fe(II) oxidation but also by the cysteine concentration, in a pH-controlled system. Due to the continuous supply

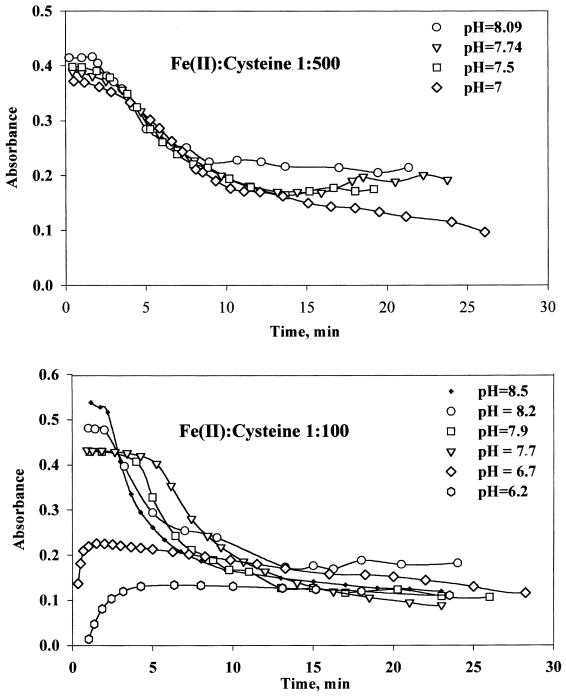

Fig. 7. Fe(III)–cysteine complex reduction kinetics ($A = 492$ nm) in 0.7 m NaCl and 0.009 M HCO_3^-. Effect of pH at 1:100 and 1:500 Fe(II):cysteine initial ratios. $[Fe(II)]_o = 20$ μM, $t = 25$°C.

of Fe(III) from the oxidation of Fe(II), a pseudo steady-state concentration of the complex is observed at times lower than 5–8 min, decreasing as both pH and cysteine concentration increase.

The second, decay, part of the curves represent a very fast initial reduction, followed by a much slower reaction, resulting in a stable concentration of the complex after approximately 10 min (Fig. 7). Similar findings were observed by Voelker and Sulzberger (1996) in the presence of fulvic acid. For the studies where cysteine was in large excess, straight lines were obtained for the $\ln A$ vs. time in the initial reduction step, indicating first order kinetics (Fig. 8). The rate of the Fe(III) complex reduction decreases as cysteine concentration increase. In studies carried out by Jamenson et al. (1988a) at pH over 8 and without oxygen, the complex formed disappears with time. In our case, the Fe(II), produced in the decomposition of the complex, is reoxidated to Fe(III) in the oxygenated medium, and a relatively high steady concentration of complexed iron can be maintained in the system as long as the organic material is not fully oxidized.

The following scheme rationalizes the experimental observations for the complex formation reaction, after the oxidation of Fe(II) with O_2.

$$Fe(II) + O_2 + H^+ \overset{K}{\rightarrow} Fe(III) \quad (19)$$

$$Fe(OH)_2^+ + H_2O \overset{K_H}{\leftrightarrow} Fe(OH)_3 + H^+ \quad (20)$$

$$H_2L \overset{K_{2A}}{\leftrightarrow} HL^- + H^+ \quad (21)$$

The two species of both Fe(III) and cysteine will react to form the intermediate.

$$Fe(OH)_2^+ + H_2L \overset{k_1}{\leftrightarrow} Fe(OH)L + H_2O + H^+ \quad (22)$$

$$Fe(OH)_3 + H_2L \overset{k_2}{\leftrightarrow} Fe(OH)L + 2H_2O \quad (23)$$

$$Fe(OH)_2^+ + HL^- \overset{k_3}{\leftrightarrow} Fe(OH)L + H_2O \quad (24)$$

$$Fe(OH)_3 + HL^- + H^+ \overset{k_4}{\leftrightarrow} Fe(OH)L + 2H_2O \quad (25)$$

The redox reactions of this complex can be described by Eqs. 26–29, where the reaction proceeds via the formation of an intermediate radical, which (resonance between (*a*) and (*b*) forms) subsequently

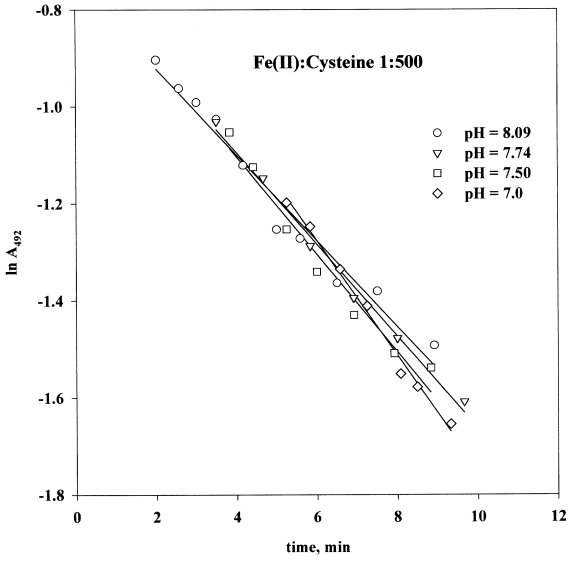

Fig. 8. Pseudo-first-order rate constant determination for the first fast reduction of the Fe(II)–cysteine complex at different pH values. $[Fe(II)]_o = 20$ μM, Fe(II):cysteine ratio is 1:500.

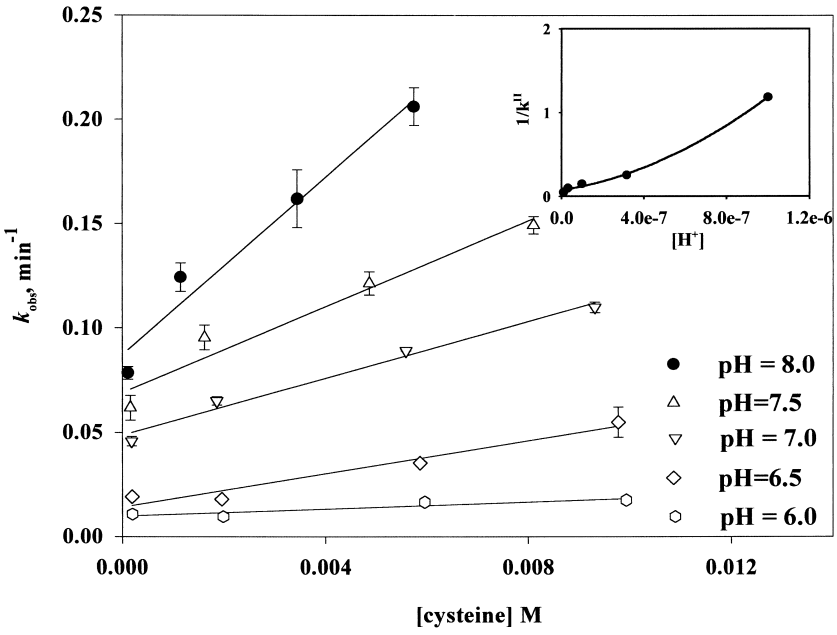

Fig. 9. Pseudo-first-order rate constant for the first fast reduction of the Fe(III)–cysteine complex at different pH values as a function of cysteine ($[H_2L]) = [H_2L]_0/(1 + K_{2A}[H^+] - 1$), where $[H_2L]_0$ is the initial cysteine concentration, $Fe[(II)]_o = 20$ μM, $t = 25$°C. Inset: plot of $(k^{II})^{-1}$ as a function of $[H^+]$ for the reduction step in the reaction of Fe(II) with cysteine according to Eq. 34.

reacts very rapidly with another Fe(III) center to give the disulfide, while Fe(II) will be reincorporated to step (1).

$$Fe(OH)L + H_2L \overset{k_5}{\leftrightarrow} Fe(OH)L_2^{2-} + 2H^+ \quad (26)$$

$$Fe(OH)L + HL^- \overset{k_6}{\leftrightarrow} Fe(OH)L_2^{2-} + H^+ \quad (27)$$

$$Fe(OH)L_2^{2-} \overset{k_7}{\rightarrow} Fe(II) + \left(L^{\cdot} - L \overset{a}{\leftrightarrow} L \overset{b}{-} L^{\cdot}\right) \quad (28)$$

$$Fe(III) + L^{\cdot} - L + O_2 \overset{fast}{\rightarrow} Fe(II) + L - L + H_2O_2 \quad (29)$$

The kinetic law, with the assumption of the steady state condition for the species $Fe(OH)L_2^{2-}$ is given by Eq. 30

$$\frac{d[Fe(OH)L_2^{2-}]}{dt} = 0 = \left(k_5 + k_6 K_{2A}[H^+]^{-1}\right) \times [Fe(OH)L][H_2L] - \left(k_7 + k_{-6}[H^+] + k_{-5}[H^+]^2\right) \times [Fe(OH)L_2^{2-}] \quad (30)$$

where the observed pseudo-first-order rate constant is equal to Eq. 31.

$$\text{Rate} = \frac{d[L - L]}{dt} = -\frac{1}{2}\frac{d[Fe(OH)L]}{dt} = \frac{1}{2}k_{obs}[Fe(OH)L] = k_7[Fe(OH)L_2^{2-}] = k_7\frac{k_5 + k_6 K_{2A}[H^+]^{-1}}{k_{-5}[H^+]^2 + k_{-6}[H^+] + k_7} \times [Fe(OH)L][H_2L] \quad (31)$$

A linear plot was obtained for the observed rate constant vs. the cysteine concentration, where $[H_2L] = [H_2L]_0/(1 + K_{2A}[H^+]^{-1})$ (Fig.9). The effect of the continuous oxidation of the Fe(II) that is regenerated can account for the observed increase in the

intercept of the plot related with the pH of the solution. Eq. 31 can be expressed as

$$\frac{1}{2}k_{obs} = k_7 \frac{k_5 + k_6 K_{2A}[H^+]^{-1}}{K_{-5}[H^+]^2 + k_{-6}[H^+] + k_7}[H_2L] \quad (32)$$

where k_{obs} is a linear function of $[H_2L]$, but the slope (the specific second order rate constant k^{II}) has a complex functional form. By putting

$$\frac{2}{k^{II}} = \frac{[H^+]\left(k_{-5}[H^+]^2 + k_{-6}[H^+]\right)}{k_7\left(k_5[H^+] + k_6 K_{2A}\right)} + \frac{[H^+]}{k_5[H^+] + k_6 K_{2A}} \quad (33)$$

assuming $k_6 K_{2A} \ll k_5[H^+]$, one obtains

$$\frac{2}{k^{II}} = \frac{1}{k_5} + \frac{k_{-6}}{k_7 k_5}[H^+] + \frac{k_{-5}}{k_7 k_5}[H^+]^2. \quad (34)$$

Plot of $(k^{II})^{-1}$ vs. $[H^+]$ (Fig. 9, inset) gives a second-degree fit, which allows us to determine the values of k_5 and the ratios k_{-6}/k_7 and k_{-5}/k_7, where

$$\frac{1}{k^{II}} = 7.25 \cdot 10^{-2}(\pm 0.018) + 3.77 \cdot 10^5(\pm 3.8 \cdot 10^4)[H^+] + 7.33 \cdot 10^{11}(\pm 1.57 \cdot 10^6)[H^+]^2 \quad (35)$$

and

$$k_5 = 6.897\,M^{-1}\,min^{-1}$$

$$k_{-6}/k_7 = 5.20 \cdot 10^6$$

$$k_{-5}/k_7 = 1.01 \cdot 10^{13}$$

Eq. 29 involves the reaction between molecular oxygen and the bis-cystine radical. In this case, the oxidation involves the transfer of two electrons from the co-ordinated cysteine ligands through the oxygen molecule yielding peroxide. The last assumption adopted in deriving Eq. 34 is quite reasonable, since the protonated species of the reductant with no charge, has more chances of approaching the complex Fe(OH)L. The k_5 value affects the equilibrium constant of formation of the complex, and as a consequence, markedly affects the concentration available for the subsequent reaction step, that is the active species for the redox step. The high value of the k_{-5}/k_7 ratio confirms the slow complex decomposition shown in Fig. 7. It is difficult to compare our results to literature results made under different conditions and with other mercaptocarboxylic acids. Baiocchi et al. (1983) found values for the k_5 rate constant in the order of 10^4 M^{-1} min^{-1} in perchlorate media and different mercaptocarboxylic acids than cysteine and anoxic conditions. Our value of 6.9 M^{-1} min^{-1} is the result of not only the pH effect on the reduction rate but also the iron (III)-catalyzed oxidation of cysteine by molecular oxygen.

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