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The oxidation of Fe(II) in NaCl–HCO₃[–] and seawater solutions in the presence of phthalate and salicylate ions: a kinetic model

J. Magdalena Santana-Casiano^{a,*}, Melchor González-Dávila^a, Frank J. Millero^b

^aDepartamento de Química, Facultad de Ciencias del Mar, Universidad de Las Palmas de Gran Canaria, Las Palmas de Gran Canaria 35017, Spain

^bRosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA

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Abstract

The oxidation of Fe(II) by molecular oxygen in NaCl–HCO₃[–] and natural seawater solutions and in the presence of phthalic and salicylic acid has been studied at different pH_F and Fe(II)–organic compounds ratios. These two compounds have been selected as simple organic model compounds in order to describe the effect of organic ligands on the oxidation rates of Fe(II) in the environment. A kinetic model including the speciation of Fe(II) and the organic species interacting with the major ions in solution was developed to describe the oxidation rate in any media. The model successfully describes Fe(II) behavior in both NaCl–bicarbonate solutions and seawater in the absence and in the presence of the selected compounds. The second-order rate constants for oxidation of the different species by oxygen are the same for all the experimental conditions studied; the speciation of the species accounts for the differences observed for each selected media. The Fe(OH)₂ species is the most significant contributor to the overall oxidation rate in 0.002 m NaHCO₃ solution, concentration found in natural seawater. Phthalate ion decreases the Fe(II) oxidation rate in the selected media, while salicylate ion increases oxidation as a result of the formation of the Fe(II)–salicylate complex. The oxidation rate for the Fe(II)–phthalate is close to zero accounting for the lower rate than in pure Fe(II) solution. Salicylate ion forms a 1:1 complex with an oxidation rate $k_L = 6.62 \times 10^5 \pm 300 \text{ M}^{-1} \text{ min}^{-1}$. The higher rate is probably related to the formation of a stable Fe(III)–salicylate complex.

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Keywords: Fe(II); Oxidation; Speciation; Kinetic model; Phthalic acid; Salicylic acid

1. Introduction

Natural organic matter can play an important role in regulating the speciation of metals in the environment, thereby affecting its solubility, adsorption

capacities, oxidation rates, and rates of geochemical reactions. As degradation products of organic matter, the humic and fulvic acids are present in the natural waters. The exact structure of humic and fulvic acids is unknown and it varies according to source (Thurman, 1985). Various functional groups, such as carbonyls, alcoholic and phenolic hydroxyls, carboxylates, amines, and amides, have been characterized in these acids (Suzuki et al., 2001). These functional groups have a high capacity to form complexes with

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

E-mail address: jmsantana@dqui.ulpgc.es (J.M. Santana-Casiano).

metal ions (Smith and Martell, 1989). However, little attention has been paid to studies of the physical–chemical behavior of metals, like iron, in the presence of organic ligands. Iron is present in all natural systems and it plays a key role in redox processes in natural environments. It is an essential element required by organisms. Iron availability has been shown to limit phytoplankton biomass in high-nutrient low-chlorophyll (HNLC) regions (Martin and Fitzwater, 1988; Martin and Gordon, 1988) and fertilization studies have been carried out in order to confirm this hypothesis (IRONEX experiments). Different studies have shown that most of the dissolved iron in open ocean waters is bound to strong organic ligands (Rue and Bruland, 1995; van den Berg, 1995; Wu and Luther, 1995; Nolting et al., 1998; Witter et al., 2000) reducing the concentration of inorganically bound iron. The kinetics of oxidation of Fe(II) has been studied in fresh water (Stumm and Lee, 1961; Ghost, 1974; Tamura et al., 1976; Sung and Morgan, 1980; Davidson and Seed, 1983) and seawater (Kester et al., 1975; Murray and Gill, 1978; Millero, 1989; Millero et al., 1987; Millero and Izaguirre, 1989). The studies of Millero et al. (1987) have demonstrated the importance of hydroxyl-Fe(II) species, FeOH^+ and Fe(OH)_2 in order to explain the kinetic of oxidation reactions of Fe(II) as a function of pH in different media. The studies of inorganic speciation of Fe(II) in seawater solutions (Millero et al., 1995) show that other inorganic complexes of Fe(II), like FeCO_3 and FeHCO_3 can be also important (Millero and Izaguirre, 1989).

Studies carried out at different carbonate solutions by King (1998) have shown increases in the rate of oxidation of Fe(II) due to the formation of $\text{Fe(CO}_3)_2^{2-}$.

In this paper, the contribution of the different inorganic species of Fe(II) to the oxidation kinetic of iron has been studied in order to elucidate the importance of hydroxyl and carbonate species of Fe(II) in the control of Fe(II) oxidation. A kinetic model, which takes into account all the species present in NaCl-HCO_3^- and seawater solutions, has been developed in order to explain the observed behavior. Moreover, considering that the rates of oxidation of Fe(II) have been shown to be affected by the presence of organic compounds in water (Theis and Singer, 1973, 1974), in NaCl solutions

(Santana-Casiano et al., 2000), and in seawater (Millero et al., 1987), this study also considers the effect of the presence of organic ligands in the oxidation kinetic of Fe(II). For that reason, and given that two of the most abundant binding sites found in the humic and fulvic compounds are carboxylic ($-\text{COOH}$) and phenolic ($-\text{C}_6\text{H}_4\text{OH}$) groups similar to those in *o*-phthalic and salicylic acids, these two compounds were selected for the present study. The oxidation rate of Fe(II) in NaCl-HCO_3^- and seawater media was studied in the presence of different Fe(II)-organic ligand ratios as a function of pH. The kinetic model for the Fe(II) oxidation in aerate solutions based on thermodynamic and kinetic information, which considers the effects of solution composition and pH, was also applied to the presence of Fe(II)-complexes.

2. Experimental

Chemicals: Fe(II) stock solutions (0.05M) were prepared using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck), acidified with HCl. The organic ligands under investigation (Sigma) were used without further purification. The available complexation constants for the organic compounds studied with Fe(II) and Fe(III) are listed in Table 1.

Oxygen concentration: All measurements were made in solutions saturated with air at 25 °C by bubbling with air.

pH measurements: Since the oxidation of Fe(II) in aqueous solutions is strongly dependent upon pH (Stumm and Lee, 1961; Davison and Seed, 1983), the solutions were buffered with 0.009 and 0.002 m NaHCO_3 . This buffer system can adequately control the pH to ± 0.01 during an experimental run (Millero et al., 1987). TRIS–NaCl buffers (Millero, 1986) and TRIS–seawater buffers (DOE, 1994) were used to calibrate the electrode system and calculate the pH of the solution. pH was measured in the free scale in NaCl solution and in total scale in seawater, being converted to free scale following Millero (2001). pH was measured with an Orion pHmeter 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.

Oxidation experiments: Fe(II) oxidation experiments were performed by adding 20 μM Fe(II) to

Table 1

Stability constants for the formation of Fe(II) and Fe(III) complexes considered for the kinetic model

No.	Species	log <i>K</i> (0.7 m, 25 °C)	Reference
1	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	– 13.72	Millero, 1995
2	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	– 6.005	
3	$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	– 9.6	
4	$\text{Na}^+ + \text{HCO}_3^- \rightleftharpoons \text{NaHCO}_3$	– 0.53	Millero and Schreiber, 1982
5	$\text{Na}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NaCO}_3^-$	0.42	
6	$\text{Ca}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CaHCO}_3^+$	0.33	
7	$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$	2.1	
8	$\text{Mg}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{MgHCO}_3^+$	0.28	
9	$\text{Mg}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{MgCO}_3$	1.94	
10	$2\text{Mg}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{Mg}_2(\text{CO}_3)^{2+}$	2.59	
11	$\text{Mg}^{2+} + \text{OH}^- \rightleftharpoons \text{MgOH}^+$	2.2	
12	$\text{Fe}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{FeHCO}_3^+$	0.97	Millero and Hawke, 1992
13	$\text{Fe}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{FeCO}_3$	4.33	After King, 1998
14	$\text{Fe}^{2+} + 2 \text{CO}_3^{2-} \rightleftharpoons \text{Fe}(\text{CO}_3)_2$	6.09	
15	$\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{OH}^- \rightleftharpoons \text{Fe}(\text{CO}_3)(\text{OH})^-$	8.90	
16	$\text{Fe}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})^+ + \text{H}^+$	– 9.66	Millero et al., 1995
17	$\text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2 \text{H}^+$	– 20.87	
18	$\text{Fe}^{2+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^+$	– 0.12	After King, 1998
19	$\text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeSO}_4$	0.96	
20	$\text{Fe}^{3+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{2+}$	0.57	Millero et al., 1995
21	$\text{Fe}^{3+} + 2 \text{Cl}^- \rightleftharpoons \text{FeCl}_2^+$	0.13	
22	$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})^{2+} + \text{H}^+$	– 2.62	
23	$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	– 6.0	
24	$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{H}^+$	– 12.5	
25	$\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_4^+ + 4\text{H}^+$	– 21.8	
<i>Phthalic acid</i> = <i>P</i>			
26	$\text{H}_2\text{P} \rightleftharpoons \text{HP}^- + \text{H}^+$	– 2.72	Smith and Martell, 1989 ^a
27	$\text{HP}^- \rightleftharpoons \text{P}^{2-} + \text{H}^+$	– 4.7	
28	$\text{P}^{2-} + \text{Na}^+ \rightleftharpoons \text{PNa}^-$	0.675	
29	$\text{P}^{2-} + \text{K}^+ \rightleftharpoons \text{PK}^-$	0.575	
30	$\text{P}^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{Pca}$	0.97	
31	$\text{P}^{2-} + \text{Mg}^{2+} \rightleftharpoons \text{PMg}$	0.97 ^b	
32	$\text{P}^{2-} + \text{Fe}^{2+} \rightleftharpoons \text{Pfe}$	2.68	This work
<i>Salicylic acid</i> = <i>Sa</i>			
33	$\text{H}_2\text{Sa} \rightleftharpoons \text{HSa}^- + \text{H}^+$	– 2.72	Smith and Martell, 1989 ^a
34	$\text{HSa}^- \rightleftharpoons \text{Sa}^{2-} + \text{H}^+$	– 13.62	
35	$\text{HSa}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaHSa}^+$	– 0.14	

Table 1 (continued)

No.	Species	log <i>K</i> (0.7 m, 25 °C)	Reference
<i>Salicylic acid</i> = <i>Sa</i>			
36	$\text{Sa}^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaSa}$	4.16	
37	$\text{HSa}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaSa} + \text{H}^+$	– 8.85	
38	$\text{Sa}^{2-} + \text{Mg}^{2+} \rightleftharpoons \text{MgSa}$	5.06	
39	$\text{Sa}^{2-} + \text{Fe}^{2+} \rightleftharpoons \text{FeSa}$	6.48	
40	$2 \text{Sa}^{2-} + \text{Fe}^{2+} \rightleftharpoons \text{FeSa}_2$	11.13	
41	$\text{Sa}^{2-} + \text{Fe}^{3+} \rightleftharpoons \text{FeSa}^+$	16.26	
42	$2\text{Sa}^{2-} + \text{Fe}^{3+} \rightleftharpoons \text{FeSa}_2^-$	28.83	
43	$\text{SaH}^- + \text{Fe}^{3+} \rightleftharpoons \text{FeHSa}^{2+}$	4.12	

^a Davies equation was used to compute equilibrium constants at 0.7 m.^b Phthalate complex formation with Mg^{2+} considered to be similar to that for Ca^{2+} .

both the O₂-saturated 0.7 m NaCl solutions buffered with HCO_3^- and to the O₂-saturated seawater solutions. Prior to the addition of iron, the pH of the air-saturated solutions containing the organic ligand was adjusted by adding NaOH or HCl from 0.1 M solutions. Reactions were studied in a 500-ml thermostatically controlled glass 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–CO₂ mixture through the solutions, two for the glass and reference electrodes and one to insert a 10-cm³ calibrated automatic repipette from which samples were taken. The solutions were stirred with a teflon-coated magnetic stirrer.

Fe(II) analysis: Total Fe(II) concentrations in NaCl and seawater solutions were determined spectrophotometrically using the bathophenanthroline technique (Sung and Morgan, 1980; Millero et al., 1987) and the ferrozine technique (Gibbs, 1976). Absorbance was measured at 511 nm (bathophenanthroline) and at 562 nm (ferrozine) on a Hewlett Packard Diode-array Spectrophotometer 8453 with an automatized system which pumped the sample through a 5-cm path length quartz flow-cell.

2.1. Kinetic analysis

The effect of pH on the Fe(II) oxidation by oxygen in NaCl media in the presence of carbonate species has been described by a rate law with an overall Fe(II)

oxidation rate (k_{app}) that considers different Fe(II) complexes

$$-\frac{d\{\text{Fe(II)}\}}{dt} = k_{\text{app}}[\text{O}_2]\{\text{Fe(II)}\} \quad (1)$$

$$k_{\text{app}} = 4(k_1\alpha_{\text{Fe}^{2+}} + k_2\alpha_{\text{FeOH}^+} + k_3\alpha_{\text{Fe(OH)}_2} + k_4\alpha_{\text{FeHCO}_3^+} + k_5\alpha_{\text{Fe(CO}_3\text{)}} + k_6\alpha_{\text{Fe(CO}_3\text{)}_2^{2-}} + k_7\alpha_{\text{Fe(CO}_3\text{)OH}^-} + k_8\alpha_{\text{FeCl}^+}) \quad (2)$$

where α_i is the fraction of each Fe(II) species in the solution and a function of the ionic media. k_i is the second-order rate constant for oxidation by oxygen and $\{\text{Fe(II)}\}$ is the total Fe(II) concentration in the solution. The factor 4 reflects the stoichiometry of Fe(II) oxidation by oxygen (King, 1998; Santana-Casiano et al., 2000). To verify this rate law and to determine the rate constants, we have defined a kinetic model with all pertinent dissociation, complex formation (Table 1) and oxidation reactions for the different Fe(II) species involved in the solution. We also considered the complex formation reaction between carbonate species and sodium as described in Table 1. Gepasi Version 3.21 (Mendes, 1997), a software system for the simulation of chemical and biochemical kinetics, was used to compute the time-dependent concentrations of all reactants. A response surface methodology (Box and Draper, 1987) and the Statistica Program for Windows (1995) inserted initial conditions and varied k_i values until the sum of squared residuals from the difference between model and data was minimised for the entire set of experiments, for each pH and carbonate concentration. In the Gepasi software, chemical equilibrium is treated as a series of forward and backward reactions with bimolecular rate constants of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the acid–base and complex formation backward reactions following Buerge and Hug (1998). The k_i constants are obtained by adjusting the observed $\{\text{Fe(II)}\}$ concentrations/time pair of data with the kinetic model output. All eight kinetic constants in the NaCl solutions were considered as part of the adjustment exercise. The FeSO_4 oxidation rate, which should be also considered in seawater solution, was computed in 0.03 m Na_2SO_4 –0.61 m NaCl solutions (Ionic strength 0.7 m) in the pH range 6–8.

In seawater media (salinity 36.7), the same set of dissociation, complex formation and redox reactions were considered as in 0.7 m NaCl solution. The apparent rate constant includes the presence of nine Fe(II) species

$$k_{\text{app}} = 4(k_1\alpha_{\text{Fe}^{2+}} + k_2\alpha_{\text{FeOH}^+} + k_3\alpha_{\text{Fe(OH)}_2} + k_4\alpha_{\text{FeHCO}_3^+} + k_5\alpha_{\text{Fe(CO}_3\text{)}} + k_6\alpha_{\text{Fe(CO}_3\text{)}_2^{2-}} + k_7\alpha_{\text{Fe(CO}_3\text{)OH}^-} + k_8\alpha_{\text{FeCl}^+} + k_9\alpha_{\text{FeSO}_4}) \quad (3)$$

Moreover, the presence of the different major inorganic species Ca^{2+} , Mg^{2+} , plus Na^+ affecting carbonate speciation (Millero and Schreiber, 1982) were also considered (Table 1) in order to account for the decrease in the observed rate constant in seawater by comparison with NaCl with similar ionic strength. Other major species in seawater were not considered, as association constants were not available.

In the presence of organic ligands, we expected Fe(II) organic complexation to influence the kinetics in a similar way. The overall Fe(II) oxidation rate would now include the weighted sum of the oxidation rates of the inorganic and organic Fe(II) species

$$k_{\text{app}} = 4(k_1\alpha_{\text{Fe}^{2+}} + k_2\alpha_{\text{FeOH}^+} + k_3\alpha_{\text{Fe(OH)}_2} + k_4\alpha_{\text{FeHCO}_3^+} + k_5\alpha_{\text{Fe(CO}_3\text{)}} + k_6\alpha_{\text{Fe(CO}_3\text{)}_2^{2-}} + k_7\alpha_{\text{Fe(CO}_3\text{)OH}^-} + k_8\alpha_{\text{FeCl}^+} + k_9\alpha_{\text{FeSO}_4} + \sum_i k_{L_i}\alpha_{\text{FeL}_i}) \quad (4)$$

where FeL_i are different Fe(II)–organic ligands complexes in the solution, with a rate constant k_{L_i} . The presence of the different major inorganic species Ca^{2+} , Mg^{2+} , K^+ and Na^+ affecting ligand speciation (Table 1) were also considered.

3. Results and discussion

In order to study the effect of the inorganic speciation of Fe(II) in the oxidation kinetics of Fe(II), studies were carried out in 0.7 m NaCl solutions including both 0.009 and 0.002 m

NaHCO₃ solutions in the absence of any organic compounds. Fig. 1 shows the experimental results for the oxidation of Fe(II) in 0.7 m NaCl solution carried out at different pH in 0.009 m NaHCO₃ solutions (see Appendix A). Table 2 presents the observed pseudo-first order rate constants determined in the different experimental conditions carried out in this study.

An important decrease in the Fe(II) oxidation rate is clearly observed as pH decreases (Table 2) due to changes in the speciation distribution of the Fe(II) species in solution. Our studies also show the important effect of carbonate ion when the concentration changes from 0.009 to 0.002 m NaHCO₃ (ionic media 2 and 3, respectively, Table 2). At pH 8, the pseudo-first order oxidation rate decreases from $k' = 1.64 \text{ min}^{-1}$ at 0.009 m NaHCO₃ to 0.63 min^{-1} at 0.002 m NaHCO₃. Most of the studies carried out until the present work were done in pure water with different NaHCO₃ solutions, very far from the ionic strength found in natural seawater. Only a value of $\log k = 15.43 \pm 0.07$ ($k' = 1.7 \pm 0.2 \text{ min}^{-1}$) has been found in the literature (Millero and Izaguirre, 1989) at the same 0.7 m NaCl–0.009 m NaHCO₃ solution,

similar to our experimental value of 1.64 min^{-1} (Table 2, pH=8.13).

In order to gain insight in the role played by carbonate ions in the oxidation kinetic of Fe(II), we determine the speciation of the different iron species in the selected media. Fig. 2 shows the Fe(II) speciation in 0.009 and 0.002 m NaHCO₃ solutions between pH 6 and 8.5 using the constants presented in Table 1. Fe(CO₃) is the most important Fe(II) species in solution above pH 7.3 in 0.009 m NaHCO₃ solution. However, the Fe(CO₃) concentration is higher than Fe²⁺ only at pH over 8.1 in 0.002 m NaHCO₃. Fe(OH)₂ and Fe(CO₃)₂²⁻ concentrations increase by 98% and Fe(CO₃)OH⁻ by 99.7%, when the pH changes from 7 to 8. Using the adjustment procedure describe above for the studies carried out at different pH and NaHCO₃ solutions, the computed rate constants for the oxidation of the eight Fe(II) species are shown in Table 3. The accuracy of these rate constants describing the experimental data is shown in Fig. 1, where the lines represent the outputs from the kinetic model. The relative contribution of the inorganic Fe(II) species to the total observed oxidation rate is shown in Fig. 3 in both 0.009 and

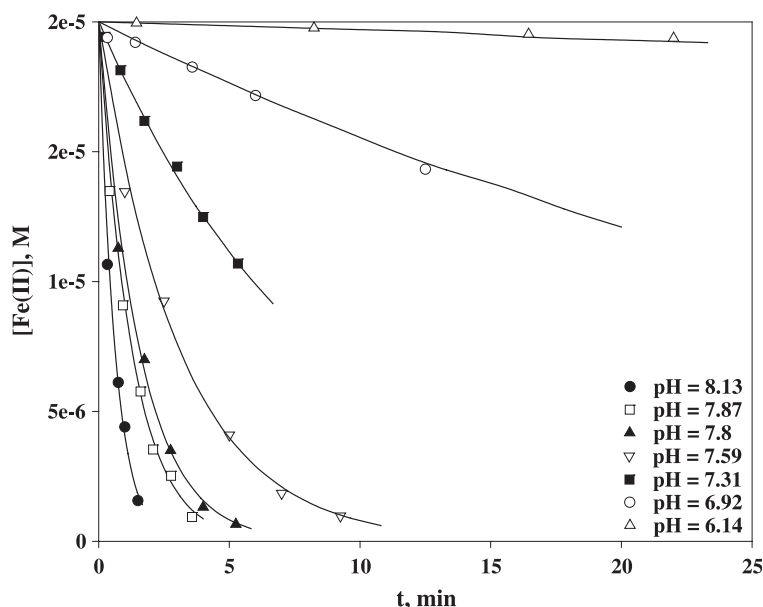


Fig. 1. Kinetics of oxidation of Fe(II) (20 μM) at different pH_F in 0.7 m NaCl and 0.009 m NaHCO₃ and $t = 25^\circ\text{C}$. The lines represent the kinetic model output for the experimental conditions as shown in Table 3.

Table 2

Fe(II) oxidation rates ($k' = k_{\text{app}}[\text{O}_2]$) and oxidation model fits for 0.7 m NaCl and seawater solutions ($[\text{Fe(II)}]_0 = 20 \mu\text{M}$) in the absence and in the presence of phthalate and salicylate ions

Ionic media	Fe(II)/L	pH _F	k' (min ⁻¹)	k' (min ⁻¹), model
1	1:0	7.98	0.57	0.58
1	1:0	8.00	0.634 ^a	0.60
1	1:0	7.18	0.021	0.02
1	1:0	7.20	0.015 ^a	0.02
1	1:0	6.12	1.3×10^{-4}	1.85×10^{-4}
1	1:0	6.24	1.34×10^{-4a}	2.1×10^{-4}
2	1:0	8.13	1.64	1.60
2	1:0	8.0	1.7 ± 0.2^b	1.57
2	1:0	7.31	0.115	0.12
2	1:0	6.11	1.45×10^{-3}	1.7×10^{-3}
3	1:0	7.98	0.63	0.61
3	1:0	7.40	0.062	0.060
1	1:0	8.13	0.89	0.88
4	1:10	8.13	0.85	0.86
4	1:100	8.12	0.80	0.80
4	1:1000	8.14	0.47	0.45
5	1:1000	8.05	0.93	0.94
5	1:1000	7.41	0.097	0.091
5	1:1000	6.87	7.9×10^{-3}	8.1×10^{-3}
5	1:1000	6.59	2.4×10^{-3}	2.1×10^{-3}
5	1:1000	6.12	1.7×10^{-4}	1.85×10^{-4}
5	1:500	8.05	1.05	1.08
5	1:100	8.05	1.24	1.23
3	1:0	8.05	0.77	0.78
6	1:100	8.05	0.66	0.70
6	1:1000	8.05	0.42	0.41
7	1:100	8.16	4.63	4.58
7	1:100	7.14	0.56	0.60
1	1:0	7.14	0.014	0.017
7	1:50	8.17	2.21	2.11
7	1:10	8.09	0.93	0.89
1	1:0	8.09	0.88	0.85

Published rate constants from Millero et al. (1987) compared with model predictions are also included.

(1) Natural seawater. (2) 0.7 m NaCl, 0.009 m NaHCO₃. (3) 0.7 m NaCl, 0.002 m NaHCO₃. (4) Fe(II)/Phthalate, in seawater. (5) Fe(II)/Phthalate, 0.7 m NaCl, 0.009 m NaHCO₃. (6) Fe(II)/Phthalate, 0.7 m NaCl, 0.002 m NaHCO₃. (7) Fe(II)/Salicylate, in seawater.

^a Millero et al. (1987).

^b Millero and Izaguirre (1989).

0.002 m NaHCO₃ solutions. At 0.009 m NaHCO₃ and for pH values of more than 6.5, Fe(CO₃)₂²⁻ contributes 80% to the observed Fe(II) oxidation rate while Fe(OH)₂'s contribution to the observed overall rate is 15%. The most reactive species Fe(OH)₂, with an oxidation rate of $4.6 \times 10^8 \text{ M}^{-1} \text{ min}^{-1}$ in 0.7 m NaCl solutions, is present in solution at a concentration of

less than 10^{-10} m . Both species, Fe(CO₃)₂²⁻ and Fe(OH)₂, present a second-order dependence in relation to pH which is consistent with the oxidation rate described by Stumm and Lee (1961) in water (pH 5 to 7), by Millero et al. (1987) in water and seawater ($S=0$ to 40 and pH 6 to 8.5) and by Millero and Izaguirre (1989) in NaCl and NaClO₄ solutions,

$$-\frac{d[\text{Fe(II)}]}{dt} = k[\text{O}_2][\text{Fe(II)}][\text{OH}^-]^2 \quad (5)$$

In a solution containing 0.002 m NaHCO₃, a similar concentration than that found in seawater solutions, the pattern is just the opposite. At pH over 6.5, Fe(OH)₂ contributes nearly 80% to the observed oxidation rate while Fe(CO₃)₂²⁻ contributes 15%, which is also consistent with the general oxidation rate expression. These results are in accordance with the kinetic model proposed by King (1998) who studied the role of carbonate speciation on the oxidation rate of Fe(II) and determined the contribution of each species. The individual oxidation rates determined by this author considered studies carried out in the absence of NaCl and were corrected for ionic strength effects by considering a quadratic ionic strength dependence in $I^{1/2}$ for all rate constants. In our study, the values determined in our fitting procedure correspond directly with those at the ionic strength of 0.7 m. The three most reactive species are also Fe(CO₃)₂²⁻, Fe(OH)₂ and Fe(CO₃)OH⁻. Moreover, we consider both the interaction between Na⁺ and carbonate ions in solutions (Eqs. (4) and (5), Table 1) and the equilibrium constants valid at this ionic strength, which affect the carbonate speciation and consequently, the reaction rates determined with our kinetic model, changing the log $k(\text{Fe(CO}_3)_2^{2-})$ from 5.10 to 5.78, log $k(\text{Fe(OH)}_2)$ from 7.00 to 8.66 and log $k(\text{Fe(CO}_3)\text{OH}^-)$ from 3.2 to 3.95. The most important increase in the log k for Fe(OH)₂ is responsible for the observed effect in the 0.002 m NaHCO₃ solution and makes this species the most significant contributor to the overall rate at low NaHCO₃ concentration, like in seawater which is consistent with results presented by Millero (1989).

Different studies were carried out in oceanic seawater ($S=36.7$, 5-m depth) sampled at the time

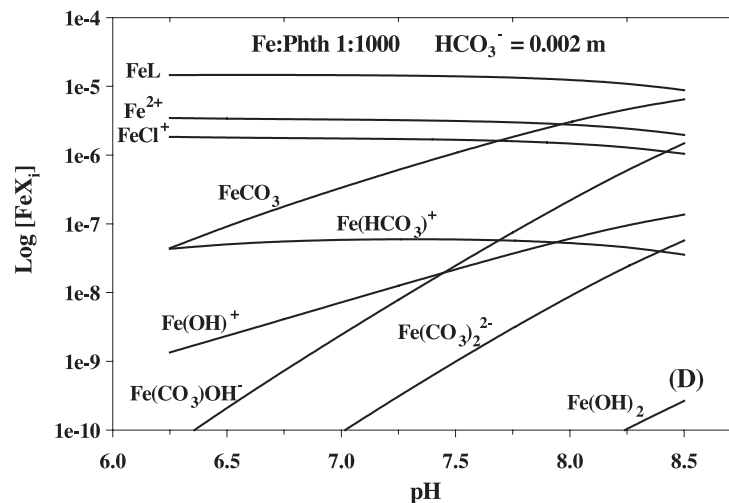
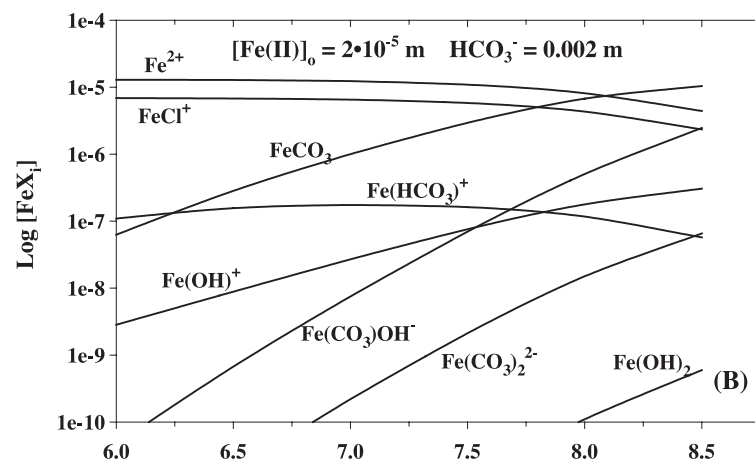
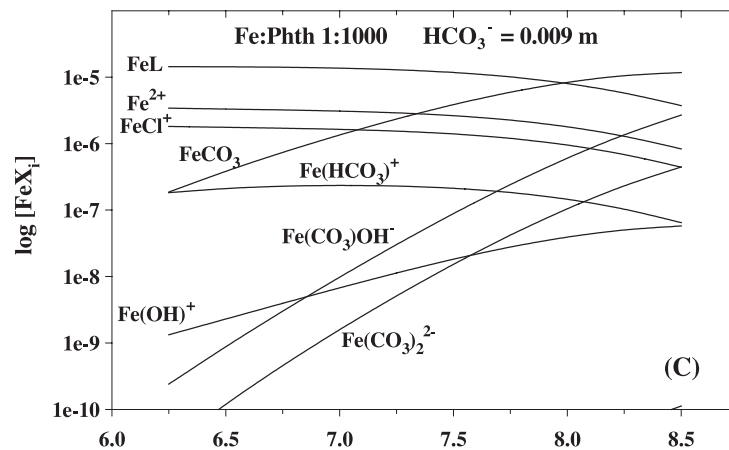
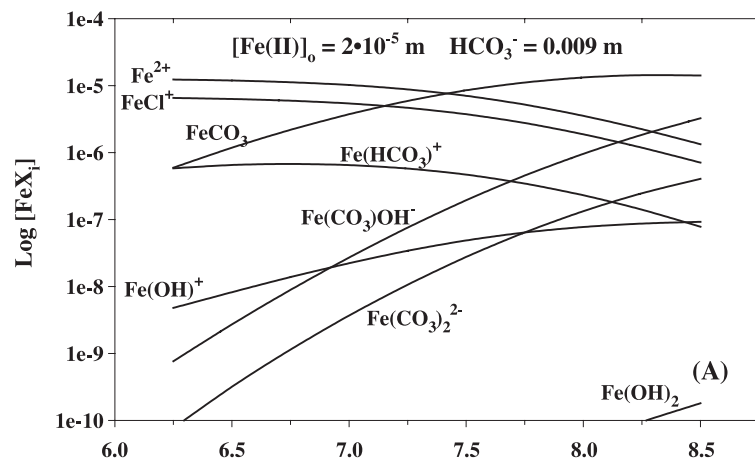


Fig. 2. Fe(II) speciation in 0.7 m NaCl solutions as a function of pH_F: (A) with 0.009 m NaHCO₃, (B) with 0.002 m NaHCO₃, (C) with 0.009 m NaHCO₃ and 2×10^{-2} m phthalic acid and (D) with 0.002 m NaHCO₃ and 2×10^{-2} m phthalic acid.

Table 3

Fe(II) oxidation rates with molecular oxygen at 25 °C for the pH range 6–8 calculated from the kinetic model considering the equilibrium constants of Table 1 in a 0.7 m ionic strength medium and experimental values presented in Table 2

No.	Species	k (M ⁻¹ min ⁻¹)
1	Fe ²⁺	0.12 ± 0.08
2	FeHCO ₃ ⁺	0.2 ± 0.1
3	FeCO ₃	0.2 ± 0.1
4	Fe(CO ₃) ₂ ²⁻	6 (± 0.3) × 10 ⁵
5	Fe(CO ₃)(OH) ⁻	9 (± 0.2) × 10 ³
6	Fe(OH) ⁺	300 ± 25
7	Fe(OH) ₂	4.6 (± 0.01) × 10 ⁸
8	FeCl ⁺	0.12 ± 0.08
9	FeSO ₄	0.12 ± 0.08
10	Fe–Phthalate	0.06 ± 0.06
11	Fe–salicylate, FeSa	6.6 × 10 ⁵ ± 300

series station (ESTOC) north of the Canary Islands. At pH_F 7.98 in seawater (Table 2), an overall rate of 0.57 min⁻¹ is determined, lower than the value 0.63 min⁻¹ determined in 0.7 m NaCl–0.002 m NaHCO₃. Millero et al. (1987) found values of 0.31 min⁻¹ at pH_F 7.93 and of 0.63 min⁻¹ at pH_F 7.998, with a value of 0.50 ± 0.08 min⁻¹ at pH_F 7.98 (by using Eq. (27) from Millero et al., 1987) similar to our value of 0.57 min⁻¹ (Table 2). A good agreement between their values and our values at lower pH is also shown in Table 2. In order to explain the observed behavior for the oxidation of Fe(II) in seawater solutions, the kinetic model was applied to the different experimental conditions presented in Table 2. The same individual kinetic constants obtained in NaCl–NaHCO₃ solutions, together with the nonreactive FeSO₄ species (log $k = -0.92 \pm 0.22$, Table 3) and the ion-pairing formation between carbonate- and hydroxide-ions with the major ions in seawater shown in Table 1, describe the observed Fe(II) oxidation process. These results are consistent with the role of Fe(OH)₂ and Fe(II)-carbonate complexes in 0.002 m NaHCO₃ and the ionic interactions between major ions with Fe(II) and carbonate ions. The correlation between our experimental results and those determined in seawater by Millero et al. (1987) together with the predicted values determined by using our model in both studies is shown in Table 2. The oxidation rates for each species presented in Table 3 describe the behavior observed in all the studies, showing the

important role played by the carbonate species in both the speciation and oxidation rate of Fe(II) in solutions with similar ionic strength than that found in seawater and confirming the Fe(OH)₂ species is the most active species contributing to the oxidation rate determined at the 0.002 m NaHCO₃ concentration typically found in seawater.

3.1. Phthalic acid

Phthalic acid has two carboxylic groups in ortho-position with pK_a* values of 2.72 and 4.7 in 0.7 m NaCl solution and 25 °C (Table 1). Table 2 shows the oxidation rate constants of Fe(II) (20 μM) in 0.7 m NaCl and 0.009 and 0.002 m HCO₃⁻ in the presence of different phthalic acid concentrations at 25 °C. In the presence of phthalic acid and at pH_F = 8, a decrease in the oxidation rate as ligand concentration increases from a ratio Fe(II)/ligand, 1:100 to 1:1000 is observed in both HCO₃⁻ concentrations. No stability constants are available in the references considered for this study. However, our kinetic model allows us to determine a value for the formation constant for the FeL complex and its oxidation rate valid in all the experimental conditions presented in this work. A conditional complex formation constant of log K_{FeL}* = 2.68 at an ionic strength of 0.7 m and 25 °C is obtained. The oxidation of this complex does not occur at any appreciable rate; the observed rate of Fe(II) decreases as a result of the change in speciation of Fe(II) in solution. The most reactive species are clearly affected by the presence of phthalic acid in the NaCl media. When phthalic acid is added to the 0.7 m NaCl–0.009 m HCO₃⁻ solution up to 2 × 10⁻² m (1:1000 Fe/phthalic acid ratio), final pH_F = 8.0 (Fig. 2), Fe(OH)₂, Fe(CO₃)₂²⁻ and Fe(CO₃)OH⁻ concentrations decrease by 18%, while the Fe(II) complexed by phthalate becomes 28% (5.55 × 10⁻⁶ M) of the initial {Fe(II)} added to the solution. At pH_F = 7, FeL concentration reaches 1.05 × 10⁻⁶ M, which is nonreactive in these experimental conditions. The observed increase in the oxidation rate from pH 7 to pH 8 (Fig. 4, Appendix B) is closely related to the increase in the concentration of the reactive species Fe(OH)₂ and Fe(CO₃)₂²⁻. The pH dependence of the Fe(II) phthalate concentration fully explains the pH dependence of the reaction when all the species affecting the Fe(II) and phthalic acid concentration are taken into account. The contribution

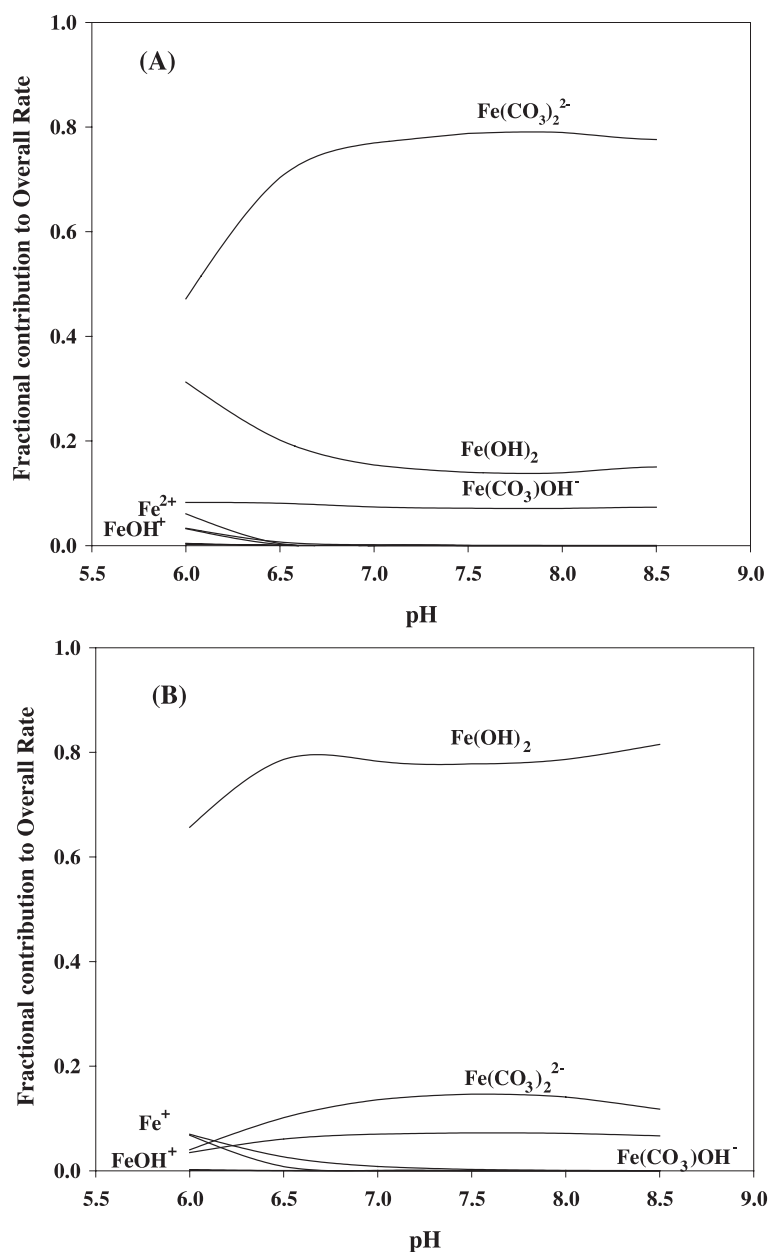


Fig. 3. Contribution of specific Fe(II) species in total Fe(II) oxidation rate by oxygen. Calculations are for (A) 0.7 m NaCl and 0.009 m NaHCO₃, and (B) 0.7 m NaCl and 0.002 m NaHCO₃.

of the individual species to the overall rate is similar to that obtained for Fe(II) in the absence of any organic compounds (Fig. 3), owing to its behavior as a nonreactive species ($k \approx 0$). Due to the relatively high value of $k(\text{Fe}(\text{CO}_3)_2^{2-})$, the product $k\alpha$ dominates the

weighted sum of the all Fe(II) species, representing 72% of the observed rate. Fe(OH)₂'s contribution to the observed rate is 20% in the pH range between 7.0 and 8.5. This behavior is consistent with the second-order OH⁻ dependence on Fe(II) oxidation, which is

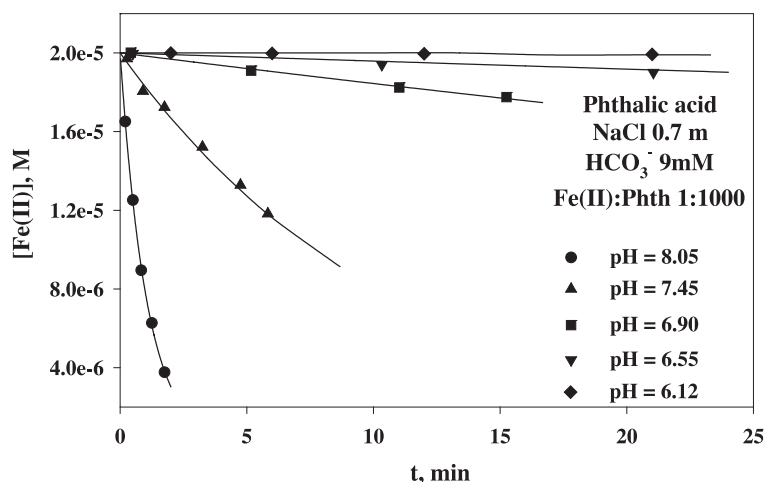


Fig. 4. Effect of pH_F in the oxidation kinetics of Fe(II)/phthalic acid 1:1000 in NaCl 0.7 m and 0.009 m HCO_3^- . The lines represent the kinetic model output for the experimental conditions as shown in Table 3.

followed in the presence of phthalic acid ($k' = k_{\text{app}}[\text{O}_2]$ in min^{-1})

$$\log k' = 15.35(\pm 0.57) + 1.92(\pm 0.08)\text{pH} \quad (r^2 = 0.995, n = 5)$$

In seawater media, the decrease in the oxidation rate of Fe(II) as phthalic acid concentration increases is similar to that found in NaCl– HCO_3^- solutions (see Table 2). In the presence of phthalic acid, the major cations (Ca^{2+} and Mg^{2+}) may also be complexed by the organic ligand capable of complexing Fe(II). Our model including all the HCO_3^- major ion interactions, phthalic acid-major ion complexes, the FeL complex (Table 1) and oxidation rates (Table 3) fit the experimental results for the different Fe(II):phthalic acid ratios considered (Table 2). At pH 7, the slowest oxidation rate in natural seawater (pseudo-first order rate constant $k' = 0.015 \text{ min}^{-1}$ at $\text{pH}_F = 7.11$) is reduced in the presence of phthalic acid $2 \times 10^{-2} \text{ m}$ ($k' = 6.2 \times 10^{-3} \text{ min}^{-1}$). The bar diagram in Fig. 5 depicts the effect of the presence of phthalic acid in Fe(II) speciation at pH 8 and 7.11 in seawater media. The decrease in concentration of the active carbonate- and hydroxyl-Fe(II) species ($\text{Fe}(\text{CO}_3)_2^{2-}$ from 0.08% to $7 \times 10^{-4}\%$, $\text{Fe}(\text{CO}_3)(\text{OH})^-$ from 3.2% to 0.025%, and $\text{Fe}(\text{OH})_2$ from $8.8 \times 10^{-4}\%$ to $5.9 \times 10^{-6}\%$) explains the

slower kinetics of Fe(II) in seawater. This decrease is followed by an increase in the Fe(II) phthalate complex concentration from 14.9% to 21.7% (also by the less active Fe(II) species), which accounts for the slower oxidation rate. A linear relationship between $\log k'$ and pH gives a slope of 1.88 ± 0.03 .

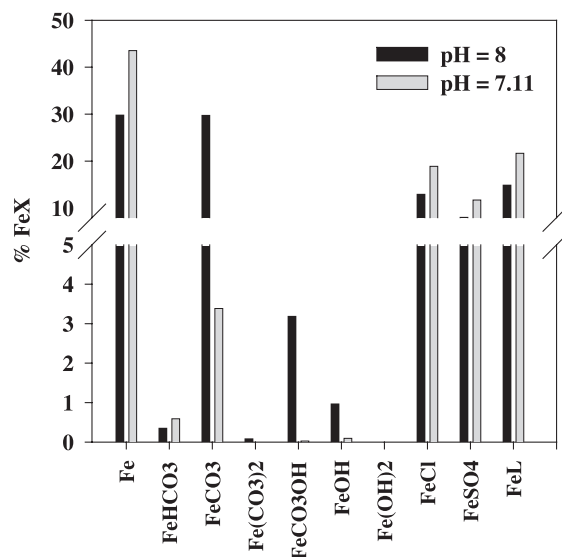


Fig. 5. Bar diagram for Fe(II) speciation in the presence of phthalic acid (ratio 1:1000) at pH_F 8.0 and 7.11 in seawater solutions at 25 °C and $S = 36.7$.

This finding supports the second-order rate constant for oxidation of Fe(II) by oxygen in seawater both in the absence and in the presence of phthalic acid. The coincidence between the experimental values and the model output in the pH range studied (Table 2), confirms the assumption considered in the proposed model even taking into account the fact that some other species presented in seawater may affect the speciation of HCO_3^- and the organic ligand.

3.2. Salicylic acid

Salicylic acid with a carboxylic and a hydroxyl group in ortho-position is present in natural seawater pH as the carboxylate anion with a fraction higher than 90%. In seawater, complexes with calcium and magnesium have already been described (Smith and Martell, 1989). MgL accounts for 7% of the total while CaL and CaHL represent around 1%. In this media, iron complexes, FeSa and FeSa₂, only contribute, respectively, 0.026% and $2.83 \times 10^{-5}\%$ to the salicylic acid speciation, according to the speciation model (Table 4). However, when we study the oxidation of Fe(II) in seawater, $\text{pH}_F = 8.1$, $S = 36.7$ and $t = 25^\circ\text{C}$, an increase in the oxidation rate is observed (Fig. 6, Appendix C) (Table 2). When the ratio Fe(II)/salicylic acid was as high as 1:1000, Fe(II) becomes oxidized in a few seconds. At $\text{pH}_F = 7.14$, the slowest Fe(II) oxidation rate in pure seawater increased from 0.017 to 0.603 min^{-1} in the presence

of $2.0 \times 10^{-3} \text{ M}$ salicylic acid, in both cases assuming a pseudo-first order behaviour. Table 4 also shows the effect of the presence of $2.0 \times 10^{-3} \text{ M}$ salicylic acid in the Fe(II) speciation in seawater. In our speciation model, the presence of the major ions Ca^{2+} and Mg^{2+} complexed with salicylic acid were considered (Table 1). At $\text{pH}_F = 8.14$, iron speciation is dominated by the less-reactive species ($k \approx 0$) of Fe(II), Fe^{2+} , FeCO_3 , FeCl^+ and FeSO_4 while the most reactive species $\text{Fe}(\text{CO}_3)_2^{2-}$, $\text{Fe}(\text{CO}_3)\text{OH}^-$ and $\text{Fe}(\text{OH})_2$ with a composition of 0.09%, 3.45% and $9 \times 10^{-4}\%$, respectively, dominate the weighted sum of all Fe(II) $k_i\alpha_i$ products. In the presence of salicylic acid, these three species slightly decrease their concentrations, and Fe(II) is also present in the mono- and bis-salicylate complexes as 2.57% and $2.83 \times 10^{-3}\%$, respectively (Table 4). The smaller percentage in the species with larger k_i values ($\text{Fe}(\text{CO}_3)_2^{2-}$, $\text{Fe}(\text{CO}_3)\text{OH}^-$ and $\text{Fe}(\text{OH})_2$) would decrease its oxidation rate unless the salicylic complexes participated actively in the oxidation process, favoured also by the formation of the strong Fe(III)–salicylate ion complexes (Table 1). In order to account for this finding, the kinetic model in seawater was applied. All the species with known complexing constants (Table 1) were considered and the oxidation rate for the Fe(II)–salicylic acid complexes were determined to fit the experimental values with different salicylic acid concentrations and seawater pH conditions. The oxidation of the mono-salicylic com-

Table 4

Speciation (%) of Salicylate ion (pH=8) and Fe(II) (pH=8 and pH=7) in 0.7 m ionic strength considering equilibrium constants given in Table 1

Speciation of salicylate			Speciation of Fe(II)				
Species	Without Fe(II)	With Fe(II)	Species	pH = 8		pH = 7	
				No Sa	With Sa	No Sa	With Sa
H ₂ Sa	3.51×10^{-4}	3.51×10^{-4}	Fe ²⁺	35.26	34.31	55.5	55.4
HSa [−]	92.2	92.1	FeHCO ₃	0.44	0.429	0.785	0.783
Sa ^{2−}	1.23×10^{-3}	1.24×10^{-3}	FeCO ₃	34.86	34.01	4.525	4.50
CaSa	0.170	0.170	Fe(CO ₃) ₂	0.093	0.091	9.9×10^{-4}	9.9×10^{-4}
MgSa	7	7	Fe(CO ₃)OH	3.485	3.396	0.033	0.033
CaHSa	0.635	0.635	FeOH	1.065	1.035	0.122	0.121
FeSa		0.026	Fe(OH) ₂	9.1×10^{-4}	8.8×10^{-4}	7.5×10^{-6}	7.4×10^{-6}
FeSa ₂		2.83×10^{-5}	FeCl	15.3	14.9	24.1	23.95
			FeSO ₄	9.5	9.25	14.95	14.92
			FeSa		2.566		0.32
			FeSa ₂		2.8×10^{-3}		2.7×10^{-5}

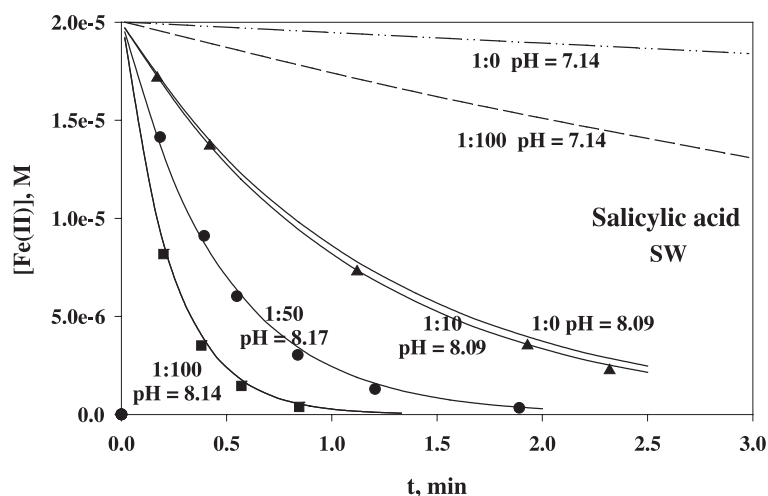


Fig. 6. Kinetics of oxidation of Fe(II) (20 μM) in the presence of different Fe(II)/salicylate ratios in seawater solutions ($S = 36.7$) at $\text{pH}_F = 8.0$ and $t = 25^\circ\text{C}$. The lines represent the kinetic model output for the experimental conditions.

plex, FeSa, with a second-order rate constant of $6.624 \times 10^5 \text{ M}^{-1} \text{ min}^{-1}$ (Table 3), fits the experimental results in the pH (7 to 8.2) and salicylic acid concentration range studied, while the FeSa_2^{2-} complex acts as a nonreactive species under these experimental conditions. At $\text{pH}_F = 7.1$, the important decrease in the concentration of carbonate- and hydroxyl-Fe(II) species, which explains the slower kinetics of Fe(II) in seawater (from 0.89 min^{-1} at pH 8.13 to 0.014 min^{-1} at pH 7.14, Table 2), is only followed by a decrease in the concentration of the salicylate complex FeSa from 2.56% to 0.32%. In this case, the product $k_{\text{FeSa}}\alpha_{\text{FeSa}}$ becomes similar in magnitude to the other active inorganic Fe(II) species ($\text{Fe}(\text{CO}_3)_2^{2-}$, $\text{Fe}(\text{CO}_3)\text{OH}^-$ and $\text{Fe}(\text{OH})_2$) in the oxidation of Fe(II). This behavior explains the value of $k' = 0.56 \text{ min}^{-1}$ (Table 2) in the presence of $2.0 \times 10^{-3} \text{ M}$ salicylate ion at $\text{pH}_F = 7.14$ with respect to a value of only 0.014 min^{-1} in seawater.

3.3. Environmental significance

This study provides a chemical model for Fe(II) oxidation with a quantitative understanding of Fe(II) oxidation by oxygen in organic-rich environments. The model is consistent with the experimental rate measurements as a function of pH for natural and seawater solutions. The model improves previous

Fe(II) oxidation rate models (King, 1998) by considering the full speciation of both inorganic iron and organic ligands and by working in a media of similar ionic strength to that found in natural seawater.

The role of two related organic compounds in seawater, generally used as model of organic compounds has been studied. Phenols and other benzoic derivatives are naturally present in surface waters as degradation products of lignin and other plant materials. In addition, anthropogenic inputs of these benzoic compounds and industrial wastes may be important in coastal waters. Environmental phthalates have become common in seawater where they scavenge metals that would otherwise be available to microorganisms (Chang and Zylstra, 1999). Some microorganisms are able to metabolise phthalates (Chang and Zylstra, 1999) by transporting them across their cell membrane. While salicylic acid favours Fe(II) oxidation, phthalate ion decreases Fe(II) oxidation rates making ferrous iron more available to microorganism. This study has been carried out under micromolar levels of iron. More studies are planned with these and other natural organic ligands by improving the analytical techniques to be able to work at nanomolar levels of Fe(II) concentrations with capillary longpath cells and UV–visible spectrophotometric detection.

Acknowledgements

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Appendix A

Experimental data for Fig. 1. $[\text{Fe(II)}]_0 = 2.0 \times 10^{-5}$ M in 0.7 m NaCl and 0.009 m NaHCO_3 and $t = 25^\circ\text{C}$.

	t (min)	$[\text{Fe(II)}]$
pH=8.13	0.33	$1.0659\text{e}-05$
	0.75	$6.1116\text{e}-06$
	1	$4.4004\text{e}-06$
pH=7.87	1.5	$1.5646\text{e}-06$
	0.42	$1.3487\text{e}-05$
	0.93	$9.086\text{e}-06$
	1.6	$5.7708\text{e}-06$
pH=7.8	2.083	$3.5362\text{e}-06$
	2.77	$2.5211\text{e}-06$
	3.57	$9.3315\text{e}-07$
	0.75	$1.1283\text{e}-05$
	1.75	$6.9971\text{e}-06$
	2.75	$3.4986\text{e}-06$
pH=7.59	4	$1.312\text{e}-06$
	5.25	$6.5598\text{e}-07$
	1	$1.3463\text{e}-05$
	2.5	$9.2488\text{e}-06$
	5	$4.0874\text{e}-06$
	7	$1.8449\text{e}-06$
pH=7.31	9.25	$9.7163\text{e}-07$
	0.23	$1.9425\text{e}-05$
	0.83	$1.8137\text{e}-05$
	1.75	$1.6188\text{e}-05$
	3	$1.4429\text{e}-05$
	4	$1.2485\text{e}-05$
pH=6.92	5.33	$1.0696\text{e}-05$
	0.33	$1.9391\text{e}-05$
	1.4	$1.9207\text{e}-05$
	3.58	$1.8255\text{e}-05$
	6	$1.7161\text{e}-05$
pH=6.14	12.5	$1.4325\text{e}-05$
	1.45	$1.9958\text{e}-05$
	8.24	$1.9762\text{e}-05$
	16.45	$1.9529\text{e}-05$
	22	$1.9372\text{e}-05$

Appendix B

Experimental data for Fig. 4. $\text{Fe(II)/phthalic acid}$ 1:1000 in 0.7 m NaCl and 0.009 m HCO_3^- , $[\text{Fe(II)}]_0 = 2.0 \times 10^{-5}$ M and $t = 25^\circ\text{C}$.

	t (min)	$[\text{Fe(II)}]$
pH=8.05	0.2	$1.6512\text{e}-05$
	0.5	$1.2518\text{e}-05$
	0.83	$8.9511\text{e}-06$
	1.25	$6.2749\text{e}-06$
	1.75	$3.7667\text{e}-06$
pH=7.45	0.27	$1.9708\text{e}-05$
	0.9	$1.8053\text{e}-05$
	1.75	$1.7237\text{e}-05$
	3.25	$1.5216\text{e}-05$
	4.75	$1.3282\text{e}-05$
	5.83	$1.1821\text{e}-05$
pH=6.90	0.42	$2.0011\text{e}-05$
	5.17	$1.9097\text{e}-05$
	11.02	$1.8245\text{e}-05$
	15.25	$1.7752\text{e}-05$
pH=6.55	0.5	$1.9971\text{e}-05$
	10.33	$1.9402\text{e}-05$
	21.05	$1.9\text{e}-05$
pH=6.12	2	$1.9993\text{e}-05$
	6	$1.9978\text{e}-05$
	12	$1.9956\text{e}-05$
	21	$1.9922\text{e}-05$

Appendix C

Experimental data for Fig. 6. Fe(II)/salicylate in 0.7 m NaCl and 0.009 m HCO_3^- , $[\text{Fe(II)}]_0 = 2.0 \times 10^{-5}$ M and $t = 25^\circ\text{C}$.

1:100, pH=8.14	0.2	$8.18\text{e}-06$
	0.38	$3.52\text{e}-06$
	0.57	$1.46\text{e}-06$
	0.84	$3.87\text{e}-07$
1:50, pH=8.17	0.18	$1.41\text{e}-05$
	0.39	$9.11\text{e}-06$
	0.55	$6.03\text{e}-06$
	0.84	$3.04\text{e}-06$
	1.21	$1.30\text{e}-06$
1:10, pH=8.09	1.89	$3.40\text{e}-07$
	0.17	$1.72\text{e}-05$
	0.42	$1.37\text{e}-05$
	1.93	$3.51\text{e}-06$
	2.32	$2.25\text{e}-06$
	1.12	$7.28\text{e}-06$

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