University of Groningen

Kinetics of the reaction of Fe-II(EDTA) with oxygen in aqueous solutions

Gambardella, Francesca; Ganzeveld, I.J.; Winkelman, Jos; Heeres, E.J.

Published in:
Industrial and Engineering Chemistry Research

DOI:
[10.1021/ie050448e](https://doi.org/10.1021/ie050448e)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gambardella, F., Ganzeveld, I. J., Winkelman, J., & Heeres, E. J. (2005). Kinetics of the reaction of Fe-II(EDTA) with oxygen in aqueous solutions. *Industrial and Engineering Chemistry Research*, 44(22), 8190-8198. <https://doi.org/10.1021/ie050448e>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Kinetics of the Reaction of Fe^{II}(EDTA) with Oxygen in Aqueous Solutions

Francesca Gambardella, Ineke J. Ganzeveld, Jos G. M. Winkelman, and Erik J. Heeres*

Department of Chemical Engineering, Stratingh Institute, RijksUniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

The kinetics of the reaction of oxygen with aqueous Fe^{II}(EDTA) solutions has been determined in a range of process conditions ($C_{\text{Fe}^{\text{II}}(\text{EDTA})} = 15\text{--}60 \text{ mol/m}^3$, $P_{\text{O}_2} = 5\text{--}20 \text{ kPa}$, $\text{pH} = 5\text{--}8$, $T = 298\text{--}328 \text{ K}$, $C_{\text{NaCl}} = 0\text{--}15 \text{ kg/m}^3$) using a gas–liquid stirred cell reactor. The oxygen absorption rates were modeled using an expression derived by De Coursey using the penetration theory of mass transfer. Within the range of process conditions applied, the reaction was shown to be first order in oxygen and second order in iron chelate. The temperature dependence of the kinetic constant may be expressed as ($\text{pH} = 7$, no salt addition): $k_{12} = 5.3 \times 10^3 \text{ e}^{-4098/T} \text{ m}^6/(\text{mol}^2 \cdot \text{s})$. The kinetic constant is essentially independent of the pH in the range $5 < \text{pH} < 8$. When applying a NaCl concentration of 15 kg/m^3 , the kinetic constant increases $\sim 35\%$ ($T = 328 \text{ K}$). The oxidation of Fe^{II}(EDTA) to Fe^{III}(EDTA) is not the sole oxygen-consuming reaction. The extent of side reactions, possibly related to EDTA ligand degradation, is a function of the pH and the oxygen concentration. A remarkable, unprecedented step change in the selectivity of the reaction was observed when the reaction was performed at a higher oxygen concentration.

1. Introduction

A number of treatment technologies have been developed to remove NO from flue gas.¹ Selective catalytic reduction is now widely used on a large scale. Novel concepts such as wet removal technologies have been proposed in the literature. Here, the NO gas is absorbed in an aqueous solution with a suitable reactant. Particularly, Fe^{II} chelates based on ethylenediaminetetraacetic acid derivatives (EDTA) and related compounds such as NTA (nitrilotriacetic acid) are very effective and lead to high NO absorption rates and removal efficiencies.^{2,3} However, to be cost effective, the Fe chelate needs to be regenerated and reused in the process. Various recycle options have been proposed. In the BiodeNOx process, NO absorption in an Fe^{II}(EDTA) solution is coupled with a biological regeneration of the loaded Fe-chelate solution, using denitrifying microorganisms.⁴ Various other components are present in flue gas, which can interfere with the BiodeNOx process and give rise to undesired side reactions with the iron chelate. One of the major components is molecular oxygen, which is typically present in amounts between 2 and 10 vol %. Oxygen reacts with the iron chelate to form Fe^{III}(EDTA) according to the overall reaction:

This complex is not able to bind NO, and for this reason, the efficiency of the BiodeNOx absorption unit may decrease. The presence of oxygen in the flue gas cannot be avoided, and the rate of oxidation compared to the rate of NO absorption has to be reduced as much as possible by the proper selection of the process conditions and the absorber configuration. For this purpose, reliable

kinetic data on the oxidation reaction in the BiodeNOx operating window are required.

The reaction has been the object of several studies. A summary of the literature available is represented in Table 1 and the kinetic data are shown in Table 2. A considerable spread in the orders of the reactants has been observed.

In some cases, the reaction was observed to be first order in iron chelate, in other cases it was second order. This change in the order in iron chelate appears to be a function of the concentration of ferrous chelate.^{8,9} At low concentrations, the reaction seems to be first order in iron chelate, whereas the order changes to 2 at increasing Fe^{II}(EDTA) concentrations. Mechanistic proposals have been put forward to explain this effect.^{8,9} Recent studies suggest that the order in iron is 2 when using iron concentrations relevant for the BiodeNOx process ($10 < \text{Fe} < 100 \text{ mol/m}^3$).⁹ In addition, all studies imply that the reaction is first order with respect to oxygen.^{5–10}

This work describes a kinetic study on the reaction of $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ with oxygen under conditions relevant to the BiodeNOx process ($C_{\text{Fe}^{\text{II}}(\text{EDTA})} = 15\text{--}60 \text{ mol/m}^3$, $P_{\text{O}_2} = 5\text{--}20 \text{ kPa}$, $\text{pH} = 5\text{--}8$, $T = 298\text{--}328 \text{ K}$, and $C_{\text{NaCl}} = 0\text{--}15 \text{ kg/m}^3$). Although various studies have been performed in the past, the results are not always reliable because of improper attention to mass transfer issues. In addition, a lack of kinetic information was found for the typical BiodeNOx process conditions ($T > 300 \text{ K}$, $\text{pH} \neq 7.5$, and an iron chelate concentration $> 10 \text{ mol/m}^3$).

Special attention is given to pH effects and the effects of salts in the aqueous phase on the oxygen absorption rates. The flue gas often contains acidic components such as HF and HCl, and these may reduce the pH of the solution. This could possibly lead to negative effects on the absorption rates and microbial growth. To avoid these effects, a constant pH is desired and buffering and/or the addition of bases is required. This

* To whom correspondence should be addressed. Fax: +31 50 363 4479. E-mail: h.j.heeres@rug.nl.

Table 1. Overview of Literature Studies Performed on the Oxidation of Fe^{II}(EDTA) in Water

author	<i>T</i> (K)	pH	system	<i>C</i> _{Fe^{II}(EDTA)} (mol/m ³)	<i>C</i> _{O₂} ⁱ (mol/m ³)	ratio EDTA/Fe
Travin and Skurlatov ⁵	295	2–6	stopped flow	0.1–0.2	0.25	1–40
Sada and Kumazawa ⁶	293–333	6–8	bubble column	<20	0.018–0.064	1–2
Brown and Mazzarella ⁷	298	3–7	bubble column	2.5	0.125–1.5	5
Zang and van Eldik ⁸	286–323	2–7	stopped flow	2.5–20	0.125	1–20
Wubs and Beenackers ⁹	293–331	7.5	stirred cell	0–100	0–1.25	1.2
Seibig and van Eldik ¹⁰	298	1–6	stopped flow	2.5	0.125	1

Table 2. Orders in Reactants for the Reaction between Fe^{II}(EDTA) and Oxygen

author	<i>T</i> (K)	pH	order in Fe ^{II} (EDTA)	order in O ₂
Travin and Skurlatov ⁵	295	6	1	1
Sada and Kumazawa ⁶	293–330	6–8	0.5	1
Brown and Mazzarella ⁷	298	4.5–7	1–2	1
Zang and van Eldik ⁸	286.5–322	5	1–2	1
Wubs and Beenackers ⁹	293–361	7.5	2	1
Seibig and van Eldik ¹⁰	298	2.5–6	1	1

will evidently lead to high salt concentrations in the Fe-chelate solution and this might have an effect on the oxygen absorption rates. The influence of denitrifying microorganisms on the absorption rates will be reported separately.

2. Experimental Section

2.1. Chemicals. FeCl₂·4H₂O (p.a.), titriplex (EDTA–Na₂) (p.a.), and Na₂CO₃ were obtained from Merck, NaOH (33% in water) was obtained from Boom, and Ce(SO₄)₂·4H₂O (>99%) was obtained from Acros. N₂O (>99%), O₂ (>99.99%), and N₂ (>99.99%) were obtained from Hoek Loos. Reverse osmosis water was applied to prepare the various solutions.

2.2. Preparation of the Fe^{II}(EDTA) Solution. Aqueous solutions of Fe^{II}(EDTA) are extremely air-sensitive and were handled under a protective nitrogen atmosphere. The Fe^{II}(EDTA) solution was prepared by dissolving a predetermined amount of titriplex in degassed water (1.5 × 10^{−4} m³). The turbid solution turned transparent when the pH was increased from 4 to 9 by carefully adding some drops of a 4 M NaOH solution. The appropriate amount of FeCl₂·4H₂O (Fe/EDTA = 1:1.2 mol/mol) was added to the EDTA solution, giving a slightly green, clear solution with a pH of ~3. Next, the solution was diluted with degassed water to 9 × 10^{−4} m³. At this stage, the pH was adjusted to the desired value by the addition of a NaOH solution. Finally, degassed water was added to adjust the total volume to 10^{−3} m³.

2.3. Experimental Setup and Instrumentation. The kinetic experiments were carried out using two different stirred-cell reactors, both made of glass. The two reactors differed in dimensions and in the layout of the mechanical stirring devices. Both reactors were equipped with four glass baffles and could be operated in batch as well as in continuous mode with respect to the gas phase and in batch mode with respect to the liquid phase. A schematic representation of reactor 1 is given in Figure 1.

The stirrer of reactor 1 had six blades for the gas phase and six smaller ones for the liquid phase. For reactor 2, a stainless steel turbine impeller was used for the gas phase, while a magnetic stirrer in combination with an external magnetic drive was used for the liquid phase. The rotation speed of the magnetic drive was determined using a stroboscope (Philips PR 9107). The double wall of the reactors allowed the use of water

to regulate the temperature in the reactor (Julabo, MV basis). Typical dimensions of the stirred-cell contactors are given in Table 3. A temperature indicator (PT-100) and a pressure transducer (Trafag, ECO 2.5 A) were used to monitor the temperature and pressure during an experiment.

Figure 1. Stirred-cell reactor (reactor 1) used in this study: 1, 2 = magnetic valve for the gas inlet and outlet; 3 = metal cover; 4 = double-walled glass reactor 5 = stirring device; 6, 7 = gas- and liquid-phase stirrer; 8 = temperature sensor; and 9 = pressure indicator.

2.4. Constant Pressure Experiments. The constant pressure experiments were performed in reactor 1. An experimental procedure described in detail by Wubs and Beenackers⁹ was applied. Before starting an experiment, the headspace of the reactor was evacuated to remove the air, until the vapor pressure of water was established. At this point, oxygen gas was supplied to the reactor until the desired pressure was reached. Subsequently, the inlet valve was closed, the stirrer was activated, and the absorption was started. The experiment was allowed to proceed until the pressure reached a preset minimum value, after which extra gas was supplied until the original preset maximum pressure was reached again. By repeating this procedure several times, the pressure profile appeared as a sawtooth-like curve.

2.5. Decreasing Pressure Experiment. A number of physical absorption experiments using inert N₂O were performed in order to determine the solubility of the gas in the various solutions and the hydrodynamics of both reactor setups. These experiments were carried out at decreasing pressure. The gas was supplied to the reactor until the pressure reached a preset value. At this point,

Table 3. Characteristics of the Stirred Cell Contactors

	reactor 1	reactor 2
total reactor volume (m ³)	1.98 × 10 ^{−3}	1.245 × 10 ^{−3}
liquid volume (m ³)	10 ^{−3}	0.3 × 10 ^{−3}
interfacial area (m ²)	8.34 × 10 ^{−3}	7.79 × 10 ^{−3}
gas impeller (m)	six-blade turbine, <i>d</i> = 6 × 10 ^{−2}	six-blade turbine, <i>d</i> = 6 × 10 ^{−2}
liquid impeller (m)	six-blade turbine, <i>d</i> = 4 × 10 ^{−2}	magnetic stirrer, <i>d</i> = 2 × 10 ^{−2}
<i>N_S</i> liquid stirrer (min ^{−1})	120	100
<i>N_S</i> gas impeller (min ^{−1})	120	2000

the inlet valve was closed, the stirrer was activated, and the absorption was started. The absorption was allowed to proceed until the pressure inside the reactor reached a constant value. A typical pressure profile is given in the Supporting Information. A similar procedure was applied when performing oxygen absorption experiments at decreasing pressure.

2.6. Determination of the Concentration of Fe^{II} in Solution. The concentration of Fe^{II} in the solution was determined before and after every oxidation experiment by titration using a 0.1 M Ce(SO₄)₂ solution. A 0.025 M ferroine solution was used as the redox indicator. To obtain reproducible results, the iron-chelate sample was diluted with an ~10-fold volume of sulfuric acid (2 M) and degassed by adding ~1 g of NaHCO₃. After adding some drops of the ferroine indicator, the color of the solution turned red/orange. At this point, the titration was started by the dropwise addition of the cerium solution until the color of the solution changed from red-orange to clear blue-green.¹¹

3. Theory

3.1. Calculation of the Kinetics of the Oxidation Reaction at Various Process Conditions. The enhancement factor E_A for reactive absorption processes is generally defined as:

$$E_A = \frac{J_{\text{reaction}}}{J_{\text{physical}}} \Big|_{\text{at the same driving force}} \quad (2)$$

E_A may be determined experimentally for each absorption experiment using the following relation:

$$E_A = \frac{J_{\text{reaction}}}{J_{\text{physical}}} = \frac{J_{\text{O}_2}}{k_L C_{\text{O}_2}^i} = \frac{1}{k_L a} \frac{He_{\text{O}_2}}{P_{\text{O}_2}} \cdot \frac{V_G}{RTV_L} \left(-\frac{dP_{\text{O}_2}}{dt} \right) \quad (3)$$

The various theories for mass transfer accompanied by chemical reaction in parallel have provided relations between E_A and the Hatta (Ha) number.¹² Here, the Ha number for reaction 1 is defined as

$$Ha = \frac{1}{k_L} \sqrt{\frac{2}{q+1} D_{\text{O}_2} k_{pq} C_{\text{FeII(EDTA)}}^p C_{\text{O}_2}^{i,q-1}} \quad (4)$$

where p and q represent the orders of the reaction with respect to O₂ and Fe^{II}(EDTA), respectively, and k_{pq} is the kinetic rate constant.¹² When the Ha number is known, the kinetic constant may be determined using eq 4.

In the case that $Ha < 0.2$, the oxygen absorption rate is not enhanced by chemical reaction and the enhancement factor $E_A = 1$. In the case that $2 < Ha \ll E_{A\infty}$, the reaction takes place in the fast regime and $E_A = Ha$. Here $E_{A\infty}$ is defined as¹²

$$E_{A\infty} = \frac{1}{\sqrt{r_B}} + \frac{\sqrt{r_B} C_{\text{FeII(EDTA)}}}{\nu_B C_{\text{O}_2}^i} \quad (5)$$

In the case where $Ha \gg E_{A\infty}$, the absorption process occurs in the instantaneous reaction regime and $E_A = E_{A\infty}$.

As shown later, the intermediate regime between the fast and instantaneous regimes appears to be of par-

ticular interest for this study. Several relations between E_A and Ha have been derived for this regime. A useful relation is an explicit expression derived by De Coursey using the penetration theory of Dankwerts.¹³

$$E_A = -\frac{Ha^2}{2(E_{A\infty} - 1)} + \sqrt{\frac{Ha^4}{4(E_{A\infty} - 1)^2} + \frac{E_{A\infty} Ha^2}{(E_{A\infty} - 1)} + 1} \quad (6)$$

The relation was derived for reacting components having equal diffusivities and extended to compounds with different diffusivities. The maximum inaccuracy of this expression is ~13% for a ratio of diffusion coefficients in the order of 0.02, and it decreases to 6% for equal diffusivities. Later, the authors derived a refined, implicit relation, which is more accurate for species with unequal diffusivities.¹⁴ In the case of an irreversible reaction, this relation can be written as

$$\frac{1}{Ha^2} + \frac{1}{q(E_A \sqrt{r_B} + 1)} = \frac{1}{E_A^2 - 1} \quad (7)$$

where

$$q = \frac{C_{\text{FeII(EDTA)}}}{\nu_B C_{\text{O}_2}^i} \quad (8)$$

and

$$r_B = \frac{D_{\text{FeII(EDTA)}}}{D_{\text{O}_2}} \quad (9)$$

The equation is valid for any value of Ha and can be extended to an irreversible reaction of any order, taking into consideration the correct definition of Ha . This implicit relation is in good agreement with the results based on numerical solutions using a rigorous mass balance approach, and a mean deviation of 11% was observed.¹⁵

3.2. Solubility and Mass Transfer Coefficients.

Knowledge of the solubility of oxygen and the hydrodynamics in the stirred-cell contactor as a function of the process conditions is required to determine the kinetics of the oxidation reaction. The solubility of oxygen in the liquid phase may be described by the Henry coefficient, which is defined as the ratio of the partial pressure of a gas and its concentration in the bulk liquid at equilibrium:

$$He = \left(\frac{P_{\text{O}_2}}{C_{\text{O}_2}^i} \right)_{\text{eq}} \quad (10)$$

For physical absorption of a gas in a batch setup, a mass balance gives the following relation for the Henry coefficient:

$$He = \frac{P^\infty - P_w}{P^0 - P^\infty} \frac{RTV_L}{V_G} \quad (11)$$

In the case of oxygen, the solubility cannot be measured directly because of the fact that oxygen reacts with Fe^{II}(EDTA). To determine the He value for O₂, physical absorption experiments using an inert gas (nitrous oxide) are performed. The measured solubility

of the inert gas may be used to calculate the oxygen solubility using the following relation:

$$\left(\frac{He}{He_w}\right)_{O_2} = A_G \left(\frac{He}{He_w}\right)_{N_2O} \quad (12)$$

The term A_G represents a correction term, which is a function of the total ion concentration and temperature. A_G was estimated using well-established relations (see Supporting Information). The solubility of N_2O in water is given by Versteeg and van Swaaij.¹⁶ The solubility of oxygen in water is given by Benson and Krause.¹⁷

The mass transfer coefficient of oxygen in the liquid phase (k_L) is a function of the temperature, the composition of the liquid phase, and the stirrer speed and geometry. k_L may be obtained experimentally by performing physical absorption experiments using an inert gas such as N_2O in the batch setup. A mass balance leads to the following relation,

$$k_L a t = \left(\frac{\alpha}{\alpha + 1}\right) \ln \left(\frac{P_{O_2}^0}{(\alpha + 1)P_{O_2} - \alpha P_{O_2}^0} \right) \quad (13)$$

with

$$\alpha = \frac{V_G He}{V_L R T} \quad (14)$$

The $k_L a$ for oxygen can be calculated from the experimentally determined value for N_2O using the following relation:¹²

$$(k_L a)_{O_2} = (k_L a)_{N_2O} \sqrt{\frac{D_{O_{2w}}}{D_{N_2O_w}}} \quad (15)$$

$D_{N_2O_w}$ is given by Versteeg and van Swaaij.¹⁶ $D_{O_{2w}}$ may be calculated using the relation given by St-Denis and Fell.¹⁸ The diffusion coefficient of oxygen in $Fe^{II}(EDTA)$ solutions (D_{O_2}) may be calculated from $D_{O_{2w}}$ using a relation given by Ho et al.¹⁹

3.3 Determination of the Stoichiometric Coefficient. To obtain information of possible other oxygen-consuming reactions besides the main reaction, the stoichiometric coefficient of iron for the reaction has to be determined experimentally. For the reaction

the stoichiometric coefficient ν_B may be calculated considering that

$$C_{Fe^{II}(EDTA)} \cdot V_L = C_{Fe^{II}(EDTA)}^0 \cdot V_L - \nu_B N_{O_2} \quad (17)$$

The concentrations of the iron chelates before and after reaction ($C_{Fe^{II}(EDTA)}^0$ and $C_{Fe^{II}(EDTA)}$) were determined experimentally by titration, while the total number of moles of oxygen absorbed, N_{O_2} , was calculated from the absorption profiles of decreasing pressure experiments.

4. Results and Discussion

Absorption experiments were performed using pure oxygen at pressures ranging from 5 to 20 kPa and initial $Fe^{II}(EDTA)$ concentrations in the range of 15 and 60 mol/m³. In all cases, an EDTA–Fe molar ratio of 1.2:1

Figure 2. First-order dependency of the reaction in oxygen: $T = 328$ K, $C_{Fe^{II}(EDTA)}^0 = 50$ mol/m³, pH = 7, and $C_{O_2}^i = 0.036$ mol/m³.

was applied. A first group of experiments was carried out at different temperatures (298–328 K) and a fixed pH = 7 to determine the temperature dependence of the kinetic constant of the reaction. Subsequently, experiments with a variable pH (5–8) were applied at 328 K to probe possible pH effects on the kinetics. Finally, experiments in the presence of NaCl (5–15 kg/m³) were performed (328 K) to determine any effect of the presence of salt on the gas absorption rates and the intrinsic kinetics.

4.1. Determination of Reaction Orders and Absorption Regime. To determine the absorption regime and, subsequently, the kinetic data, the order in reactants needs to be known. The order in oxygen may be obtained from decreasing pressure experiments. For such experiments, a mass balance for oxygen for the gas phase leads to

$$-\frac{dP_{O_2}}{dt} = cP_{O_2} \quad (18)$$

A plot of $\ln(P_{O_2}^0/P_{O_2})$ versus time is expected to give a straight line, provided that c is independent of the initial oxygen partial pressure. This is the case when the reaction is first order in oxygen and when the reaction takes place in the fast regime ($E_A \ll E_{A\infty}$). For a typical experiment in the fast regime, a linear relation between $\ln(P_{O_2}^0/P_{O_2})$ and the time was observed (Figure 2), and this confirms that the reaction is first order in oxygen.

In our studies, $C_{Fe^{II}(EDTA)}$ always exceeded 10 mol/m³ and, as a consequence, an order in Fe of 2 was assumed. The validity of this assumption will be discussed later on. When the reaction is first order in oxygen and second order in iron, the Ha number for the system is defined as

$$Ha = \frac{C_{Fe^{II}(EDTA)}}{k_L} \sqrt{D_{O_2} k_{12}} \quad (19)$$

Knowledge on the regime of absorption may be obtained from the theory of mass transfer and reaction in parallel. In the case that the absorption occurs in the fast regime, $E_A = Ha$ and eq 19 may be rewritten as

$$C_{O_2}^i \frac{dE_A}{dC_{Fe^{II}(EDTA)}} = \frac{C_{O_2}^i}{k_L} \sqrt{D_{O_2} k_{21}} \quad (20)$$

In this regime, $C_{O_2}^i (dE_A/dC_{Fe^{II}(EDTA)})$ is expected to vary linearly with $C_{O_2}^i$.

In the case that the absorption process takes place in the instantaneous regime, eq 5 holds, and this may be rewritten as

$$C_{O_2}^i \frac{dE_A}{dC_{Fe^{II}(EDTA)}} = \frac{\sqrt{r_B}}{\nu_B} \quad (21)$$

Absorption experiments were performed in reactor 2 to determine E_A as a function of $C_{O_2}^i$. The results are given in Figure 3.

A linear dependency was observed at low $C_{O_2}^i$, whereas a leveling off occurs at higher $C_{O_2}^i$ values. Although not conclusive, this suggests that the reaction takes place in the fast regime at low $C_{O_2}^i$ and that the regime changes from fast to instantaneous at higher oxygen concentrations. Additional evidence that the reaction takes place in a regime between fast and instantaneous is obtained when considering E_A as a function of $C_{O_2}^i$ (Figure 4). In the case that the reaction is a fast first-order reaction in oxygen, the E_A is expected to be independent of the $C_{O_2}^i$ (eq 19). In the case that the reaction is instantaneous, a plot of $\ln(E_A)$ vs $\ln(C_{O_2}^i)$ is expected to give a straight line with a slope of -1 (eq 5). The observed slope is -0.15 , which is, again, a strong indication that the reaction takes place in the intermediate regime between fast and instantaneous. On the basis of these findings, it seems appropriate to apply the implicit de Coursey relation (eq 7) to describe the absorption process in the stirred-cell contactor.

4.2. Determination of the Kinetic Constant of the Oxidation Reaction at Various Temperatures.

A set of experiments at different temperatures was performed in reactor 2 to determine the temperature dependence of the kinetic constant. The experiments were carried out at an initial pH = 7, an initial $Fe^{II}(EDTA)$ concentration of 50 mol/m³, and $C_{O_2}^i$ between 0.04 and 0.4 mol/m³. The rate constant at different temperatures may be calculated by combining eqs 7 and 19. This results in

$$k_{12} = \frac{k_L^2}{C_{Fe^{II}(EDTA)}^2 D_{O_2}} \cdot \frac{(E_A^2 - 1)q(E_A \sqrt{r_B} + 1)}{q(E_A \sqrt{r_B} + 1) - E_A^2 + 1} \quad (22)$$

The experimentally determined k_{12} values at various temperatures are graphically provided in the form of an Arrhenius plot (Figure 5). In this figure, earlier data provided by Wubs and Beenackers⁹ and Zang and van Eldik⁸ are also given.

The activation energy (E_a) and the preexponential factor of the oxidation reaction were calculated to be 34.1 (± 0.4) kJ/mol and 5326 (± 2) m⁶/(mol²·s), respectively. Our results are within the broad range of values reported in the literature (see Figure 5 for details). Zang and van Eldik reported an E_a of 36.6 kJ/mol,⁸ which is close to the value found by us; however, the kinetic constants are significantly higher than our values. van Eldik used a different experimental technique (single-phase system and stopped flow) compared to the multiphase stirred-cell contactor used in this study. Their

Figure 3. Determination of the reaction regime for the reaction between $Fe^{II}(EDTA)$ and oxygen: $C_{Fe^{II}(EDTA)}^0 = 50$ mol/m³, $T = 328$ K, and pH = 7. ■: measured; solid line: for illustrative purposes only.

Figure 4. Enhancement factor as a function of the interfacial oxygen concentration: $C_{Fe^{II}(EDTA)}^0 = 50$ mol/m³, $T = 323$ K, and pH = 7.

kinetic data were analyzed assuming pseudo-first-order reactions, which is only correct when one of the reactants is in large excess. These conditions are not always fulfilled in their study. In addition, when determining the order in oxygen, first-order behavior in $Fe^{II}(EDTA)$ was assumed, whereas in a subsequent stage, it is concluded that an order of 2 in Fe is more appropriate.

The low-temperature kinetic constants are in close agreement with earlier studies by Wubs and Beenackers.⁹ However, the high temperature results deviate considerably, and the E_a reported by Wubs (27.2 kJ/mol) is significantly lower than that found by us. These differences are likely related to the differences in calculation procedures. Wubs applied the explicit relation by De Coursey (eq 6) to calculate the kinetic data, which is less accurate in the case of unequal diffusivities. Moreover, a value of $\nu_B = 2$, instead of $\nu_B = 4$, was applied in the calculation, which is not appropriate.

4.3. pH Effects on the Absorption Rates and the Intrinsic Kinetics.

A number of constant-pressure

Figure 5. Arrhenius plot for the reaction of oxygen with $\text{Fe}^{\text{II}}(\text{EDTA})$. Solid line: $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 50 \text{ mol/m}^3$, $\text{pH} = 7$ (this study); dotted line: $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 100 \text{ mol/m}^3$, $\text{pH} = 7.5$ (Wubs and Beenackers);⁹ dashed line: $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 20 \text{ mol/m}^3$, $\text{pH} = 5$ (Zang and van Eldik).⁸

Figure 6. E_A as a function of $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ at $\text{pH} = 5$: ■, experimental data, $T = 328 \text{ K}$, $C_{\text{O}_2}^i = 0.158 \text{ mol/m}^3$; solid line, calculated according to eq 7, $T = 328 \text{ K}$, $k_{12} = 0.030 \text{ m}^6/\text{mol}^2 \text{ s}$, $k_L = 2.40 \times 10^{-5} \text{ m/s}$, $P_{\text{O}_2} = 18 \text{ kPa}$, $D_{\text{O}_2} = 2.05 \times 10^{-9} \text{ m}^2/\text{s}$, $r_B = 0.213$,²⁰ $v_b = 4$; and dotted line, calculated according to eq 7 for a 1,1 order reaction with $k_{1,1} = 0.95 \text{ m}^3/(\text{mol} \cdot \text{s})$.

experiments in reactor 1 at 328 K were performed to determine the influence of pH variation (5–8) on the kinetics of the oxidation of $\text{Fe}^{\text{II}}(\text{EDTA})$. A $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0$ between 15 and 60 mol/m^3 and a P_{O_2} of 18 kPa were used. The results were compared with the experiments obtained at $\text{pH} = 7$. E_A was calculated as a function of $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ using eq 3. An overview of the experimental results is provided in Figures 6 ($\text{pH} = 5$) and 7 ($\text{pH} = 8$). The maximum E_A was ~ 17 for both experimental series.

The kinetic constants of the reaction at various pHs were calculated using eq 22. To do so, He_{O_2} and k_L as a function of the pH need to be known. These were determined experimentally; further details are given in the Supporting Information. The kinetic constant values at 328 K were subsequently calculated from the experimental enhancement factors, using eq 22. The results are provided in Table 4.

Figure 7. E_A as a function of $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ at $\text{pH} = 8$: ■, experimental points, $T = 328 \text{ K}$, $C_{\text{O}_2}^i = 0.158 \text{ mol/m}^3$; solid line, calculated according to eq 7, $T = 328 \text{ K}$, $P_{\text{O}_2} = 18 \text{ kPa}$, $k_{12} = 0.024 \text{ m}^6/(\text{mol}^2 \cdot \text{s})$, $k_L = 2.40 \times 10^{-5} \text{ m/s}$, $D_{\text{O}_2} = 2.05 \times 10^{-9} \text{ m}^2/\text{s}$, $r_B = 0.213$,²⁰ $v_b = 4$; and dotted line, calculated according to eq 7 for a 1,1 order reaction with $k_{1,1} = 0.81 \text{ m}^3/(\text{mol} \cdot \text{s})$.

Table 4. k_{12} at $T = 328 \text{ K}$ as a Function of the pH

pH	$C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0$ (mol/m^3)	k_{12} ($\text{m}^6/(\text{mol}^2 \cdot \text{s})$)
8 ^a	60	0.024 ± 0.005
7 ^b	50	0.020 ± 0.001
5 ^a	60	0.030 ± 0.005

^a Constant pressure experiment, $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 15\text{--}60 \text{ mol/m}^3$ and $C_{\text{O}_2}^i = 0.158 \text{ mol/m}^3$ (reactor 1). ^b Decreasing pressure experiments, $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 50 \text{ mol/m}^3$ and $C_{\text{O}_2}^i = 0.036\text{--}0.16 \text{ mol/m}^3$ (reactor 2).

It appears that the pH effects on k_{12} are relatively small and within the error of the determination. Brown and Mazzarella⁷ observed that the kinetic constant for the oxidation reaction is pH independent for a $\text{pH} > 5$ ($T = 298 \text{ K}$). Zang and van Eldik⁸ studied the effect of the pH in the range of 1–7. The kinetic constant was not pH dependent at pH values > 5 . However, upon further lowering the pH, the kinetic constant increases until a $\text{pH} = 3$. Upon further lowering the pH, the k_{12} decreases again.

With the experimentally determined dependency of E_A versus $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ (Figures 6 and 7), the assumption that the reaction is indeed second order in iron and not first order in the experimental range of conditions can be verified. In the case that the reaction is first order in oxygen, the dependency of the E_A versus the $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ may be predicted using eq 7, taking into account the correct definition of Ha . The results for both pH series are given in Figures 6 and 7. Qualitatively, the experimental profiles are more in line with a second-order reaction in iron than for a first-order dependency. Statistical analyses using the sum of squares method also indicates that the model assuming a second-order dependency in iron describes the experimental points more satisfactorily.

4.4. Effect of Salt Addition on the Absorption Rate and the Kinetics of the Reaction. A number of constant-pressure absorption experiments were performed in the presence of various amounts of NaCl (5, 10, and 15 kg/m^3) to probe the effects of salinity on the gas absorption rates and the intrinsic reaction kinetics (328 K, $\text{pH} = 7$, $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 50 \text{ mol/m}^3$, and $P_{\text{O}_2} = 18$

Figure 8. E_A values at different C_{NaCl} values, $T = 328$ K, $\text{pH} = 7$. ■, $C_{\text{NaCl}} = 5$ kg/m³; ●, $C_{\text{NaCl}} = 10$ kg/m³; ▲, $C_{\text{NaCl}} = 15$ kg/m³; lines, calculated according to eq 7, $C_{\text{O}_2}^i = 0.156$ mol/m³, $D_{\text{O}_2} = 2.05 \times 10^{-9}$ m²/s, $r_B = 0.213$,²⁰ $v_B = 4$; solid line, $k_{12} = 0.019$ mol⁶/(m³·s), $k_L = 2.40 \times 10^{-5}$ m/s; dotted line, $k_{12} = 0.022$ mol⁶/(m³·s), $k_L = 2.31 \times 10^{-5}$ m/s; and dashed line, $k_{12} = 0.027$ mol⁶/(m³·s), $k_L = 2.11 \times 10^{-5}$ m/s.

kPa. The observed E_A values as a function of $C_{\text{Fe}^{\text{II}}(\text{EDTA})}$ are given in Figure 8.

It is clear that E_A increases with increasing salt concentration. This effect may be the result of changes in either the physical and hydrodynamics properties of the liquid (e.g., k_L) and/or the effects on the intrinsic kinetics. To gain more insights into these effects, the k_L and gas solubility of oxygen at various salt loadings were determined ($T = 328$ K, $C_{\text{Fe}^{\text{II}}(\text{EDTA})} = 50$ mol/m³, and $\text{pH} = 7$). The He_{O_2} was rather insensitive to the salt concentration in the concentration range applied. k_L decreased when increasing the salt loading (see Supporting Information for more details), in line with an observed reduction of the D_{O_2} at higher salt concentrations.²¹ Here, the $D_{\text{O}_2, \text{w}}$ decreased up to 5% when increasing the salt concentration from 5 to 16 kg/m³.

With the k_L and the solubility of oxygen in the presence of salts known, the kinetic constants at various salt concentrations may be calculated using eq 22. The results are given in Figure 9. Despite the relatively large error, k_{12} appears to increase with C_{NaCl} .

4.5. Side Reactions. There is considerable evidence in the literature that the reaction of an Fe chelate with oxygen leads not only to iron oxidation but also to the formation of degradation products.^{22,23} However, the type and number of oxygen-consuming side reactions is still not clear to date, although it appears that chelate degradation may be involved as well. Information on the extent of other oxygen-consuming side reactions may be obtained by determination of the stoichiometric coefficient of iron. If only iron oxidation takes place, the stoichiometric coefficient $v_B = 4$ (see reaction 1). If other oxygen-consuming reactions occur simultaneously, the experimentally determined v_B is reduced.

v_B was determined using eq 17 for a number of absorption experiments performed in reactor 2 using different oxygen pressures (between 5 and 45 kPa) and pH values between 5 and 8, at a constant $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 50$ mol/m³ and $T = 328$ K (see Figure 10). The v_B values

Figure 9. k_{12} versus C_{NaCl} at $T = 328$ K, $\text{pH} = 7$, $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 50$ mol/m³, and $C_{\text{O}_2}^i = 0.156$ mol/m³.

Figure 10. v_B as a function of $C_{\text{O}_2}^i$ for different initial pH values: $C_{\text{Fe}^{\text{II}}(\text{EDTA})}^0 = 50$ mol/m³, $T = 328$ K. ■, $\text{pH} = 7$; ●, $\text{pH} = 8$; and ▲, $\text{pH} = 5$.

ranged from 3 to 4 and are dependent on $C_{\text{O}_2}^i$. At low $C_{\text{O}_2}^i$, v_B is close to 4, indicating that other oxygen-consuming reactions only take place to a minor extent. Upon increasing $C_{\text{O}_2}^i$, v_B drops rapidly and subsequently levels off to a value ~ 3 . This remarkable sudden step change in the v_B as a function of the $C_{\text{O}_2}^i$ has not been reported to date. So far, we do not have a sound explanation for this observation. Variations of v_B of reaction 1 as a function of experimental conditions have been observed in the literature.^{9,24} However, the wider range of $C_{\text{O}_2}^i$ applied in those studies and the scatter in the data did not allow the observation of the clear step change in v_B as a function of $C_{\text{O}_2}^i$.

The shape of the curves is also a function of the pH. At low pH, the sudden drop of v_B occurs at a lower $C_{\text{O}_2}^i$ value. Hence, the extent of side reactions may be reduced by working at relatively high pH while keeping the oxygen concentrations low.

Further studies to gain more insights into the side reactions taking place when treating aqueous $\text{Fe}^{\text{II}}(\text{EDTA})$ solutions with molecular oxygen, and particularly those on EDTA degradation, are in progress and will be reported in forthcoming papers.

5. Conclusions

The kinetics of the reaction of oxygen with $\text{Fe}^{\text{II}}(\text{EDTA})$ at conditions that are typical for the BiodeNOx process ($C_{\text{Fe}^{\text{II}}(\text{EDTA})} = 15\text{--}60 \text{ mol/m}^3$, $\text{pH} = 5\text{--}8$, $T = 328 \text{ K}$, and $P_{\text{O}_2} = 5\text{--}20 \text{ kPa}$) has been determined. In this experimental range, the reaction is first order in oxygen and second order in iron chelate. At $\text{pH} = 7$, the temperature dependence of the kinetic constant ($298 < T < 328 \text{ K}$) may be expressed as: $k_{12} = 5.3 \times 10^3 \text{ e}^{-4098/T} \text{ m}^6/(\text{mol}^2 \text{ s})$.

The value of the kinetic constant appears to be independent of the pH in the range $5\text{--}8$. The kinetic constant is a function of the salt loading, and a 35% increase was observed when performing the reaction in a $15 \text{ kg/m}^3 \text{ NaCl}$ solution.

The overall stoichiometric coefficient of the reaction deviates from the theoretical value of 4, suggesting that other oxygen-consuming reactions take place as well. A remarkable, unprecedented step change in the ν_B as a function of the C_{O_2} was observed. Higher oxygen concentrations and, to a lesser extent, low pH values promote the side reactions and cause the stoichiometric coefficient to drop to ~ 3 . The side reactions may involve reactions of oxygen with the EDTA chelate, leading to the undesired degradation of the EDTA ligand. This study suggests that the EDTA degradation rates may be reduced by working at a relatively high pH value and low oxygen concentrations.

The experimental data obtained in this study will be applied for the design of a reactive NO absorption unit using $\text{Fe}^{\text{II}}(\text{EDTA})$ as the reactant. Here, the oxidation reaction is an undesirable side reaction which needs to be suppressed to enhance NO absorption rates.

Acknowledgment

The research was financially supported by The Netherlands Technology Foundation (STW).

Supporting Information Available: The Supporting Information includes adsorption profiles, the determination of the effect of salts on the solubility of gases, and the effects of pH and salinity on the solubility and mass transfer coefficient of O_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

Symbols

A_G = salt correction coefficient
 a = specific interfacial area, m^{-1}
 C = concentration, $\text{mol}\cdot\text{m}^{-3}$ or $\text{kg}\cdot\text{m}^{-3}$
 c = numeric constant
 D = diffusion coefficient, $\text{m}^2\cdot\text{s}^{-1}$
 d = diameter, m
 E_A = enhancement factor
 E_a = activation energy, J/mol
 h_G = gas specific parameter
 $h_{G,0}$ = reference parameter
 h_i = ion specific parameter
 h_T = temperature parameter
 Ha = Hatta number
 He = Henry coefficient, $\text{Pa}\cdot\text{m}^3\cdot\text{mole}^{-1}$
 J = mole flux, $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
 k = mass transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
 k_{12} = kinetic constant for the reaction of order 1, 2, $\text{m}^6\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$
 N_{O_2} = number of moles absorbed
 N_S = stirrer speed, min^{-1}

P = pressure, Pa

R = gas constant = $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

r = ratio of the diffusion coefficient

T = temperature, K

t = time, s

V = volume, m^3

ν_B = stoichiometric coefficient

Subscript

∞ = final value for $t = \infty$

G = gas phase

L = liquid phase

N_2O = nitrous oxide

O_2 = oxygen

p = order of the reaction with respect to the gas reactant

q = order of the reaction with respect to the liquid reactant

w = value relative to water

Superscript

0 = initial value for $t = 0$

b = bulk

i = interface

Literature Cited

- (1) *Technical Assessment of NOx removal processes for utility application*. Report EPA-600/7-77-127; U.S. Environmental Protection Agency, Electric Power Research Institute, Tennessee Valley Authority, 1977.
- (2) Chang, S. G.; Littlejohn, D. The potential of a wet process for simultaneous control of SO_2 and NO_x in flue gas. *Am. Chem. Soc., Div. Fuel Chem., Prepr. Pap.* **1985**, 30, 119.
- (3) Smith, K. J.; Tseng, S.; Babu, M. Enhanced NOx removal in wet scrubbers using metal chelates. Presented at 86th Air and Waste Management Association Annual Meeting, Denver, CO, 1986.
- (4) Buisman, C. J.; Dijkman, H.; Verbaak, P. L.; Den Hartog, A. J. Process for purifying flue gas containing nitrogen oxides. Patent BO1D 53/84, 53/56, 53/60. WO 96/24434, 1996.
- (5) Travin, S. O.; Skurlatov, Yu. I. Kinetics and mechanism of the reaction of iron(II) ethylenediaminetetraacetate ($\text{Fe}^{2+} + \text{EDTA}$) with molecular oxygen in the presence of ligands. *Russ. J. Phys. Chem.* **1981**, 55, 815.
- (6) Sada, E.; Kumazawa, H. Oxidation kinetics of $\text{Fe}^{\text{II}}\text{EDTA}$ and $\text{Fe}^{\text{II}}\text{NTA}$ chelates by dissolved oxygen. *Ind. Eng. Chem. Res.* **1987**, 26, 1468.
- (7) Brown, E. R.; Mazzarella, J. D. Mechanism of oxidation of ferrous polydentate complexes by dioxygen. *J. Electroanal. Chem.* **1987**, 222, 173.
- (8) Zang, V.; van Eldik, R. Kinetics and mechanism of the autoxidation of iron(II) induced through chelation by ethylenediaminetetraacetate and related ligands. *Inorg. Chem.* **1990**, 29, 1705.
- (9) Wubs, H. J.; Beenackers, A. A. C. M. Kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution. *Ind. Eng. Chem. Res.* **1993**, 32 (11), 2580.
- (10) Seibig S.; van Eldik, R. Kinetics of $[\text{Fe}^2(\text{EDTA})]$ oxidation by molecular oxygen revisited. New evidence for a multistep mechanism. *Inorg. Chem.* **1997**, 36, 4115.
- (11) Vogel, A. I. *Vogel's textbook of quantitative chemical analysis*; Longman: London, England, 1978.
- (12) Westerterp, K. R.; van Swaaij, W. P. M.; Beenackers, A. A. C. M. *Chemical Reactor Design and Operation*. Wiley: New York, 1984.
- (13) De Coursey, W. J. Absorption with chemical reaction: Development of a new relation for the Dankwerts model. *Chem. Eng. Sci.* **1974**, 29, 1867.
- (14) De Coursey, W. J.; Thring, R. W. Effect of unequal diffusivities on enhancement factors for reversible and irreversible reaction. *Chem. Eng. Sci.* **1989**, 44, 1715.
- (15) Winkelman, J. G. M.; Brodsky S. J.; Beenackers, A. A. C. M. Effect of unequal diffusivities on enhancement factors for reversible reactions: Numerical solutions and comparison with DeCoursey's method. *Chem. Eng. Sci.* **1992**, 47, 485.

- (16) Versteeg, G. F.; van Swaaij, W. P. M. Solubility and diffusivity of acid gases (CO₂, N₂O) in aqueous alkanolamine solutions. *J. Chem. Eng. Data* **1988**, *33*, 29.
- (17) Benson, B. B.; Krause, D., Jr. Empirical laws for dilute aqueous solutions of non polar gases. *J. Chem. Phys.* **1982**, *64*, 689.
- (18) St-Denis, C. E.; Fell, C. J. D. Diffusivity of oxygen in water. *Can. J. Chem. Eng.* **1971**, *49*, 885.
- (19) Ho, C. S.; Ju, L. K.; Baddour, R. F.; Wang, D. I. C. Simultaneous measurements of oxygen diffusion coefficients and solubilities in electrolyte solutions with a polarographic oxygen electrode. *Chem. Eng. Sci.* **1990**, *43*, 3093.
- (20) O'Connor, G. A.; Lindsay, W. L.; Olse, S. R. Diffusion of iron and iron chelate in soil. *Soil Sci. Soc. Am. Proc.* **1971**, *35*, 407.
- (21) Van Stroe, A. J.; Janssen, L. J. J. Determination of the diffusion coefficient of oxygen in sodium chloride solutions with a transient pulse technique. *Anal. Chim. Acta* **1993**, *279*, 213.
- (22) Chen, D.; Martell, A. E.; McManus, D. Studies on the mechanism of chelate degradation in iron based, liquid redox H₂S removal processes. *Can. J. Chem.* **1995**, *73*, 264.
- (23) Moteikatis, R. J.; Martell, A. E.; Hayes, D. The iron(III)-catalyzed oxidation of EDTA in aqueous solution. *Can. J. Chem.* **1980**, *58*, 1999.
- (24) Burkitt, M. J.; Gilbert, B. C. The autoxidation of iron(II) in aqueous system: The effects of iron chelation by physiological, nonphysiological and therapeutic chelators on the generation of reactive oxygen species and the inducement of biomolecular damage. *Free Radical Res. Commun.* **1991**, *14*, 107.

Received for review April 14, 2005

Revised manuscript received July 20, 2005

Accepted August 10, 2005

IE050448E