Chapter 2

Experimental and Modeling Studies on the Absorption of NO in Aqueous Ferrous EDTA Solutions

Abstract
This work describes an experimental and modeling study on an industrial relevant process, i.e. the absorption of NO in aqueous Fe\textsuperscript{II}(EDTA) solutions, to accurately determine the equilibrium constant of the reaction in the temperature range 299 - 329 K. The experiments were carried out in a stirred cell contactor using a pH of 7 and an initial Fe\textsuperscript{II}(EDTA) concentration of 7 - 9 mol/m\textsuperscript{3}. A dynamic reactor model was developed to describe the experimental absorption profiles. Mass transfer effects were taken into account using the penetration theory for mass transfer. Excellent fits were obtained between measured and modeled profiles when assuming that the reaction takes place in the instantaneous regime. The following temperature dependence for the $K$ value was obtained: $K = \exp\left(\frac{4702}{T} - 8.534\right)$. Dynamic reactor modeling not only allowed calculation of the equilibrium constants of the reaction but also provided accurate values for the ratio of the diffusivity of Fe\textsuperscript{II}(EDTA) and NO ($r_P$) at various temperatures. This ratio is of extreme importance for the design of a reactive NO absorption unit and could be expressed as: $r_P = -1.778 \times 10^{-4} \cdot T^2 + 0.11 \cdot T - 16.93$.
2.1 Introduction

Metal chelate solutions rapidly react with the absorbed NO gas to form stable metal-nitrosyl complexes. Absorption rates using these metal complexes are significantly higher than in pure water. Particularly, Fe\(\text{II}\) chelates based on ethylene-diamine-tetraacetic acid (EDTA) and related compounds like NTA (nitrilotriacetic acid) were proven to be very effective \[41, 42\]:

\[
\text{Fe}^{\text{II}}(\text{EDTA}) + \text{NO} \rightleftharpoons \text{Fe}^{\text{III}}(\text{EDTA})(\text{NO})
\]  \hspace{1cm} (1)

It should be noted that the actual ferrous complex is a seven coordinate species, Fe\(\text{II}(\text{EDTA})(\text{H}_2\text{O})\), and that the produced NO complex is formally an Fe\(\text{III}\) species, Fe\(\text{III}(\text{EDTA})(\text{NO}^-)\) \[46, 61, 63\]. However, to be consistent with earlier literature on the reaction, these species will be denoted as shown in reaction (1).

In this chapter, we have studied the absorption of NO gas in aqueous Fe\(\text{II}(\text{EDTA})\) solutions in more detail. The reaction of NO with Fe\(\text{II}(\text{EDTA})\) has been studied by various research groups using different reactor configurations and experimental conditions. An overview is given in Table 1.

Table 1. An overview of experimental studies on NO absorption in aqueous Fe\(\text{II}(\text{EDTA})\) solution.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>T (K)</th>
<th>pH</th>
<th>(C_{\text{Fe}^{\text{II}}}) (mol/m(^3))</th>
<th>(C_{\text{NO}}) (mol/m(^3))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble column</td>
<td>288 - 308</td>
<td>2 - 10</td>
<td>10 - 30</td>
<td>((4 - 30) \cdot 10^{-4})</td>
<td>Teramoto et al. [64]</td>
</tr>
<tr>
<td>Stirred cell</td>
<td>311 - 343</td>
<td>1 - 6</td>
<td>8 - 36</td>
<td>((8.3 - 24) \cdot 10^{-4})</td>
<td>Hishinuma and Kaji [65]</td>
</tr>
<tr>
<td>Stirred cell</td>
<td>298</td>
<td>1.5 - 10</td>
<td>10-50</td>
<td>((1.4 - 20) \cdot 10^{-4})</td>
<td>Sada et al. [66]</td>
</tr>
<tr>
<td>Bubble column</td>
<td>308</td>
<td>6 - 8</td>
<td>10</td>
<td>(17 \cdot 10^{-4})</td>
<td>Sada et al. [67]</td>
</tr>
<tr>
<td>Stirred cell</td>
<td>298 - 353</td>
<td>7</td>
<td>10 - 50</td>
<td>((5 - 50) \cdot 10^{-4})</td>
<td>Yih and Lii [68]</td>
</tr>
<tr>
<td>Stirred cell</td>
<td>298 - 348</td>
<td>2 - 10</td>
<td>10 - 50</td>
<td>((0.5 - 7.9) \cdot 10^{-4})</td>
<td>Huasheng and Wenchi [69]</td>
</tr>
<tr>
<td>Bubble column</td>
<td>277 - 363</td>
<td>n.a.(a)</td>
<td>10 - 100</td>
<td>((2.0 - 8.0) \cdot 10^{-4})</td>
<td>Nymoen et al. [70]</td>
</tr>
<tr>
<td>Stirred reactor</td>
<td>298</td>
<td>&lt;1</td>
<td>4 - 12</td>
<td>1.9</td>
<td>Shy et al. [71]</td>
</tr>
<tr>
<td>Stirred cell</td>
<td>293 - 333</td>
<td>7 - 8</td>
<td>5 - 100</td>
<td>(0.13 - 0.49)</td>
<td>Demmink [44]</td>
</tr>
<tr>
<td>Stopped flow,</td>
<td>298</td>
<td>4.9 - 7.2</td>
<td>2</td>
<td>0 - 1.8</td>
<td>Schneppe... et al. [46, 61, 63]</td>
</tr>
</tbody>
</table>

(a): n.a.= not provided in original literature source

All studies conclude that the reaction is first order in both reagents. However, the resulting kinetic and thermodynamic data show considerable spreading (Table 2). One reason for this scatter is probably the high rate of the reaction of NO with Fe\(\text{II}(\text{EDTA})\), which may result in severe mass transfer limitation of both NO and Fe\(\text{II}(\text{EDTA})\). So far, only the study of Demmink \[44\] has taken into account the effect of mass transfer limitation of the Fe\(\text{II}(\text{EDTA})\) species on the overall rate of the absorption process. He has shown that, even under low NO partial pressure, the
absorption rate is completely limited by ferrous mass transfer. However, he assumed
the reaction to be irreversible. Recent mechanistic studies by Schneppensieper et al. 
[46, 61, 63], using pulse radiolysis and stopped flow techniques, have unequivocally
proven that the reaction has to be treated as reversible.

The target of the present study is the determination of the equilibrium constants for
the reaction of NO with Fe II(EDTA) in a range of conditions that are relevant to the
BiodeNOx process (i.e. 298 < T < 328 K, C_{NO,G} = 0 - 1000 vppm, 1 < C_{FeII(EDTA)} < 50
mol/m³), taking into account the reversibility of the reaction and mass transfer
limitation of both NO and Fe II(EDTA) in the solution.

Table 2. Kinetic and equilibrium constants cited in the literature for the reaction of NO with
Fe II(EDTA).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>pH</th>
<th>k_{11} (m³/mol s)</th>
<th>k_{-1} (1/s)</th>
<th>K (m³/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>4.6 - 8.0</td>
<td>1.7 · 10⁴</td>
<td>1.5 · 10²</td>
<td>Teramoto et al. [64]</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>7.6</td>
<td>5.5 · 10²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>3</td>
<td>3.48 · 10³</td>
<td></td>
<td>Hishinuma and Kaji [65]</td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>3</td>
<td>8.59 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>243</td>
<td>3</td>
<td>3.39 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>1.5 - 2.5</td>
<td>3.29 · 10⁴</td>
<td></td>
<td></td>
<td>Sada et al. [66]</td>
</tr>
<tr>
<td>298</td>
<td>7</td>
<td>1.23 · 10⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>9.5 - 10</td>
<td>1.04 · 10⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>6 - 8</td>
<td>9.90 · 10⁵</td>
<td></td>
<td></td>
<td>Sada et al. [67]</td>
</tr>
<tr>
<td>298</td>
<td>7</td>
<td>1.24 · 10⁵</td>
<td></td>
<td></td>
<td>Yih and Lii [68]</td>
</tr>
<tr>
<td>313</td>
<td>7</td>
<td>1.35 · 10⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>7</td>
<td>1.43 · 10⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>7</td>
<td>1.47 · 10⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>n.a.⁴⁰</td>
<td>2.18 · 10³</td>
<td></td>
<td>Huasheng and Wenchi [69]</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>n.a.⁴⁰</td>
<td>1.53 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>n.a.⁴⁰</td>
<td>7.82 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>n.a.⁴⁰</td>
<td>5.31 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>348</td>
<td>n.a.⁴⁰</td>
<td>2.52 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>n.a.⁴⁰</td>
<td>1.7 · 10³</td>
<td></td>
<td>Nymoen et al. [70]</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>n.a.⁴⁰</td>
<td>3.9 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>n.a.⁴⁰</td>
<td>1.1 · 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>5.1</td>
<td>&gt; 6.0 · 10³</td>
<td>&gt; 60</td>
<td>Shy et al. [71]</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>5</td>
<td>2.4 · 10³</td>
<td>91</td>
<td>2.1 · 10³</td>
<td>Schneppensieper et al. [46, 61, 63]</td>
</tr>
</tbody>
</table>

(a): n.a. = not provided in original literature source
2.2 Experimental Section

2.2.1 Chemicals
FeCl₂·4H₂O (p.a.), titriplex (p.a.) and Na₂CO₃ were obtained from Merck, NaOH (33% in water) from Boom, CeSO₄·4H₂O (> 99%) from Acros, and N₂O (> 99%), N₂ (> 99.99 %) and NO (1008 vppm in N₂) from Hoek Loos. Reverse osmosis water was applied to prepare the various solutions.

2.2.2 Experimental set-up
The kinetic experiments were carried out in a stirred cell reactor consisting of glass, equipped with four glass baffles. The reactor could be operated in batch as well as continuous mode with respect to the gas phase and in batch mode with respect to the liquid. A stainless steel turbine impeller was used to stir the gas phase, while a magnetic stirrer (2 cm) in combination with an external magnetic drive was used for the liquid phase. The double wall of the reactor allowed the use of water to regulate the temperature in the reactor (Julabo, MV basis). Typical dimensions of the stirred cell contactor are given in Table 3. Temperature (PT-100) and pressure transducers (Trafag, ECO 2.5 A) were used to determine the temperature and pressure during an experiment. The NO concentration in the outlet was measured using an NO analyzer (Thermo Electron-Model 10).

Table 3. Dimensions and characteristics of the stirred cell contactor.

<table>
<thead>
<tr>
<th>Total reactor volume (m³)</th>
<th>1.245 · 10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial area (m²)</td>
<td>7.79 · 10⁻³</td>
</tr>
<tr>
<td>Gas impeller (m)</td>
<td>Six bladed turbine</td>
</tr>
<tr>
<td></td>
<td>dₛ = 6 · 10⁻²</td>
</tr>
<tr>
<td>Nₛ liquid stirrer (rpm)</td>
<td>100</td>
</tr>
<tr>
<td>Nₛ gas impeller (rpm)</td>
<td>2000</td>
</tr>
</tbody>
</table>

The NO analyzer was calibrated before and after every experiment using an NO gas mixture of known concentration. The NO analyzer, the temperature, and pressure transducer were connected to a computer equipped with an NI-4351 PCI (National Instrument) data acquisition card. The reactor set-up is schematically represented in Fig. 1.

2.2.3 Preparation of Fe²⁺(EDTA) solutions
Aqueous solutions of Fe²⁺(EDTA) are extremely air-sensitive and should be handled under a protective nitrogen atmosphere. The Fe²⁺(EDTA) solution was prepared by dissolving a predetermined amount of titriplex (Na₂EDTA) in degassed water (10⁻⁴ m³). The turbid solution turned transparent when the pH was increased from 4 to 9 by carefully addition of some drops of a 4 M NaOH solution. The appropriate amount of FeCl₂·4H₂O (Fe : EDTA ratio = 1 : 1.2 mol/mol) was added to the EDTA solution, giving a slightly green, clear solution with a pH of about 3. Next, the solution was diluted further with degassed water to 2·10⁻⁴ m³. At this stage, the pH was adjusted to the desired value by the addition of a 4 M NaOH solution. Finally, degassed water was added to adjust the total volume to 3·1
2.2.4. Physical absorption experiment

Physical absorption experiments were performed using N$_2$O gas. The reactor was operated in batch mode, both with respect to the gas and the liquid phase. The reactor was filled with the iron-chelate solution and thoroughly degassed for about 15 minutes. Next, the reactor was filled with N$_2$O gas until the desired pressure was reached. The experiment was initiated by starting the gas and liquid stirrers. The pressure inside the reactor was measured using a pressure transducer and recorded by a computer.

2.2.5 Determination of the gas phase mass transfer coefficients

Gas phase mass transfer coefficients at various experimental conditions were obtained by measuring the evaporation rate of water into an air stream. The reactor outlet was connected to 2 cold traps in series cooled with ice. The amount of evaporated liquid was obtained by determining the weight increase of the cold traps.

2.2.6 Equilibrium absorption experiments

During the reactive absorption experiments, the liquid phase was operated in batch mode while the gas phase was operated continuously. The reactor was filled with the appropriate amount of solution and degassed under vacuum for about 15 minutes.
After degassing, the reactor was filled with nitrogen gas until atmospheric pressure was reached. The reactor was heated to the desired temperature. A gas mixture of NO in N₂ was initially bypassed around the reactor to the analysis unit. The NO concentration in the gas stream was regulated using two mass flow controllers and the composition of the mixture gas was determined using the NO analyser. The actual absorption was started by closing the bypass valves and admitting the NO in nitrogen mixture gas to the reactor. The NO concentration of the outlet flow was measured as a function of the time. The experiment was terminated when the outlet NO concentration was equal to the inlet value. Desorption experiments were performed by switching the gas stream from NO/N₂ to pure N₂, after establishment of equilibrium. The NO concentration in the outlet stream was monitored as a function of time.

2.2.7 Determination of the Fe⁺⁺ content in the solution

The concentration of Fe⁺⁺ in the solution was determined before every absorption experiments by titration with a 0.1 M Ce(SO₄)₂ solution, using a 0.025 M ferroine as indicator [72]. To obtain reproducible results, the iron-chelate sample was diluted with an approximate 10-fold volume of sulphuric acid (2 - 4 kmol/m³) and subsequently degassed by adding approximately 1 g of NaHCO₃ prior to the titration.

2.3 Theory

The overall rate of NO absorption in an aqueous solution of Fe⁺⁺(EDTA) is a function of the intrinsic reaction rate of the reaction between Fe⁺⁺(EDTA) and NO and the rate of mass transfer of the various components. To model the absorption profile, expressions for the NO flux are required. A general equation for the flux of NO, here denoted as component A, in a reactive gas-liquid system may be given by [73]:

\[
J_A = \left( \frac{1}{mk_L E_A} + \frac{1}{k_G} \right)^{-1} \left( C_{A,G}^b - \frac{C_{A,L}^b}{m} \right)
\]  

The enhancement factor, \(E_A\), is a function of the absorption regime and is defined as [73]:

\[
E_A = \frac{J_{A \text{ with reaction}}}{J_{A \text{ without reaction}}}
\]  

If the reaction is slow compared to diffusional transport, \(E_A\) equals 1 and the absorption may be regarded as a physical absorption process. If the chemical reaction is much faster than the mass transfer process, \(E_A\) is larger than 1 and the mass transfer is enhanced by the reaction.

Various theoretical mass transfer models have provided expressions for the enhancement factor for the absorption process described in eq. (5) and (6):

\[
A_G \rightarrow A_L
\]  

\[
A_L + B_L \rightarrow P_L
\]
Onda et al. [74] obtained an expression for the \( E_A \) using the film theory and by assuming that the concentration of \( \text{Fe}^{III}(\text{EDTA}) \) in the reaction zone is constant:

\[
E_A = \frac{1 + r_p \cdot K \cdot C_{B,L}^i}{1 + r_p \cdot K \cdot C_B^i \cdot \tanh(\Theta)} \left[ r_p \frac{K \cdot C_{B,L}^i \cdot C_{A,L}^b - C_{P,L}^b}{C_{A,L}^i - C_{A,L}^b} \right] \left[ 1 - \frac{1}{\cosh(\Theta)} \right] \tag{7}
\]

where the reaction factor, \( \Theta \), is defined as:

\[
\Theta = \frac{1}{k_L} \left( k_{11} \cdot D_A \cdot C_{B,L}^i \left( 1 + \frac{1}{r_p \cdot K \cdot C_{B,L}^i} \right) \right) \tag{8}
\]

However, if the reaction is extremely fast, the assumption of a constant Fe concentration in the film is not valid. In this so called instantaneous regime, \( E_A \) can be expressed as [73]:

\[
E_A = E_A^{\infty} = 1 + r_p \frac{K C_{B,L}^b}{1 + \frac{r_p}{r_B} K C_{A,L}^i} \tag{9}
\]

Related expressions using the penetration theory instead of the film theory have been derived. De Coursey and Thring [75] developed an approximate analytical solution for \( E_A \) and Winkelman et al. [76] demonstrated the viability of this approximation, and showed it could be written as:

\[
\frac{q_A}{C_{B,L}^b \beta K} \left( \frac{E_A^2 - 1}{q_A (E_A \sqrt{r_p} + 1)} - \frac{q_A C_{A,L}^b}{C_{B,L}^b} \right) = \left[ 1 + \frac{1}{\beta \cdot Ha^2} \right] \left[ 1 - \frac{E_A}{\sqrt{1 + \beta Ha^2}} \right] \tag{10}
\]

where the Hatta number is defined as:

\[
Ha = \sqrt[2]{\frac{k_{11} D_A C_{B,L}^b}{k_L^2}} \tag{11}
\]

In case the reaction is instantaneous, the following approximate solution may be applied [73]:

\[
E_A = E_A^{\infty} = \left( 1 + \frac{r_p}{r_B} \frac{K C_{B,L}^b}{1 + \frac{r_p}{r_B} K C_{A,L}^i} \right)^{0.5} \tag{12}
\]
2.4 Physical properties and mass transfer coefficients

2.4.1 Solubility of NO in Fe\(^{II}\)(EDTA) solutions

Direct determination of the solubility of NO in iron-EDTA solutions is not possible due to the reactive nature of the system. However, indirect determination is possible when performing absorption experiments with N\(_2\)O instead of NO. According to Demmink [44], the Henry coefficient of NO may be obtained using:

\[
He_{\text{NO}} = A_g \left( He_{\text{NO},w} \right) \left( \frac{He_{\text{NO}}}{He_{\text{N}_2\text{O},w}} \right)
\]

(13)

Here, \(He\) is the Henry coefficient defined as:

\[
He_A = \frac{P_A}{C_{A,L}}
\]

(14)

\(A_g\) is a gas specific salting out parameter [44] which is close to unity for NO at 298 K, whereas the solubility of N\(_2\)O in water (\(He_{\text{N}_2\text{O},w}\)) is given by Versteeg and van Swaaij [77]. The solubility of NO in pure water (\(He_{\text{NO},w}\)) is given by Fogg and Gerrard [78].

The Henry coefficient of N\(_2\)O in an iron-chelate solution was determined experimentally using the reactor set up as described in the experimental section. The absorption experiments were carried out in a batch mode, both for the gas and liquid phase. The pressure in the reactor was measured as a function of the time, allowing calculation of the He-coefficient using:

\[
He = \frac{P^\infty - P_w}{P^0 - P^\infty} \cdot \frac{RT V_L}{V_G}
\]

(15)

Fig. 2 shows the experimentally obtained solubilities of N\(_2\)O in solutions of Fe\(^{II}\)(EDTA) solutions at various temperatures (298 – 328 K) and Fe concentrations (25 - 100 mol/m\(^3\)). As expected, the \(He\) coefficient increases at higher temperatures. However, a clear relation between the \(He_{\text{N}_2\text{O}}\) and the concentration of the iron chelate, probably also due to some experimental errors, appears to be absent in this concentration range. When assuming that the He is not affected for Fe\(^{II}\) loadings below 100 mol/m\(^3\), the following relation for the temperature dependency of the \(He\) coefficient of N\(_2\)O may be calculated:

\[
He_{\text{N}_2\text{O}} = 2.35 \cdot 10^7 e^{-2544/T}
\]

(16)
Figure 2. Henry coefficient of N₂O in Fe²⁺(EDTA) solution as a function of the temperature. ○: $C_{Fe(EDTA)} = 100 \text{ mol/m}^3$, x: $C_{Fe(EDTA)} = 75 \text{ mol/m}^3$, ♦: $C_{Fe(EDTA)} = 50 \text{ mol/m}^3$, □: $C_{Fe(EDTA)} = 25 \text{ mol/m}^3$. The dotted line represents the results obtained by Wubs [57] for $C_{Fe(EDTA)} = 100 \text{ mol/m}^3$. The continuous line represents eq. (16).

These results are in fairly good agreement with the results obtained by Wubs [57]:

$$He_{N_2O} = 7.51 \cdot 10^6 e^{-2195/T}$$

Subsequently, the Henry coefficients for NO in Fe²⁺(EDTA) solutions at various temperatures were calculated using eq. (13). The results are represented in Fig. 3.

### 2.4.2 Diffusion coefficients

The values for the diffusion coefficient of NO in water at various temperatures may be estimated using the following relation [79]:

$$D_{NO,w} = 0.00398 \cdot e^{-3.510^4 / R_T}$$

A correction for the fact that the reaction takes place in an electrolyte solution consisting of Fe²⁺(EDTA) instead of pure water is applied using a relation given by Ho et al., which is valid for $0 < C_{salt} < 4 \cdot 10^3 \text{ mol/m}^3$ [80]:

$$D_{NO} = D_{NO,w} \left( \frac{\mu_w}{\mu_{Fe(EDTA)}} \right)^{0.62}$$

Here, $\frac{\mu_w}{\mu_{Fe(EDTA)}}$ represents the relative viscosity of the Fe²⁺(EDTA) solution which was measured by Wubs [57] for a $C_{Fe(EDTA)}$ of 100 mol/m³.
2.4.3 Mass transfer coefficients

The liquid phase mass transfer coefficients for NO at different temperatures and Fe(II)(EDTA) concentrations were calculated from physical absorption experiments of pure N$_2$O. The $k_L$ values for N$_2$O were obtained from the pressure vs. time curves using:

$$\ln \left( \frac{P_{N_2O}}{(\alpha + 1) P_{N_2O}^0 - \alpha P_{N_2O}^0} \right) = \left( \frac{\alpha}{\alpha + 1} \right) + \left( \frac{RTV_{He}}{V_L} \right)$$

with:

$$\alpha = \frac{V_G}{V_L} \frac{He}{RT}$$

According to the penetration theory, the $k_L$ values for NO are related to those of N$_2$O by the following expression [73]:

$$k_{L(NO)} = k_{L(N_2O)} \cdot \frac{D_{NO}}{D_{N_2O}}$$

The experimental values of the mass transfer coefficients for NO as a function of the temperature are given in Fig. 4.

The gas phase mass transfer coefficients at various conditions were obtained by measuring the rate of evaporation of pure water into an air stream [81]. The $k_G$ values of water in air were calculated using a balance for the vapour content of the carrier gas stream combined with the weight of the condensed vapour:
\[
\Phi_G P_{w}^{sat} = k_G a V_L \left( P_{w}^{sat} - P_w \right) \left( 1 - \frac{P_w}{P_{tot}} \right) \tag{23}
\]

\[
\frac{W}{M_w \cdot t} = \frac{\Phi_G P_w}{1 - \frac{P_w}{P_{tot}}} RT \tag{24}
\]

According to the penetration theory, the gas phase mass transfer coefficient of NO in N\textsubscript{2} \((k_{G, NO-N2})\) is related to the experimentally determined value for water in air by:

\[
k_{G, NO-N2} = k_{G, w-air} \sqrt{\frac{D_{NO-N2}}{D_{w-air}}} \tag{25}
\]

where \(D_{w-air}\) is provided by Janssen and Warmoeskerken [82] and the \(D_{NO-air}\) is estimated using the relation given by Reid et al. [83]. The experimental values for the \(k_G\) of water in air and the derived values for the \(k_G\) of NO in nitrogen are represented in Fig. 5.

**Figure 4.** Calculated \(k_L\) values for NO in Fe\textsuperscript{II}(EDTA) solutions. ○: \(C_{Fe(EDTA)} = 100\) mol/m\textsuperscript{3}; x: \(C_{Fe(EDTA)} = 75\) mol/m\textsuperscript{3}; ♦: \(C_{Fe(EDTA)} = 50\) mol/m\textsuperscript{3}; □: \(C_{Fe(EDTA)} = 25\) mol/m\textsuperscript{3}. 

35
2.5 Results and Discussion

2.5.1 Determination of the equilibrium constant of the reaction at equilibrium conditions

Equilibrium experiments were performed to determine the equilibrium constant at various temperatures, and at initial pH of 7. The reaction was allowed to proceed until the concentration in the outlet stream was equal to the inlet concentration. Reaction times of up to 7 hours were required to establish equilibrium. A summary of the experiments is given in Table 4.

Table 4. Overview of experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>299</td>
<td>304</td>
<td>314</td>
<td>313</td>
<td>329</td>
</tr>
<tr>
<td>( V_L ) (m³)</td>
<td>2.05 ( \cdot 10^{-4} )</td>
<td>1.65 ( \cdot 10^{-4} )</td>
<td>1.65 ( \cdot 10^{-4} )</td>
<td>1.45 ( \cdot 10^{-4} )</td>
<td>2.45 ( \cdot 10^{-4} )</td>
</tr>
<tr>
<td>( V_G ) (10³ m³)</td>
<td>1.04 ( \cdot 10^{-3} )</td>
<td>1.08 ( \cdot 10^{-3} )</td>
<td>1.08 ( \cdot 10^{-3} )</td>
<td>1.10 ( \cdot 10^{-3} )</td>
<td>1.00 ( \cdot 10^{-3} )</td>
</tr>
<tr>
<td>( C_{Fe^{II}(EDTA)} ) (mol/m³)</td>
<td>8.1</td>
<td>8.8</td>
<td>7.9</td>
<td>7.4</td>
<td>8.5</td>
</tr>
<tr>
<td>( \Phi_G ) (m³/s)</td>
<td>8.74 ( \cdot 10^{-6} )</td>
<td>8.85 ( \cdot 10^{-6} )</td>
<td>9.11 ( \cdot 10^{-6} )</td>
<td>9.12 ( \cdot 10^{-6} )</td>
<td>9.57 ( \cdot 10^{-6} )</td>
</tr>
<tr>
<td>( C_{NO_{in}} ) (mol/m³)</td>
<td>413</td>
<td>407</td>
<td>395</td>
<td>395</td>
<td>376</td>
</tr>
</tbody>
</table>

a: duplicate of experiment 3.
A typical experimental profile is represented in Fig. 6. A first stage with rapid concentrations changes is observed followed by second phase where a slow increase of the NO concentration up to the inlet concentration is observed. In the second stage, the actual reaction occurs and equilibrium is established. Evidence that the reaction should indeed be treated as an equilibrium reaction was obtained by performing desorption experiments. The feed composition was changed from a mixture gas of NO in N₂ to pure N₂ gas after saturation of the solution with NO and establishment of equilibrium. A rapid drop in the NO concentration in the outlet was observed to about 300 vppm, followed by a stage with a slow decrease. The latter stage suggests that NO is formed by the backward reaction and subsequently transferred to the gas phase. These findings clearly prove that the reaction should be treated as an equilibrium reaction.

The equilibrium constant for the reaction (1) is given by:

\[
K = \frac{C_{P,L}}{C_{A,L} \cdot C_{B,L}} \quad \text{at equilibrium}
\]  

The concentration of the components in the liquid at equilibrium can be rewritten as:

\[
C_{P,L} = \frac{F_G}{V_L} \left( C_{A,G}^{\text{in}} \cdot t - \int_0^{t_\text{end}} C_{A,G} \, dt \right) - \left( \frac{V_G}{V_L} + m \right) C_{A,G}^{\text{in}}
\]

\[
C_{A,L} = m \cdot C_{A,G}^{\text{in}}
\]

\[
C_{B,L} = C_{B,L}^{\text{eq}} - C_{P,L}
\]

The values of the equilibrium constant at different temperatures were determined using equations (26) – (29) and the results are given in Fig. 7. A linear relation ($R^2 = 0.996$) was observed. The equilibrium constants from previous studies have also been provided in Fig. 7. It is clear that there is a considerable spread in the data. As mentioned in the introduction, most of the experimental studies carried out so far have not properly taken into account mass transfer limitations of NO and/or the iron chelate species, which is, according to our findings, of prime importance to obtain reliable results.

2.5.2 Dynamic reactor modeling

The values of the equilibrium constants may also be obtained from the experimentally determined absorption profiles (Fig. 6). The absorption profiles were modeled assuming that the reaction between NO and Fe^{II}(EDTA) is reversible (see previous section), that the gas- and liquid phase in the stirred cell reactor are ideally mixed, which was confirmed by Residence Time Distribution (RTD) experiments and that the absorption process takes place in the instantaneous regime. The latter assumption can be justified by some very basic calculations using the Hatta number (eq. (11)). Using literature data on the diffusivity [79] and the reaction rate at 298 K [63], together with our experimental $k_L$ and $C_{Fe^{II}(EDTA)}$, the calculated $Ha$ number is ($5 \cdot 6$)$\cdot10^3$. The observed enhancement factors were always $< 10^3$. Therefore, for all experiments, $Ha >> E_A$ and we can safely assume that the absorption process takes place in the instantaneous regime [73].
Figure 6. Profile of the absorption of NO on Fe$^{II}$(EDTA) solution in the stirred cell contactor followed by desorption. $C_{Fe^{II}(EDTA)} = 7.4$ mol/m$^3$, $C_{NO_{in}} = 1000$ vppm, $T = 313$ K, pH = 7.

Figure 7. Van’t Hoff plot of the reaction of NO with Fe$^{II}$(EDTA). ▲: Hishinuma and Kaji [65], $C_{Fe^{II}(EDTA)} = 8 - 36$ mol/m$^3$, pH = 3 - 6. ●: Huasheng and Wenchi [69], $C_{Fe^{II}(EDTA)} = 10 - 50$ mol/m$^3$, pH = 5.2 - 8.2. X: Schneppensieper et al. [46, 61, 63], $C_{Fe^{II}(EDTA)} = 2$ mol/m$^3$, pH = 5. ○: Nymoen et al. [70], $C_{Fe^{II}(EDTA)} = 10 - 100$ mol/m$^3$, pH = not mentioned.

The component balance for NO in the gas phase in the stirred cell reactor is:

$$V_G \frac{dC_{A,G}^b}{dt} = F_G \left(C_{A,G}^{in} - C_{A,G}^b\right) - J_A a V_L$$

$$t = 0 \quad C_{A,G}^b = 0$$
and for the liquid phase in the stirred cell:

\[
V_L \frac{dC_{AP,L}}{dt} = J_A a V_L \\
t = 0 \quad C_{AP,L} = 0
\]  

(31)

Where \( C_{AP} = C_A^b + C_p^b \) is the total amount of absorbed NO. Assuming chemical equilibrium in the liquid phase, we can write:

\[
K C_{A,L}^b C_{B,L}^b = C_{P,L}^b
\]  

(32)

\[
C_{A,L}^b + C_{P,L}^b = C_{AP,L}^b
\]  

(33)

\[
C_{B,L}^b = C_{B,L}^0 - C_{P,L}^b
\]  

(34)

which allows for the calculation of the liquid phase concentrations once \( C_{AP} \) is known. For the mass transfer rate we have:

\[
J_A = k_G \left( C_{A,G}^b - \frac{C_{A,L}^i}{m} \right)
\]  

(35)

and

\[
J_A = k_L E_A (C_{A,L}^i - C_{A,L}^b)
\]  

(36)

where the enhancement factor \( E_A \) is given by the penetration theory of mass transfer (eq. (12)) with the assumption \( r_P = r_B \).

The set of differential equations (30), (31) and the ordinary equations (32) – (36) were solved numerically using a fourth order Runge-Kutta method. Parameters estimation was performed using a Newton-Raphson technique.

2.5.3 Parameter fitting

The two main model parameters are the value of the equilibrium constant, \( K \), and the diffusivity ratio \( r_P \). Initially, these parameters were fitted for each absorption experiment. Optimization of these parameters using the penetration theory proved very successful, and excellent fits between the measured and modelled absorption profiles were observed. A typical example is given in Fig. 8. Attempts to model the profiles using the enhancement factor for the instantaneous regime according to the film theory (eq. (9)) did not give satisfying results.

A comparison between the equilibrium constants determined using the equilibrium approach and those obtained using the dynamic reactor model is given in Fig. 9.
Figure 8. Experimental (dotted line) and modelled (continuous line) absorption profile. Experimental conditions: \( T = 299 \text{ K}, \ C_{\text{Fe(II)(EDTA)}} = 8.1 \text{ mol/m}^3, \ C_{\text{NO}_x} = 1000 \text{ vppm}, \ \text{pH} = 7. \)

Figure 9. Comparison of equilibrium constants. x: dynamic reactor modelling, (individual fit); ▲: dynamic reactor modelling (simultaneous fit); : equilibrium approach (see section 2.5.1). The dotted line represents eq. (37).

Agreement between the \( K \) values obtained by the two procedures is very satisfactory. In a second phase, all absorption experiments were fitted simultaneously. The Van’t Hoff relation for the temperature dependency of the equilibrium constants was found to be:

\[
K = \exp\left(\frac{4702}{T} - 8.534\right)
\]  

(37)
From this relation, the reaction enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were obtained as -39.1 kJ/mol and -71 J/mol K, respectively. The values for the diffusivity ratio $r_P$ at various temperatures obtained by simultaneous fitting of all experiments are given in Fig. 10. The diffusivity ratio varies between 0.07 and 0.12 and shows slight temperature dependence. There appears to be a maximum at about 315 K, at higher and lower temperatures, the ratio is lower. This trend is likely the result of the very strong temperature dependence of the diffusivity of NO in the aqueous phase. Wise et al. [79] have experimentally determined the diffusion coefficient of various gases in water and found that the diffusivity of NO is showing a very strong temperature dependence. When assuming that the temperature dependence of NO is much larger than that of the Fe species, a temperature dependence of the diffusivity ratio $r_P$ as given in Fig. 10 is expected. The temperature dependence of the diffusivity may be described by the following empirical relation:

$$r_P = -1.778 \cdot 10^{-4} \cdot T^2 + 0.11 \cdot T - 16.93$$

(38)

![Figure 10. Temperature dependence of the diffusivity ratio $r_P$. ▼: calculated values of the diffusivity ratio, individual fitting; ▲: calculated values of the diffusivity ratio, simultaneous fitting; X: Demmink [44]; ○: Huasheng and Wenchi [69].](image)

### 2.6 Conclusions

The equilibrium constants of the reaction between NO and Fe$^{II}$(EDTA) in the temperature range 299 - 329 K, and Fe$^{II}$(EDTA) concentration of 7 - 9 mol/m$^3$, an NO inlet concentration of 1000 vppm, and an initial pH of 7 at the start of the reaction, have been determined. The experiments were carried out in a stirred cell contactor operated batch with respect to the liquid phase and continuously with respect to the gas phase. Two approaches have been applied. In the first approach, experiments were carried out using long reaction times to allow for the establishment of chemical equilibrium in the set-up. The equilibrium constant was determined using the uptake
of NO and the Fe\textsuperscript{II}(EDTA) conversion. Secondly, a dynamic reactor model was developed to describe the experimental absorption profiles. Mass transfer effects were taken into account using the penetration theory for mass transfer. Excellent fits were obtained when assuming that the reaction takes place in the instantaneous regime. The dynamic approach not only allowed calculation of the equilibrium constant of the reaction at various temperatures but also provided accurate data for the diffusivity ratio $r_P$. Agreement between both approaches was excellent. The results of this study will be valuable input for subsequent experimental and modelling studies to a.o. determine the kinetic constants of the relevant reactions in the BiodeNOx process at various process conditions and an optimum BiodeNOx absorber design.