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Authors
Griffiths, E.A.
Chang, S.G.

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E.A. Griffiths and S.G. Chang

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The Effect of Citrate Buffer Additive on the Absorption
of NO by Ferrous Chelates†

E.A. Griffiths and S.G. Chang*
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Abstract

Citrate buffer in solutions can act as a ligand and compete with other ligands for complexation with ferrous ion. As a result, more than one type of ferrous chelate and/or ferrous mixed chelates may be formed. Subsequently, the absorption capacity of NO in the system is affected. The extent of the effect depends upon the stability constants of citrate and other ligands to ferrous ion, and on the stability constant of citrate ferrous chelates to NO. We have studied this effect on Fe$^{II}$(IDA), Fe$^{II}$(NTA), and Fe$^{II}$(EDTA), and determined the equilibrium constants, enthalpies and entropies for the coordination of NO to Fe$^{II}$(Cit) and to Fe$^{II}$(IDA) as a function of pH and temperature in aqueous solutions. The results are: for Fe$^{II}$(Cit)NO, $\Delta H^\circ = -8.59$ kcal. mole$^{-1}$, $\Delta S^\circ = -7.37$ e.u. and $K = 4.9 \times 10^4$ M$^{-1}$ at 25$^\circ$ C, 4 < pH < 6.5; for Fe$^{II}$(Cit)(OH)NO, $\Delta H^\circ = -3.67$ kcal. mole$^{-1}$, $\Delta S^\circ = 12.03$ e.u., and $K = 2.1 \times 10^5$ M$^{-1}$ at 25$^\circ$ C, pH > 6.5; for Fe$^{II}$(IDA)NO, $\Delta H^\circ = -9.13$ kcal. mole$^{-1}$, $\Delta S^\circ = -6.33$ e.u. and $K = 2.05 \times 10^5$ M$^{-1}$ at 25$^\circ$ C, pH 6-7; and for Fe$^{II}$(Cit)(IDA)NO, $K \geq 3.3 \times 10^5$ M$^{-1}$ at 25$^\circ$ C and $\geq 5.5 \times 10^4$ M$^{-1}$ at 55$^\circ$ C. NO absorption studies and polarographic results indicate a previously unrecognized mixed ligand complex, Fe$^{II}$(Cit)(IDA), which has a larger stability constant for NO than either Fe$^{II}$(Cit) and Fe$^{II}$(IDA) alone at 25$^\circ$ C.

Introduction

In a wet flue gas simultaneous denitrification and desulfurization system where ferrous chelates are added in the scrubbing liquor to promote the solubility of NO, nitrosyl ferrous chelates are formed (Littlejohn and Chang, 1982; Chang et al., 1982, 1983; Lin et al., 1982). The reaction between the complexed NO and HSO$_3^-$ /SO$_3^-$ ions is too slow to affect significantly the rate of absorption of SO$_2$ (Chang et al., 1983; Littlejohn and Chang, 1982). One must, instead, depend upon the buffering capacity of the solution for absorbing SO$_2$ and upon subsequent reactions for removing it from the solution. The pH of the solution in the scrubber is advantageously kept in the range 5-7. Since the acid constants of chelates commonly used for the complexation with ferrous ion, such as NTA,
EDTA and IDA, cannot provide buffering in this pH range, the buffering must be provided by adding some other soluble base to the scrubbing solution.

There has been substantial commercial experience with scrubbing $\text{SO}_2$ from stack gas with a solution containing a soluble base. Sodium citrate is an example of a base that has been employed in a process developed by the Bureau of Mines. This is a regenerable flue gas desulfurization process, where the dissolved $\text{SO}_2$ is reacted with $\text{H}_2\text{S}$ to form elemental sulfur. It has also been demonstrated in our laboratory that $\text{H}_2\text{S}$ can reduce NO in the nitrosyl ferrous chelates and regenerate ferrous chelate catalysts. The development of a regenerable flue gas denitrification and desulfurization process, based on the addition of both ferrous chelates and $\text{H}_2\text{S}$ in a wet scrubber and with sodium citrate as a buffer, sounds very promising. With this approach, a saleable form of sulfur is produced and costs may be reduced as a result. However, citrate buffer in solutions can act as a ligand and compete with other ligands for complexation with ferrous ion. Subsequently, the absorption capacity of NO in the system is affected. This paper reports the equilibrium constants of the coordination of NO to $\text{Fe}^{\text{II}}(\text{Cit})$ and $\text{Fe}^{\text{II}}(\text{IDA})$, in an aqueous solution as a function of pH and temperature, where Cit and IDA are abbreviations of citrate and iminodiacetate respectively. Also studied was the effect of citrate ions on the absorption capacity of NO by $\text{Fe}^{\text{II}}(\text{EDTA})$, $\text{Fe}^{\text{II}}(\text{NTA})$ and $\text{Fe}^{\text{II}}(\text{IDA})$, where EDTA is ethylenediaminetetraacetate and NTA is nitrilotriacetate.
Experimental Section

A. Equilibrium measurements

Aqueous solutions of the ferrous chelates were prepared under O₂-free conditions. The concentration of ferrous ion was 10⁻² M and the concentration of chelate was 10⁻¹ M. The solutions were adjusted to the desired pH by NaOH and ionic strength, 1 M, using Na₂SO₄. The NO obtained from Matheson Co. was a mixture of 2.55% NO in N₂ with NO₂ impurity of less than 255 ppm; this NO was further diluted by adding N₂ to 1000 ppm. The experimental setup was described elsewhere (Lin et al., 1982; Hishinuma et al., 1979). The experiments proceeded by bubbling a mixture of NO and N₂ of known NO concentration through a NaOH solution to absorb any NO₂ impurity in the gas and then through the ferrous chelate solution. The NO concentration in the outlet gas was measured with a Thermoelectron Model 14A chemiluminescent NOₓ analyzer. The gas flow rates were 600-810 ml.min⁻¹. Equilibrium was attained when the NO concentration in the outlet gas became equal to that of the inlet gas. The experiments were performed at 25° C and 55° C.

B. Polarographic Measurements

The ferrous chelates, 10⁻² M, and the nitrosyl complexes, were prepared on a vacuum line (Littlejohn and Chang, 1982). Sodium sulfate was employed to keep the ionic strength 1 M and as supporting electrolyte. All solutions contained 0.001% triton x 100 as a maximum suppressor. Samples of the solution were transferred to a polarographic cell and the polarograms were recorded on a PAR Model 174A polarographic analyzer. A dropping Hg electrode was used with a drop time of approximately 2 secs. A constant stream of nitrogen was passed over the solution to prevent oxidation of the ferrous chelates. An H-type cell with saturated calomel electrode was used and all measurements were made at 25° C.
Results and Discussion

The coordination of NO to ferrous chelates can be expressed by:

$$ NO + Fe(II)L \xrightarrow{k_1 \text{Fe(II)(L)NO}} $$ (1)

The equilibrium constant of this reaction can be written as:

$$ K = \frac{k_1}{k_-1} = \frac{[Fe(II)(L)NO]}{[NO][Fe(II)L]} = \frac{[Fe(II)(L)NO]}{[NO][Fe(II)L]_o - [Fe(II)(L)NO]} $$ (2)

which can be rearranged to become:

$$ \frac{[Fe(II)L]_o}{[Fe(II)(L)NO]} - 1 = \frac{1}{KHP_{NO}} $$ (3)

where L is the ligand, $[Fe(III)L]_o$ is the initial concentration of Fe(II) chelate, $[Fe(II)(L)NO]$ is the concentration of the NO adduct obtained by graphically integrating the outlet NO concentration, $P_{NO}$ is the partial pressure of NO in the gas, and $H$ is the Henry's constant for solubility of NO in water.

The equilibrium constants for the coordination of NO to Fe$^{II}$(Cit), Fe$^{II}$(Cit)(OH), Fe$^{II}$(IDA) and Fe$^{II}$(Cit)(IDA) were calculated using equation 3. The results are plotted in Figures 1 and 2, at 25°C and 55°C, respectively.

The equilibrium constant for Fe$^{II}$(Cit)NO is $4.9 \times 10^4 M^{-1}$ at 25°C and $1.3 \times 10^4 M^{-1}$ at 55°C when the pH is between 4 and 6.5. Figures 1 and 2 show that above pH 6.5, the absorption of NO increases linearly until approx. pH 8.5, where it levels off and the equilibrium constant becomes $2.1 \times 10^5 M^{-1}$ at 25°C and $1.19 \times 10^5 M^{-1}$ at 55°C. The absorbing species is Fe$^{II}$(Cit) when pH is between 4 and 6.5 and Fe$^{II}$(Cit)(OH) above pH 6.5 (Hamm et al., 1954).

The equilibrium constant for Fe$^{II}$(IDA)NO is $2.05 \times 10^5 M^{-1}$ at 25°C in the pH range 6-7 and $5.0 \times 10^4 M^{-1}$ at 55°C when pH is between 6 and 6.5. The apparent equilibrium constant for the coordination of NO to Fe$^{II}$(IDA) becomes greater with pH up to pH 6, as shown in Figures 1 and 2. This is because the stability constant of Fe$^{II}$(IDA) (Ogura and Walanabe, 1982) increases with increasing pH, (pKa's of IDA; 2.73, 9.46). At pH 6, however, the stability constant of Fe$^{II}$(IDA) is
sufficiently large for all the ferrous ion to be bound to IDA. In addition, Figures 1 and 2 illustrate the decrease in absorption of NO by Fe\textsuperscript{II}(IDA) in basic solutions. This corresponds to the ionization of the second hydrogen ion of IDA (Ringbom, 1963). We attributed this behavior to the formation of a new complex, which does not coordinate to NO.

Figures 1 and 2 show the equilibrium constant for the coordination of NO in a ferrous mixed chelate system, when equal amounts of Cit and IDA are present. When citrate ions are added to a solution of Fe\textsuperscript{II}(IDA), the equilibrium constant is 4.9 x 10\textsuperscript{4} M\textsuperscript{-1} at 25° C in the pH range 4-5.2, as shown in Figure 1. This constant is the same as that determined for Fe\textsuperscript{II}(Cit)NO. Above pH 5.2, the equilibrium constant increases with increasing pH. This is similar to the behavior observed for Fe\textsuperscript{II}(Cit)(OH)NO, although the increase for the latter only occurs at pH ≥8.5. The formation of Fe\textsuperscript{II}(Cit)(OH)NO complex can not account for the increased absorption of NO. Consequently, we propose that a mixed chelate such as Fe\textsuperscript{II}(Cit)(IDA)NO is formed. Further evidence of the formation of this mixed chelate has been obtained by polarography to be described later. When experiments were carried out at pH > 7.5 to see if the absorption of NO would change after the second hydrogen ion of IDA was ionized (Ringbom, 1963), precipitation occurred. Whereas, the Fe\textsuperscript{II}(Cit)(OH)NO complex was soluble up to pH 9.5. At 55° C, the effect due to citrate ions on the absorption of NO by Fe\textsuperscript{II}(IDA) is slightly different than that observed at 25° C, as shown in Figure 2. Below pH 5.4, the equilibrium constant can be considered to be the sum of both Fe\textsuperscript{II}(Cit) and Fe\textsuperscript{II}(IDA) absorbing NO which is dependent on their concentrations. At pH > 5.4, the mixed chelate complex, Fe\textsuperscript{II}(Cit)(IDA)NO, is formed.

In principle, the effect of citrate ions on the absorption of NO by Fe\textsuperscript{II}(EDTA), Fe\textsuperscript{II}(NTA), and Fe\textsuperscript{II}(IDA) can be calculated if there is no formation of mixed chelate ions (Intorre and Martell, 1961; Tokmadzhyan et al., 1975; Ras et al., 1982). The addition of citrate buffer causes a decrease in the value of the conditional stability constant, which is defined by the equation (Ringbom, 1963):
where \( M \) is defined as the metal, \( L \) as the ligand, \( K_{ML}' \) as the conditional stability constant and \( K_{ML} \) as the stability constant of the metal chelate. \( \alpha_{ML}, \alpha_M \) and \( \alpha_L \) are defined as the alpha coefficients of the metal chelates, metal and ligand respectively. This is a measure of the effect that interfering side reactions have on the stability constant. The alpha coefficients of the ferrous nitrosyl complexes were calculated, and those of ferrous hydroxide, ferrous citrate and ligand protonation were previously determined by Ringbom (1963). The theoretical results were calculated by substitution of these coefficients into equation 4 and are shown in Table 1.

The results indicate that all the ferrous ion will still be bound to EDTA. Consequently, the absorption will be unaffected. The conditional stability constant of \( \text{Fe}^{II}(\text{NTA}) \) decreases with pH, which means there will be less of \( \text{Fe}^{II}(\text{NTA}) \) complex formed. Hence, there will be less available for binding to NO. The free ferrous ion will coordinate to Cit and the resulting \( \text{Fe}^{II}(\text{Cit}) \) complex will also absorb NO. The observed effect, however, will be a decrease in the absorption of NO. For \( \text{Fe}^{II}(\text{IDA}) \), the conditional stability constant becomes so small that there will be no ferrous ion bound to IDA. As a result of this the ferrous ion will bind to the Cit. Therefore, the NO absorbing species will be \( \text{Fe}^{II}(\text{Cit}) \).

The experimental results for \( \text{Fe}^{II}(\text{IDA}) \) with citrate at \( \text{pH} < 5.2 \) and 25° C, concurred with the calculated result. But at \( \text{pH} > 5.2 \), a new species capable of absorbing NO efficiently is formed which is the mixed ligand complex, \( \text{Fe}^{II}(\text{Cit})(\text{IDA}) \). At 55° C and \( \text{pH} < 5.4 \), not all of the ferrous ion is bound to Cit, some ferrous ion is bound to IDA also. Consequently, both \( \text{Fe}^{II}(\text{Cit}) \) and \( \text{Fe}^{II}(\text{IDA}) \) absorb NO.

Experiments were performed on the absorption capacity of NO by \( \text{Fe}^{II}(\text{EDTA}) \) and \( \text{Fe}^{II}(\text{NTA}) \), when Cit was present to find out whether there were any mixed ligand complexes formed. The results indicate that in the presence of citrate ions, the absorption of NO by \( \text{Fe}^{II}(\text{EDTA}) \) at 25° C and 55° C is unaffected. This is in
agreement with the calculated results.

Figure 3 illustrates the effect of citrate ions on Fe$^{II}$(NTA) at 25° C and 55° C. As a result of a side reaction with citrate ions, only a fraction of the total ferrous ion is bound to NTA. Consequently, both Fe$^{II}$(NTA) and Fe$^{II}$(Cit) absorb NO. The equilibrium constants determined are the sum of the individual stability constants of NO to Fe$^{II}$(NTA) and to Fe$^{II}$(Cit), which are dependent on their concentrations. This agrees with the calculated results.

Polarography was employed to confirm that the mixed ligand chelate complex, Fe$^{II}$(Cit)(IDA), occurred at pH > 5.2. In addition, it was employed to show that only Fe$^{II}$(Cit) formed at pH < 5.2 when IDA was present in the mixed chelate system.

Figure 4 shows the half wave potentials of the ferrous chelates as a function of pH. The anodic wave for Fe$^{II}$(IDA) occurs at much more positive potentials than that of Fe$^{II}$(Cit), with a slope of 36 mV per pH unit. The half wave potential for Fe$^{II}$(Cit) is a linear function of pH, the relation being:

$$E_{1/2} = 0.217 - 0.063 \text{pH}; \quad (5)$$

when the pH < 6.5. At pH > 6.5, the slope becomes 33 mV per pH unit, which is due to the oxidation of the new species (Lingane, 1946; Meites, 1951; Hamm et al., 1954), Fe$^{II}$(Cit)(OH). When ferrous ion is in solution with equal amounts of Cit and IDA, the $E_{1/2}$ is the same as that of Fe$^{II}$(Cit) at pH < 5.2:

$$E_{1/2} = 0.212 - 0.062 \text{pH}; \quad (6)$$

At pH > 5.6, the half wave potentials are more positive than those of Fe$^{II}$(Cit). This indicates a new species that binds ferrous ion more strongly and which has a slope of 60 mV per pH unit. In the pH range 5.2 - 5.6, one observes the transition from one oxidizable species to another. We attributed this new species to Fe$^{II}$(Cit)(IDA).
Figure 5 gives further evidence for the mixed ligand complex. The polarograms of Fe\textsuperscript{II}(Cit)(IDA)NO and Fe\textsuperscript{II}(Cit)NO are recorded at pH 6. The half wave potentials of their characteristic cathodic waves (Uchiyama et al., 1977; Kaneko and Nozaki, 1977) are -0.76 V and -0.785 V, respectively. The sudden abruptness of the waves indicate a multi-electron process. In analogy to a similar system investigated, Fe\textsuperscript{II}(EDTA)NO, by linear scanning voltammetry (Uchiyama and Muto, 1981), the electrode reaction can be described by:

\[
[\text{Fe}\textsuperscript{II}(\text{Cit})\text{NO}]^1^- + 2e + H^+ \rightarrow [\text{Fe}\textsuperscript{II}(\text{Cit})\text{HNO}^-]^2-
\]  
\[
[\text{Fe}\textsuperscript{II}(\text{Cit})\text{HNO}^-]^2- + H^+ \rightarrow [\text{Fe}\textsuperscript{II}(\text{Cit})\text{NHOH}]^1-
\]  
\[
[\text{Fe}\textsuperscript{II}(\text{cit})\text{NHOH}]^1^- + e + H^+ \rightarrow [\text{Fe}\textsuperscript{II}(\text{Cit}) \text{H}]^1^- + \text{NH}_2\text{OH}
\]

Conclusion

Ferrous chelates can be used to augment the solubility of nitric oxide substantially in a wet flue gas simultaneous denitrification and desulfurization system. Both the Fe\textsuperscript{II}(Cit) and Fe\textsuperscript{II}(IDA) complexes are not as effective in absorbing NO than either Fe\textsuperscript{II}(EDTA) or Fe\textsuperscript{II}(NTA). The advantage of citrate is that it can act both as a ligand and a buffer and it is inexpensive.

The effect of citrate buffer additive on the binding of NO by ferrous chelates was calculated and examined experimentally. Consequently, the mixed chelate complex, Fe\textsuperscript{II}(Cit)(IDA) was found. The theoretical calculations applied only when there were no new species formed.

Our previous studies of the equilibrium constant of Fe\textsuperscript{II}(Cit)NO at pH 5.1 found it to be much smaller (Littlejohn and Chang, 1982) than that determined here. This is because the stability constant of ferrous citrate is small (Hamm et al., 1954), 10\textsuperscript{3.1}, and a one to one molar ratio (Littlejohn and Chang, 1982) of citrate ion to ferrous ion used in our previous studies is insufficient for all the ferrous ion to be in the form of Fe\textsuperscript{II}(Cit).
This study shows that the presence of citrate buffer additive can enhance, decrease or have no effect on the absorption of NO by ferrous chelates, depending on chelate employed and the pH of the solution.

Acknowledgements

We appreciate the support and encouragement of Earl Evans, Joseph Strakey and John Williams.
Literature Cited


Table 1

<table>
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<th>pH</th>
<th>( \log K'_{Fe^{II}EDTA} )</th>
<th>( \log K'_{Fe^{II}NTA} )</th>
<th>( \log K'_{Fe^{II}IDA} )</th>
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<td>8</td>
<td>9.5</td>
<td>3.7</td>
<td>0.26</td>
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\[ \log K_{Fe^{II}EDTA} = 14.3 \]

\[ \log K_{Fe^{II}NTA} = 8.8 \]

\[ \log K_{Fe^{II}IDA} = 5.8 \]
FIGURE CAPTIONS

Figure 1. The effect of pH on the equilibrium constants for the coordination of NO to Fe$^{II}$(Cit), (o), Fe$^{II}$(IDA), (Δ), and Fe$^{II}$(IDA) with citrate buffer, (♦), at 25° C.

Figure 2. The effect of pH on the equilibrium constants for the coordination of NO to Fe$^{II}$(Cit), (o), Fe$^{II}$(IDA), (Δ), and Fe$^{II}$(IDA) with citrate buffer, (♦), at 55° C.

Figure 3. The pH dependence on the equilibrium constants of the reversible binding of NO to Fe$^{II}$(NTA) at 25° C, (◊), and 55° C, (o), and the effect due to the addition of citrate buffer, (♦), at 25° C and (♦), 55° C.

Figure 4. The half wave potentials of Fe$^{II}$(IDA), (Δ), Fe$^{II}$(Cit), (o), and Fe$^{II}$(IDA) with citrate buffer, (♦), as a function of pH at 25° C.

Figure 5. The polarograms of Fe$^{II}$(IDA)(Cit)NO and Fe$^{II}$(Cit)NO at pH 6 and 25° C.
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