Introduction

Iron is considered the most important transition metal in biological system. Kinetic and thermodynamic data determinations of iron complex reactions with chelant agents are intensely studied with the aim of foreseeing the behaviour of this metal in biological processes such as: absorption and transport of oxygen, electron transfer and redox process that occur in live organisms.

The reactivity of iron complexes is determined for different medium and for different types of ligands, to mimic the different functions of iron in organisms.

In this work we made electrochemical and spectrophotometric equilibrium studies of the reactions occurring between [Fe(II)EDTA(H$_2$O)]$^{2-}$ complex and the diimine ligand DPEH using cyclic voltammetric and UV-Vis spectrophotometric techniques.

Experimental

The electrochemical parameters were obtained with the cyclic voltameter Bioanalytical system Inc. Mod. CV - 27 and as the auxiliary electrode the glassy carbon disk and a conventional Ag/AgCl (saturated KCl) reference electrode was used in a nonisothermal arrangement and a platinum wire was used as the auxiliary electrode. The measured potentials were converted to the normal hydrogen scale by adding 0.204V.

The spectrophotometric titration was made with a UV-Vis Shimadzu mod. UV - 190 spectrophotometer, a RB registrar and Array HP 8450A spectrophotometer.

The Na[Fe(III)EDTA(H$_2$O)]$_3$H$_2$O was synthesized as described in the literature, and reduced in situ with zinc amalgam in aqueous solution. The DPEH ligand was synthesized following the method described by by Levy.

The equilibrium constants of [Fe(II)EDTA(DPEH)$_n$]$^{2-}$ complex formation were obtained from spectrophotometric and voltammetric titration of the [Fe(EDTA)(H$_2$O)]$^{2-}$ complexes in aqueous solution, with DPEH. The DPEH solu-
tion was approximately 100 times more concentrated than the aqueous solution of [Fe(II)EDTA(H$_2$O)]$^{2-}$ complex.

**Results and Discussion**

The reaction corresponding the titrations are:

\[
\text{[Fe}^{II}\text{(EDTA)(H}_2\text{O})]^{2-} + \text{L} \xrightleftharpoons{K} \text{Fe}^{II}\text{(EDTA)L}_n
\]

- The [Fe(II)EDTA(DPEH)$_3$]$^{2+}$ complex formation in spectrophotometric titration was followed by the absorption increasing in 532 nm.

Table 1 shows the [Fe(II)EDTA(DPEH)$_3$]$^{2+}$ (n=1, 2) and [Fe(II)(DPEH)$_2$] formation constants that were obtained by the MacConnel Equations 1, using 532nm $\varepsilon = 10.200$ M$^{-1}$ cm$^{-1}$.

\[
\frac{[M][L]}{A_f - A_i} = \frac{[M] + [L]}{[M]} \frac{1}{\beta} (\varepsilon_f - \varepsilon_i)
\]

were $\varepsilon_f$ and $\varepsilon_i$ are initial and final molar coefficients; $A_f$ and $A_i$ are initial and final absorbances; $\beta$ is total formation constant equilibrium.

**Table 1. Formation constants of Fe(II) complexes in aqueous solution. I = 0.1 M KCl, t = 25 °C.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\beta_1$ (M$^{-1}$)</th>
<th>$\beta_2$ (M$^{-1}$)</th>
<th>$\beta_3$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)EDTA(DPEH)$_3$</td>
<td>1.79 x 10$^3$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(II)EDTA(DPEH)$_2$</td>
<td>3.23 x 10$^2$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(II)(DPEH)$_3$</td>
<td>-</td>
<td>1.02 x 10$^2$</td>
<td>-</td>
</tr>
</tbody>
</table>

The $\beta_3$ value indicates the occurence of [Fe(II)(DPEH)$_3$]$^{2+}$ formation with iron (II) coordinations through the diminic nitrogens of DPEH ligand, due the poor stability of pyridinic iron (II) bond in the [Fe(II)(DPEH)$_3$]$^{2+}$ complexes. Data previously obtained$^9$ reinforce this evidence when occur the quickly hydrolysis of [Fe(II)(DPEH)$_2$]$^{2+}$ in acid pH’s solution.

The inclusion of a third ligand in [Fe(II)EDTA(DPEH)$_2$]$^{2+}$ was comparatively confirmed for [Fe(II)(DPEH)$_2$]$^{2+}$ complex titration with one solution of DPEH ligand, according Eq.2.

\[
[\text{Fe(DPEH)}]^{2+} + \text{DPEH} \rightleftharpoons [\text{Fe(DPEH)}]^{3+}
\]

The $K_f = 1.0210^2$ was obtained through Eq.3

\[
\varepsilon_1 = \varepsilon_f + \varepsilon_2 K_f [\text{DPEH}]
\]

Cyclic voltammetry methods have been utilized for determination of complexation constants$^7$ and to estimate the number of ligands substituted in complexes$^8$-10. Through the thermodynamic cyclic Eqs.4 - 10, the related fact to Pearson’s theory$^{11}$, it was confirmed that soft bases (DPEH) have affinity for soft acids (iron II) and the hard bases (EDTA) for hard acids (iron III).

\[
\begin{align*}
[\text{Fe}^{2+}\text{EDTA(H}_2\text{O})]^{2-} + \text{DPEH} & \rightleftharpoons [\text{Fe}^{2+}\text{(EDTA)}\text{(DPEH)}]^{2+} & E_{1/2} = 0.101 \text{ V} & (4) \\
[\text{Fe}^{3+}\text{EDTA(H}_2\text{O})]^{3-} + \text{DPEH} & \rightleftharpoons [\text{Fe}^{3+}\text{(EDTA)}\text{(DPEH)}]^{3+} & E_{1/2} = 0.094 \text{ V} & (5) \\
[\text{Fe}^{2+}\text{(EDTA)}\text{(DPEH)}]^{2+} + \text{DPEH} & \rightleftharpoons [\text{Fe}^{2+}\text{(EDTA)}\text{(DPEH)}]^{2+} & E_{1/2} = 0.094 \text{ V} & (6) \\
[\text{Fe}^{3+}\text{(EDTA)}\text{(DPEH)}]^{3+} + \text{DPEH} & \rightleftharpoons [\text{Fe}^{3+}\text{(EDTA)}\text{(DPEH)}]^{3+} & E_{1/2} = 0.077 \text{ V} & (7) \\
[\text{Fe}^{2+}\text{(EDTA)}\text{(DPEH)}]^{2+} + \text{DPEH} & \rightleftharpoons [\text{Fe}^{2+}\text{(EDTA)}\text{(DPEH)}]^{2+} & E_{1/2} = 0.037 \text{ V} & (8) \\
[\text{Fe}^{3+}\text{(EDTA)}\text{(DPEH)}]^{3+} + \text{DPEH} & \rightleftharpoons [\text{Fe}^{3+}\text{(DPEH)}]^{3+} & E_{1/2} = 0.077 \text{ V} & (9)
\end{align*}
\]

*The potentials data is vs NHE.

Potential values obtained by voltametric titration Figure 1 and Eqs. 10 - 12, turned possible to evaluate the complexation constants ($\beta'$).
\[ E^\circ_{(1+2+)}[\text{Fe(EDTA)}]^2 = E^\circ_{[\text{Fe(EDTA)}+\text{DPEH}]} + (RT/nF) \ln \beta_1 \beta_1' \]  
(10)

\[ E^\circ_{(3+2+)}[\text{Fe(EDTA)}]^2 = E^\circ_{[\text{Fe(EDTA)}+\text{DPEH}]} + (RT/nF) \ln \beta_2 \beta_2' \]  
(11)

\[ E^\circ_{(3+2+)}[\text{Fe(EDTA)}]^2 = E^\circ_{[\text{Fe(DPEH)}]} + (RT/nF) \ln \beta_3 \beta_3' \]  
(12)

Table 2 shows the \(E^\circ\) values for the different complex obtained by cyclic voltammetry and the \(\beta\) values calculated through Equation 1 it was possible to determine the values of the complexation constants for iron (III) complexes.

**Table 2. Values of the complexation constants \(\beta\) and \(\beta'\) for iron complexes.**

<table>
<thead>
<tr>
<th></th>
<th>(\beta_1)</th>
<th>(\beta_2)</th>
<th>(\beta_3)</th>
<th>(\beta_1')</th>
<th>(\beta_2')</th>
<th>(\beta_3')</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe}^{2+})</td>
<td>1.78 x 10^3</td>
<td>3.20 x 10^2</td>
<td>1.02 x 10^2</td>
<td>1.36 x 10^3</td>
<td>1.27 x 10^2</td>
<td>8.26</td>
</tr>
<tr>
<td>(\text{Fe}^{3+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Fe(II) cation was classified as soft or intermediary acid and the DPEH ligand as soft or intermediary base, having more affinity, characteristic of covalent bonds, thus more inert. On the other hand Fe(III), hard acid, bonded to soft or intermediary base have a more coulombic character, thus more lability is present in this complex.

**Conclusion**

The reduction of \([\text{Fe(III)}\text{EDTA(H}_2\text{O)}]^2+\) complex modifies the hard acid characteristic of metallic metallic ion for the intermediary decreasing drastically the complexation constant with EDTA ligand, hard base, thus allowing the gradual substitution of the EDTA ligand by the DPEH ligand. The pyridinic bond lability in \([\text{Fe(II)}\text{DPEH}_2]{\text{]}^{2+}\) complex was observed by the disappearing of the absorption in 387 nm, characteristic of pyridinic Fe(II) interaction when the \([\text{Fe(II)}\text{DPEH}_2]{\text{]}^{2+}\) complex was titrated with DPEH ligand solution and also by quick hydrolysis of the complex in an acid solution.

The nitrogenated alfa diimine ligands, analogous to the porphyrionic macrocyclic ligands considerably affect the reactivity of iron ion in biological systems, stressing the typical intermediary characteristics of this metal.

**Acknowledgment**

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**References**