

Electrochemical and Spectrophotometric Study of Equilibrium Between $[\text{Fe(II)EDTA}]^{2-}$ and the Tridented Ligand Diacetyl Monooxim- β -Piridyl-Ethylimin in Aqueous Solution

C.C. Stadler, A.S Mangrich

Depto. de Química, Universidade Federal do Paraná, Caixa Postal 19081, 81531 Curitiba PR, Brasil

and

E. Stadler*

Depto. de Química, Universidade Federal de Santa Catarina, Caixa Postal 476, 88049 Florianópolis, SC, Brasil

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O complexo de $[\text{Fe(II)EDTA}(\text{H}_2\text{O})]^{2-}$ labil, foi obtido *in situ* por redução do complexo $[\text{Fe(III)EDTA}(\text{H}_2\text{O})]^-$ com amálgama de zinco e titulado com o ligante tridentado (DPEH) (diacetyl-monooxima- β -piridil-etilimina) formando os complexos $[\text{Fe(II)EDTA}(\text{DPEH})_n]^{2-}$ ($n=1,2$) e $[\text{Fe(II)(DPEH)}_3]^{2+}$. Os complexos mostram bandas de transferência de carga em 532 nm e 468 nm. As constantes totais de formação para os complexos Fe(II) e Fe(III) foram determinadas pelos métodos espectrofotométrico e voltamétrico. Os resultados foram analisados em termos de interação destes complexos com o ligante DPEH.

The $[\text{Fe(II)EDTA}(\text{H}_2\text{O})]^{2-}$ complex labile, was obtained *in situ* by zinc amalgam reduction of $[\text{Fe(III)EDTA}(\text{H}_2\text{O})]^-$. Under these reduction reaction conditions, the product $[\text{Fe(II)EDTA}(\text{H}_2\text{O})]^{2-}$ react with the tridentated ligand DPEH (Diacetyl-monooxim- β -piridyl-ethylimin) to form the $[\text{Fe(II)EDTA}(\text{DPEH})_n]^{2-}$ complexes ($n=1,2$) and $[\text{Fe(II)(DPEH)}_3]^{2+}$. Those complexes show charge transfer bands in 532 nm and 468 nm. The total formation constants were determined by spectrophotometric method and cyclic voltametric data. The results can be rationalized on the basis of the interaction between iron complex and DPEH.

Key words: diacetyl-monooxim- β -piridyl-ethylimin; iron(II)/(III); EDTA; equilibrium constants.

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^{1,3} 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 ligands³, to mimic the different functions of iron in organisms.

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

Experimental

The electrochemical parameters were obtained with the

cyclic voltameter Bioanalytical system Inc. Mod. CV - 27 and registrator X-Y of Houston Instruments model Omnigraphic 100, with use of a three-electrode system, where the working electrode was the glassy carbon disk and a conventional Ag/AgCl (saturated KCl) reference electrode was used in a nonisothermic 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 registrator and diode-Array HP 8450A spectrophotometer.

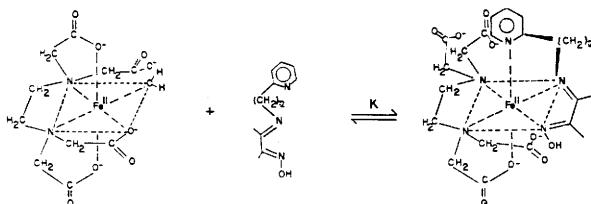
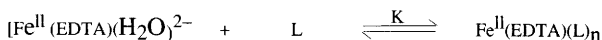
The $\text{Na}[\text{Fe(III)EDTA}(\text{H}_2\text{O})\cdot 3\text{H}_2\text{O}]$ was synthesized as described in the literature⁴, and reduced *in situ* with zinc amalgam in aqueous solution. The DPEH ligand was synthesized following the method described by Levy⁵.

The equilibrium constants of $[\text{Fe(II)EDTA}(\text{DPEH})_n]^{2-}$ complex formation were obtained from spectrophotometric and voltametric titration of the $[\text{Fe(EDTA)}(\text{H}_2\text{O})]^{2-}$ complexes in aqueous solution, with DPEH. The DPEH solu-

tion was approximately 100 times more concentrated than the aqueous solution of $[\text{Fe(II)EDTA}(\text{H}_2\text{O})]^{2-}$ complex.

Results and Discussion

The reaction corresponding the titrations are:



The $[\text{Fe(II)EDTA}(\text{DPEH})_n]^n$ complex formation in spectrophotometric titration was followed by the absorption increasing in 532 nm.

Table 1 shows the $[\text{Fe(II)EDTA}(\text{DPEH})_n]^n$ ($n=1,2$) and $[\text{Fe(II)(DPEH)}_3]$ formation constants that were obtained by the MacConel⁶ Equations 1, using 532nm $\epsilon = 10.200 \text{ M}^{-1} \text{ cm}^{-1}$.

$$\frac{[M][L]}{A_f - A_i} = \frac{[M] + [L]}{\epsilon_f - \epsilon_i} \frac{1}{\beta} (\epsilon_f - \epsilon_i) \quad (1)$$

where ϵ_f and ϵ_i are initial and final molar coefficients; A_f and A_i are initial and final absorbances; β is total formation constant equilibrium.

Table 1. Formation constants of Fe(II) complexes in aqueous solution. $I = 0.1 \text{ M KCl}$, $t = 25^\circ \text{C}$.

	β_1 (M ⁻¹)	β_2 (M ⁻¹)	b_3 (M ⁻¹)
Fe(II)EDTA(DPEH)	1.79×10^3	—	—
Fe(II)EDTA(DPEH) ₂	—	3.23×10^2	—
Fe(II)(DPEH) ₃	—	—	1.02×10^2

The β_3 value indicates the occurrence of $[\text{Fe(II)(DPEH)}_3]^{2+}$ formation with iron (II) coordinations through the diiminic nitrogens of DPEH ligand, due the poor stability of pyridinic iron (II) bond in the $[\text{Fe(II)(DPEH)}_n]^{2+}$ complexes. Data previously obtained⁵ reinforce this evidence when occur the quickly hydrolysis of $[\text{Fe(II)(DPEH)}_2]^{2+}$ in acid pH's solution.

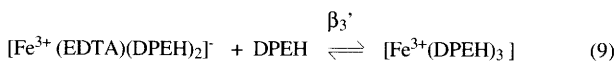
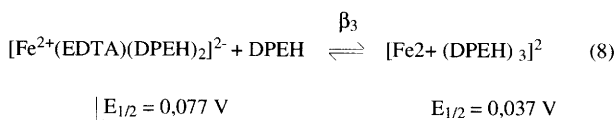
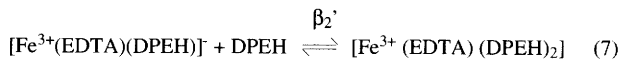
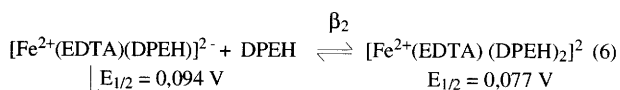
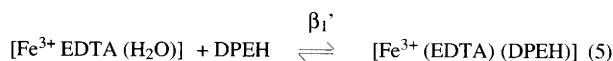
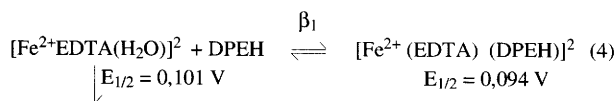
The inclusion of a third ligand in $[\text{Fe(II)EDTA}(\text{DPEH})_2]^{2-}$ was comparatively confirmed for $[\text{Fe(II)(DPEH)}_2]^{2+}$ complex titration with one solution of DPEH ligand, according Eq.2.



The $K_f = 1,0210^2$ was obtained through Eq.3

$$\epsilon_1 = \epsilon_1 + \epsilon_2 K_f [\text{DPEH}] \quad (3)$$

Cyclic voltametry methods have been utilized for determination of complexation constants⁷ and to estimate the number of ligands substituted in complexes⁸⁻¹⁰. Through the thermodynamic cyclic Eqs.4 - 10, the related fact to Pearson's theory¹¹, it was confirmed that soft bases (DPEH) have affinity for soft acids (iron II) and the hard bases (EDTA) for hard acids (iron III).



* 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 (β').

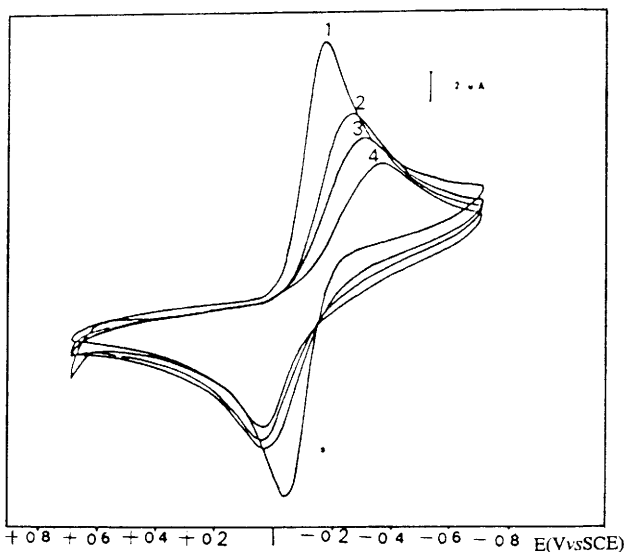


Figure 1. Voltammetric titration of $[\text{Fe}^{2+}(\text{EDTA})(\text{H}_2\text{O})]^{2-}$ with DPEH ligand. $I = 0,1 \text{ M (NaClO}_4)$, $V = 50 \text{ mV/s}$, $t = 25^\circ \text{C}$

1) $[\text{Fe}^{2+}(\text{EDTA})(\text{H}_2\text{O})]^{2-}$; 2) $[\text{Fe}^{2+}(\text{EDTA})(\text{DPEH})]^{2-}$; 3) $[\text{Fe}^{2+}(\text{EDTA})(\text{DPEH})_2]^{2-}$; 4) $[\text{Fe}^{2+}(\text{DPEH})_3]^{2+}$.

$$E^{\circ}_{(3+/2+)}[\text{Fe}(\text{EDTA})]^{2-} = E^{\circ}_{[\text{Fe}(\text{EDTA})(\text{DPEH})]} + (RT/nF) \ln \beta_1/\beta_1' \quad (10)$$

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

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

Table 2 shows the $E^{\circ}_{1/2}$ values for the different complex obtained by cyclic voltametry and the β 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 β and β' for iron complexes.

Fe^{2+}	β_1	1.78×10^3	β_2	3.20×10^2	β_3	1.02×10^2
Fe^{3+}	β_1'	1.36×10^3	β_2'	1.27×10^2	β_3'	8.26

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 $[\text{Fe}(\text{III})\text{EDTA}(\text{H}_2\text{O})]^-$ complex modifies the hard acid characteristic of 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 $[\text{Fe}(\text{II})(\text{DPEH})_2]^{2+}$ complex was observed by the disappearing of the absorption in 387 nm, characteristic of pyridinic Fe(II) interaction when the $[\text{Fe}(\text{II})(\text{DPEH})_2]^{2+}$ complex was tritrated with DPEH ligand solution and also by quick hydrolysis of the complex in an acid solution.

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

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