

Voltammetric Titration of the Complex $[(\text{Fe}^{\text{II}}\text{TIM})(\text{H}_2\text{O})_2]^{2+}$ in an Aqueous Solution

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O comportamento eletroquímico do complexo de ferro, $[(\text{Fe}^{\text{II}}\text{TIM})(\text{H}_2\text{O})_2]^{2+}$, onde TIM = 2,3,9,10-tetrametil-1,4,8,11-tetraazacicotetradeca-1,3,8,10-tetraeno, foi estudado usando como eletrólito suporte NaNO_3 ($\mu = 0.1 \text{ M}$), como eletrodo de trabalho carbono vítreo e Ag/AgCl como eletrodo de referência. Todas as soluções foram deaeradas. As constantes de protonação, foram determinadas por voltametria cíclica. Dados de espectroeletroquímica sugerem o aparecimento de um complexo com o íon metálico em baixo estado de oxidação para o acoplamento $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$, o qual pode ser observado à potenciais mais negativos nos experimentos de voltametria cíclica.

The electrochemical behavior of iron complexes with TIM macrocyclic ligands $[(\text{Fe}^{\text{II}}\text{TIM})(\text{H}_2\text{O})_2]^{2+}$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) were studied, using NaNO_3 ($\mu = 0.1$) as the supporting electrolyte on a vitreous carbon electrode, and Ag/AgCl as the reference electrode. All the solutions were deoxygenated using argon. The temperature of the cell was maintained at 25°C . The protonation constants were determined by cyclic voltammetry. Spectroelectrochemical data suggest the appearance of a metallic ion in a low oxidation state in a complex of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ couple, observed at a low potential in cyclic voltammetric experiments.

Keywords: TIM, spectroelectrochemistry, voltammetric titration

Introduction

Since they have a very simple structure, synthetic inorganic complexes can supply valuable information regarding the structure and reactivation of the metallic ion in contact with biomolecules. In this way many aspects of the chemistry of natural iron-macrocycles can be studied through complexes with synthetic ligands^{1,2}.

In this study we observe the effect of the macrocyclic ligand TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) in a speciation study of voltammetric titulation of the redox processes, obtaining different species and different states of oxidation in the macrocyclic complex. The macrocyclic ligand TIM³ offers considerable advantages, since it makes possible a rigid stereochemical control of the complex, so that the parameters of the synergetic effects that occurred among the axial

equatorial ligands in the complexes can be determined, and so that the different oxidation states such as dimeric Fe^{III} and monomeric Fe^{II} , as well as Fe^{I} , can be stabilized. While the axial effects can give us information about the capacity of the complex to undergo oxygenation, considering the relative energies and the availability of the d_{z^2} orbital with which the O_2 combines⁴ in the Fe^{III} dimeric complex, the equatorial effects can be studied for a series of axial ligand nitrogen donors^{3,5} in addition to allowing studies that involve redox potentials, metal-ligand affinity, speed of electron transfer, catalytic properties, etc^{6,7}.

Experimental

The complex $[(\text{Fe}^{\text{II}}\text{TIM})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ was synthesized by means of a condensation reaction of 1,3-diaminopropane with 2,3-butanedione, according to the Rose³ method, and characterized by CHN and IV analysis. This

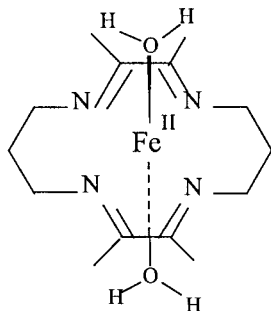


Figure 1. Macrocyclic complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$.

work was carried out using the complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$, Fig. 1, which was obtained *in situ* and under conditions of inert atmosphere, through the dissolution of the complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ in water. The cyclic voltammetric measurements were obtained on a cyclic voltammeter from Bioanalytical Systems Inc., model CV-27, coupled with an X-Y plotter from Houston Instruments, mod. Omnigraphic 100. A three electrode system was utilized, with vitreous carbon as the working electrode, saturated Ag/AgCl-KCl as the reference electrode, and platinum as the auxiliary electrode. The potential were referenced to the NHE, adding 0.204 V to the potential obtained against Ag/AgCl in a saturated solution of KCl. The voltammograms were obtained in an aqueous solution, and de-aired with ultra-pure argon. The voltammetric titration of the Fe^{II} complex was carried out in 0.1 M of NaNO_3 in a pH range of 1.5 to 10.0. Originally, the solution was acidified with HNO_3 and titrated with KOH 0.1 M. A system was assembled that made possible the reading of the pH at the same time as it was being swept with a 0.5 cm diameter glass electrode inserted in the voltammetric cell. The spectroelectrochemical data were obtained in a quartz cell, with a 0.02 cm optical path, containing a transparent gold minigrad as a working electrode, calomel as a reference electrode, and an auxiliary electrode of platinum, along with a spectrophotometer, HP-model 8450 diode array. The potential was applied with an Analytic Systems Inc., model sp-2 potentiostat.

Results and Discussion

Through the voltammetric titration of the complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$, the redox reaction and their respective pKs were determined, with voltammograms for various pHs registered within the limit of potentials +1.1 to -1.0 volts vs NHE. Typical cyclic voltammetric curves (*i* vs. *E*) of the solution of the complex are shown in Fig. 2.

For $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ oxidation states, three redox couples can be observed in the pH range of 1.50 to 7.50 (the range in which voltammograms are reversible or pseudo-reversible).

The redox processes proposed for the redox couples A, B and C follow the Nernst equation. In couple (A), Fig. 3, Table 1, the $E_{1/2}$ remained independent of $[\text{H}^+]$, in the pH

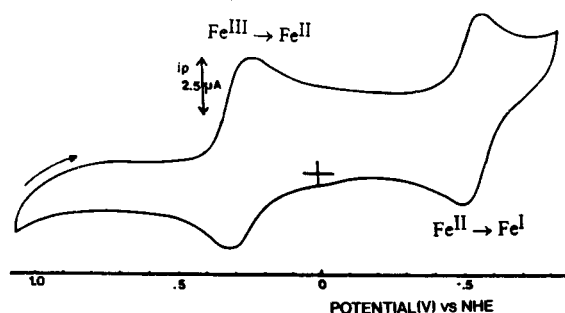


Figure 2. Cyclic Voltammetry of complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$, pH 3.71 in NaNO_3 0.1 M, 25 °C.

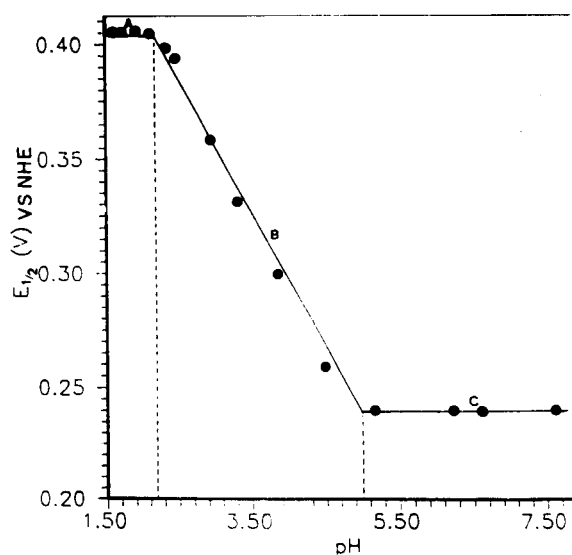
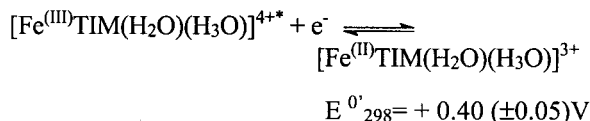


Figure 3. Dependence of $E_{1/2}$ vs. pH for the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple, of the voltammograms obtained in the range of potential 0.40 to 0.20 V vs. NHE, of the complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$, scan rate 0.1 $\text{V}\cdot\text{s}^{-1}$.

range of 1.64-2.15. The cathodic and anodic peak potentials (E_p) have been kept distant from 60-65 mV, thus establishing a reversible process of electron transfer. Considering the involvement of one electron and no proton in the electrode reaction in this pH range, the following redox process might be proposed for the couple A, where penta-coordinate species are suggested:



The couple (B), Fig. 3, shows the dependence of $E_{1/2}$ vs. pH for pHs between 2.15 and 5.17. The potentials of the cathodic and anodic peaks (ΔE_p) remain far from 60-75 mV for the voltammograms obtained up to pH 3.85, establishing a reverse process of electron transfer. Considering the transfer of an electron and a proton in the electrode

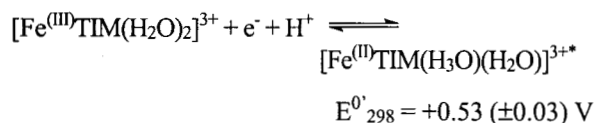
Table 1. Date of cyclic voltammetry of the $[(\text{FeTIM})(\text{H}_2\text{O})_2]^{2+}$ complex solution, $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple, NaNO_3 0.1 M, 20 °C.

| Couple | pH | $E_{1/2}$ (V) vs. NHE | ΔE_p (mv) ^a | ipc/ipa | m ^b |
|--------|------|-----------------------|--------------------------------|---------|----------------|
| A | 1.64 | 0.404 | 60 | 1.03 | 0 |
| | 1.72 | 0.404 | 60 | 1.05 | 0 |
| | 1.92 | 0.405 | 65 | 1.06 | 0 |
| | 2.15 | 0.404 | 65 | 1.04 | 0 |
| B | 2.15 | 0.404 | 65 | 1.04 | - |
| | 2.32 | 0.398 | 67 | 1.02 | 0.6 |
| | 2.47 | 0.394 | 65 | 1.02 | 0.5 |
| | 2.95 | 0.359 | 70 | 1.06 | 1.0 |
| | 3.32 | 0.332 | 70 | 1.06 | 1.0 |
| | 3.85 | 0.300 | 75 | 1.10 | 1.0 |
| | 4.47 | 0.259 | 90 | 1.11 | 1.1 |
| | 5.17 | 0.240 | 120 | 2.00 | 0.9 |
| C | 5.17 | 0.204 | 120 | 2.0 | 0 |
| | 6.22 | 0.240 | 140 | 2.4 | 0 |
| | 6.61 | 0.240 | 135 | 3.3 | 0 |
| | 7.62 | 0.240 | 130 | 3.5 | 0 |

(a) ΔE_p (mv) scan rate 0.1 V. s^{-1}

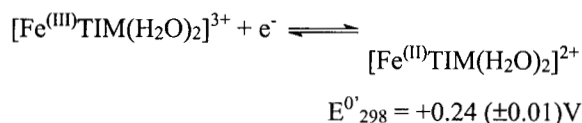
(b) m = proton number

reaction, the following redox process is proposed for the couple B:

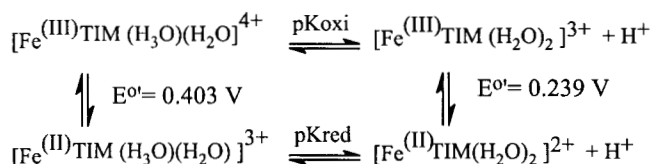


Obs: * penta-co-ordinate iron complex⁸.

The large amounts of E_p for the couple C, reveal an increasing irreversibility of the voltammetric process for $\text{pH} \geq 5$. However, we have verified that in the pH range of 5.17-7.62, the $E_{1/2}$ was independent of the pH, thus establishing a pseudo-reversible process of electron transfer without the participation of the protons in the electrode reaction. Therefore, for the couple C we propose the following redox process:



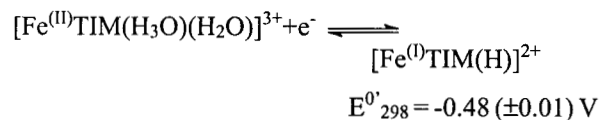
The constants in the pK dissociation were determined, considering the intersections of the straight lines of graph $E_{1/2}$ vs. pH, Fig. 3. Two pKs were obtained from the oxidated species $\text{pK}_{\text{oxi}} = 2.18 (\pm 0.09)$, from the intersection of the straight lines A and B, and $\text{pK}_{\text{red}} = 4.97 (\pm 0.09)$ of straight lines (B) and (C), according to Scheme 1.

Scheme 1.

Upon observation of the voltammogram of Fig. 2 and Table 2, another semi-reversible couple was found at more negative potentials. To characterize this voltammetric wave, the spectroelectrochemistry technique was utilized, and in this way electronic spectra of the complex at the applied potentials (in the potential range of -0.26 to -0.56 V). The electronic spectrum of the Fe^{II} complex shows a band at 648 nm ($\epsilon = 4300 \text{ M}^{-1} \text{ cm}^{-1}$) corresponding to the Fe^{II} charge transfer band macrocyclic ring. Applying the potential, Fig. 4, a new species was observed, at 525 nm, with the disappearance of the band of 648 nm, suggesting the formation of a complex on the electrode surface with a formal charge of +1⁹, consistent with the voltammetric wave in the potential range of -0.5 V, attributed to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ redox couple.

Two species were observed for the oxidation states $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$, in the 2.0 to 11.0 pH range, Fig. 5.

The following redox process is proposed in the pH range of 2.0 \approx 6.5 for the couple D:



Considering the stoichiometry of one electron, without proton transfer in the electrode reaction.

It has been shown that the E inclination values of graph $E_{1/2}$ vs. pH of Fig. 5 are inconsistent with the rates obtained from the Nernst equation. Therefore, the intersection observed for the couples D and E, Fig. 5, where a linearity

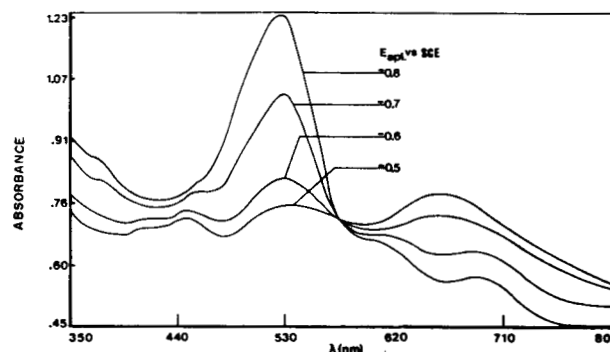


Figure 4. Electrochemical spectrum of complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$, obtained in the potential range -0.5 to -0.8 V vs. SCE. $[\text{Fe}^{\text{III}}] = 7.10 \times 10^{-4} \text{ M}$ at 20 °C and $I = 0.1 \text{ M}$ of NaNO_3 .

Table 2. Date of cyclic voltammetry of the $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$ complex solution, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ couple at 20 °C and $I = 0.1 \text{ M}$ of NaNO_3 .

| Couple | pH | $E_{1/2}$ (V) vs. NHE | ΔE_p (mv) ^a | ipc/ipa | m^b |
|--------|-------|-----------------------|--------------------------------|---------|-------|
| D | 2.95 | -0.486 | 130 | 1.36 | - |
| | 3.32 | -0.489 | 130 | 1.40 | 0.6 |
| | 3.85 | -0.486 | 130 | 1.42 | 0.5 |
| | 4.47 | -0.489 | 130 | 1.22 | 1.0 |
| | 5.17 | -0.491 | 135 | 1.21 | 1.0 |
| | 6.22 | -0.491 | 140 | 1.00 | 1.0 |
| E | 7.62 | -0.50 | 170 | - | 0.5 |
| | 8.25 | -0.52 | 170 | - | 0.5 |
| | 9.68 | -0.55 | 170 | - | 0.4 |
| | 10.44 | -0.56 | 170 | - | 0.3 |

(a) ΔE_p (mv) scan rate 0.1 V. s⁻¹

(b) m = proton number

break occurs in $\text{pH} = 6.5 (\pm 0.8)$, should be due to a dissociation of the complex with the formation of hydroxy complexes. As we can observe, the cyclic voltammetric technique is important for making the speciation for different oxidation states, including species that are only formed on the electrode surface, such as FeI . Another important observation is the characteristic of the couple $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ around $\text{pH} 7$, where the rate $E_{1/2} = +0.24 \text{ V vs. NHE}$, is within the range of "hemin" biological complexes^{8,10}, such as hemoglobin with $\approx +0.2 \text{ V vs. NHE}$ to $\text{pH} 7$. This allows us to confirm the value of the substance under study, from the electrochemical point of view, as a redox model for biological molecules.

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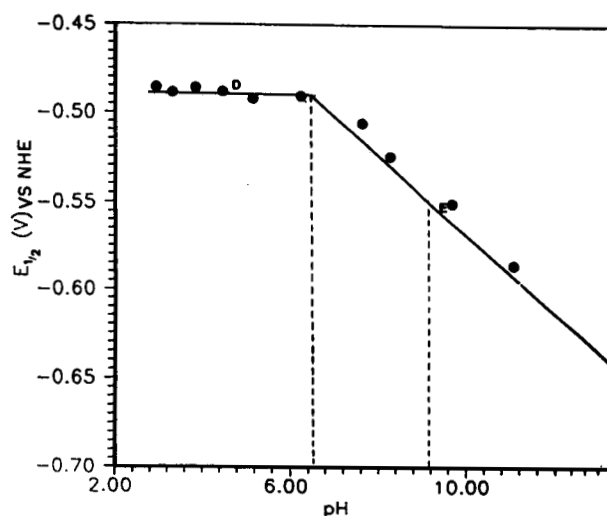


Figure 5. Dependence of $E_{1/2}$ vs. pH for the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ couple, of the voltammograms obtained in the range potential - 0.70 to - 0.45 V vs. NHE, of the complex $[\text{Fe}^{\text{II}}\text{TIM}(\text{H}_2\text{O})_2]^{2+}$, scan rate 0.1 Vs^{-1} .

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