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Preparation and characterization of the pentacyanoferrate(II) on the surface of *N*-(4-pyridilmethylidene)chitosan

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Abstract

Details of the complex formed between pentacyanoferrate(II) and chitosan $[4PMCFe(CN)_5]^{3-}$ are reported. The polymer was characterized by infrared and Mössbauer spectroscopy, and cyclic voltammetry. The infrared spectrum for $[4PMCFe(CN)_5]^{3-}$ contains a very strong band at 2041 cm^{-1} due to the C≡N stretch of the cyanide group. The cyclic voltammogram of $[4PMCFe(CN)_5]^{3-}$ shows that the half-wave potential for the couple $Fe^{II/III}$ is 250 mV versus Ag/AgCl. The Mössbauer spectra for the polymer $[4PMCFe(CN)_5]^{3-}$ show a doublet with quadrupolar splitting (Δ) of the 0.60 mm s^{-1} and isomer shift (δ) of the 0.11 mm s^{-1}. The difference in parameters in comparison with the free complex can be attributed to the matrix effect, i.e. the interaction of the cyanide group of the complex with the hydroxyl group of chitosan.

Keywords: Pentacyanoferrate(II); Mössbauer spectroscopy; Chitosan

1. Introduction

The amine group of chitosan lends itself to many reactions, such as grafting, crosslinking and Schiff reactions (Muzzarelli, 1977). We have been aiming to use it to support electrochemical sensors, especially in modified electrodes (Hikima, Kakizaki, Taga & Hasebe, 1993; Jinrui & Bin, 1994; Lasko, Pesic & Oliver, 1993; Lopes de Alba, Pacheco, Orbina & Alvarado, 1987).

In a previous work, we have shown that chitosan and some of its derivatives are used in modified electrodes as they have the capacity to pre-concentrate anions (Rodrigues, Fávere, Laranjeira & Stadler, 1993).

We have prepared chitosan derivatives by introducing pyridine groups (Rodrigues, Laranjeira, Fávere, & Stadler, 1998).

In this paper we describe the preparation and the, characterization of the complex pentacyaneferrate attached to the modified chitosan with 4-pyridinecarboxaldehyde.

2. Materials and methods

Chitosan (degree of deacetylation is 0.76; molecular weight (M_v) 65,000, determined by the Mark–Houwink equation) (Rathke & Hudson, 1994) was obtained through basic hydrolysis of chitin according to Rigby (1936). 4-pyridinecarboxaldehyde was obtained from the Aldrich Chemical Company, USA.

The chitosan derivatives, *N*-(4-pyridilmethylidene)chitosan (4PMC) were synthesized through Schiff's base reaction by a modified method (Baba, Masaki & Kawano, 1994; Rodrigues et al., 1998; Tong, Baba, Adachi & Kawazu, 1991). $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was synthesized according to previously reported methods (Brauer, 1965).

The complex was prepared by shaking with 0.1 M aqueous solution of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ for 4 h at pH 9. Afterwards the red solid was washed with water to remove excess $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ filtered and dried at 60°C for 4 h. The polymer was characterized by IR and Mössbauer spectroscopy and electrochemical parameters.

The infrared spectra were recorded using an IR-FT Bomen MB-100 spectrophotometer with a KBr pellet. The concentration of the complex in the polymer was determined using a Hitachi model Z-8000 polarized Zeeman atomic absorption spectrophotometer.

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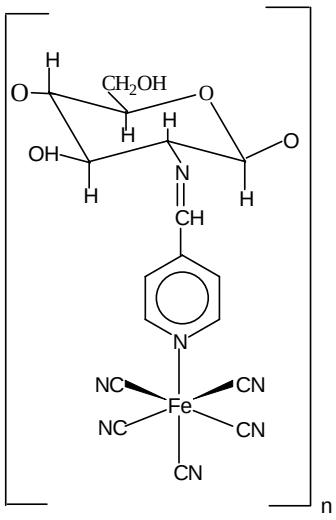

Fig. 1. Structure of $[4PMCFe(CN)_5]^{3-}$.

The cyclic voltammograms were obtained using a cyclic voltammeter model CV-27 (Bioanalytic System Inc.) coupled with an X-Y Omnigraphic 100 register (Houston Instruments). A three-electrode system was used with a carbon paste electrode as the work electrode, a (Ag/AgCl–KCl sat.) reference electrode and a platinum wire as an auxiliary electrode. The electrode modified by carbon paste (EMCP) was prepared by mixing 0.4 g of electrolytic carbon powder (Fluka Chemicals, Switzerland) with 0.2 g of mineral oil (Nujol) and 0.06 g of polymer.

Mössbauer spectroscopy measurements were obtained from solid samples of complexes with Wissel equipment operating at constant acceleration, using a source of ^{57}Co on the Rh matrix with an initial intensity of 10 mCi and 0.26 mm s^{-1} line width, measured against a sodium nitroprussiate absorber as a standard. Isomeric shifts are given relative to α-iron, at room temperature.

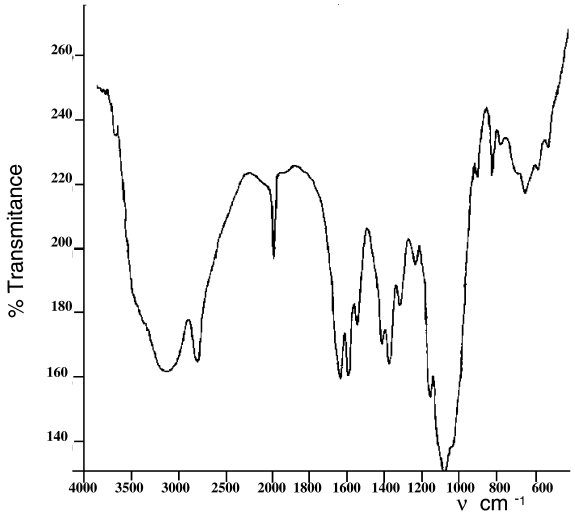

Fig. 2. Infrared spectrum of $[4PMCFe(CN)_5]^{3-}$.

3. Results and discussion

The reaction scheme of 4PMC on pentacyaneferrate in aqueous solution is shown below and the structure is shown in Fig. 1

$$[Fe(CN)_5NH_3]^{3-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} \quad (1)$$

$$[Fe(CN)_5H_2O]^{3-} + 4PMC \rightleftharpoons [4PMCFe(CN)_5]^{3-} \quad (2)$$

The chemical analysis of the pentacyanoferrate complexed to 4PMC gave 1.08×10^{-3} mol g^{-1}, as determined by atomic absorption. The quantity of pentacyanoferrate attached to the polymer is larger than that obtained by Rodrigues Filho, Gushikem, Fujiwara, Stadler and Drago (1994), in studies with organomodified silica gel and pentacyanoferrate.

The infrared spectrum for the $[4PMCFe(CN)_5]^{3-}$ contains a very strong band at 2041 cm^{-1} due to the C≡N stretch of the cyanide group, Fig. 2. This band is in the same region as that of the organomodified silica gel and pentacyanerrate compound (Rodrigues Filho et al., 1994). The observed C≡N band is shifted slightly toward higher frequencies when compared with the value for $[Fe(CN)_5NH_3]^{3-}$ and $[Fe(CN)_5py]^{3-}$ free (Macartney, 1988). The presence of the OH group of chitosan may be the responsible for the wave number shift.

The cyclic voltammogram of $[4PMCFe(CN)_5]^{3-}$ is shown in Fig. 3. The half-wave potential for the couple $Fe^{II/III}$ of the $[4PMCFe(CN)_5]^{3-}$ is 250 mV versus Ag/AgCl. The value of the half-wave of the $[4PMCFe(CN)_5]^{3-}$, is shifted to a more positive value when compared with that of free $[Fe(CN)_5H_2O]^{3-}$ (195 mV) and $[Fe(CN)_5H_2O]^{3-}$ in 4-pyridinecarboxaldehyde excess (230 mV). The shift in oxidation potential to more positive values occurs due to stabilization of Fe (II) resulting in a change of the ligand. The interaction between the cyanide group of the complex and the hydroxyls of chitosan occurs across hydrogen bridges. This interaction reduced the (σ-donor ability of the cyanides, increasing the effective nuclear charge of the metallic center, bringing about the stabilization of the lowest oxidation states, shifting the oxidation potential to more positive values (Lorencetti & Gushikem, 1993; Rodrigues, Stadler, Laranjeira & Drago, 1997; Rodrigues Filho et al., 1994).

The dependence of the current intensity in relation to the scanning rate for $[4PMCFe(CN)_5]^{3-}$, is shown in Fig. 4a. The ratio between the anodic peak currents (i_{pa}) and the cathodic (i_{pc}), in 100 mV s^{-1} is near unity. Another characteristic of a reversible system was observed, namely the linearity of the anodic current versus the square root of the scan rate, Fig. 5 (plot I_{pa} vs. $v^{1/2}$). The high value of the difference between the anodic peak potential E_{pa} and the cathodic E_{pc}, ΔE_p, 110 mV is attributed to the resistance caused by the polymeric matrix. The slight displacement of $E_{1/2}$, due to its scanning rate (range 20–1000 mV s^{-1}), shows that the complex is strongly adsorbed on the chitosan

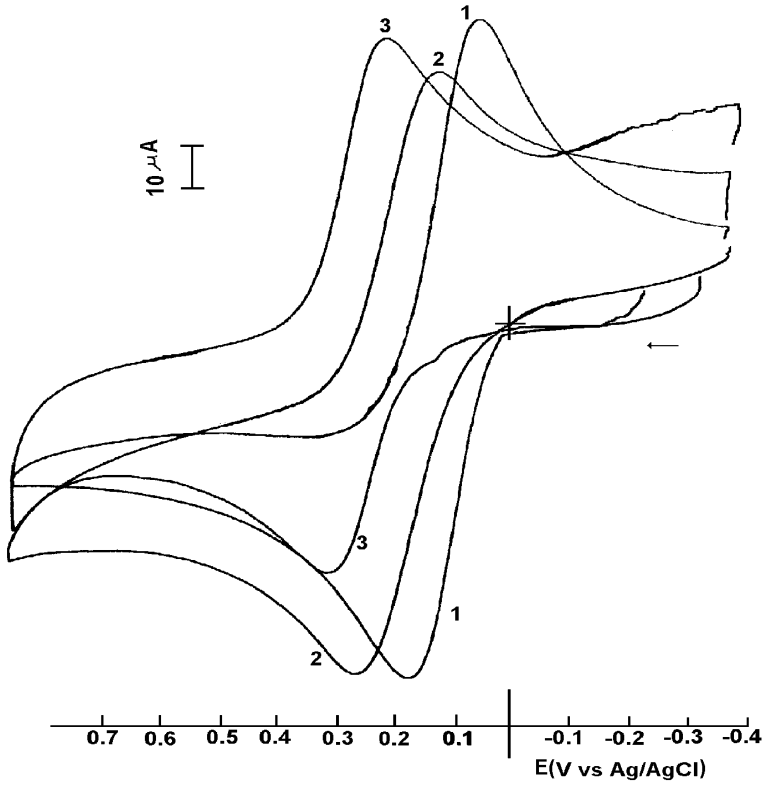

Fig. 3. Cyclic voltammogram of: (1) $[PMCFe(CN)_5]^{3-}$ in EMPC; (2) $[Fe(CN)_5NH_3]^{3-}$ (0.001 M) in glassy carbon electrode; (3) $[Fe(CN)_5NH_3]^{3-}$ and excess of 4-pyridinecarboxaldehyde in glassy carbon electrode. Electrolyte KCl 0.01 M pH 3.2 (HCl), scan rate 100 mV s^{-1}.

surface, since there is no competition between the scanning rate and the diffusion rate.

Fig. 6 shows the Mössbauer spectra already deconvoluted by the Gaussian function, the polymer $[4PMCFe(CN)_5]^{3-}$, shows a doublet with quadrupolar splitting (Δ) of the 0.60 mm s^{-1} and isomer shift (δ) of the 0.11 mm s^{-1}.

A decrease in the δ-donation or increase in the π-accepting capacity by the modification ligand caused a decrease in the density of the "s" electrons in the metal site, which should have lead to an increase in δ. This occurs when the NH_3 is substituted for pyridine in $[Fe(CN)_5NH_3]^{3-}$ ($\delta = -0.02$ mm s^{-1}) and $[Fe(CN)_5Py]^{3-}$ free (0.04 mm s^{-1}) complex. An additional increase in δ occurs due to

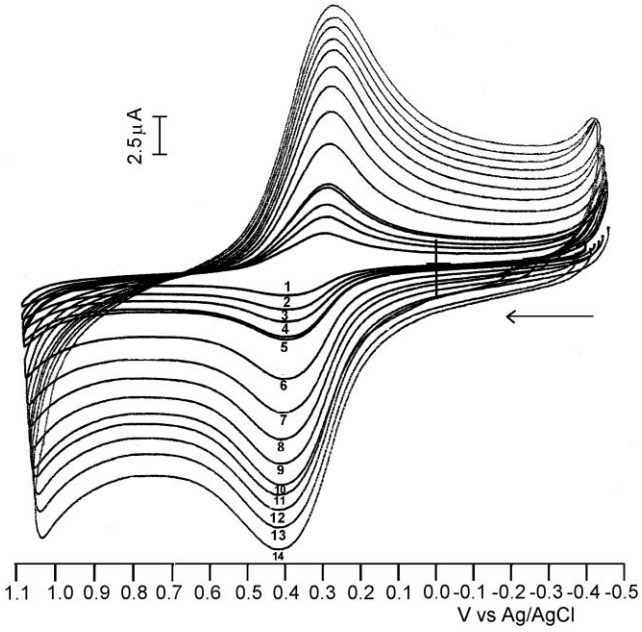

Fig. 4. Cyclic voltammograms of $[PMCFe(CN)_5]^{3-}$ at different scanning rates: 1–10, 2–20, 3–30, 4–40, 5–50, 6–60, 7–70, 8–80, 9–90, 10–100 mV s^{-1}. In KCl 0.1 M pH 3.0 with HCl.

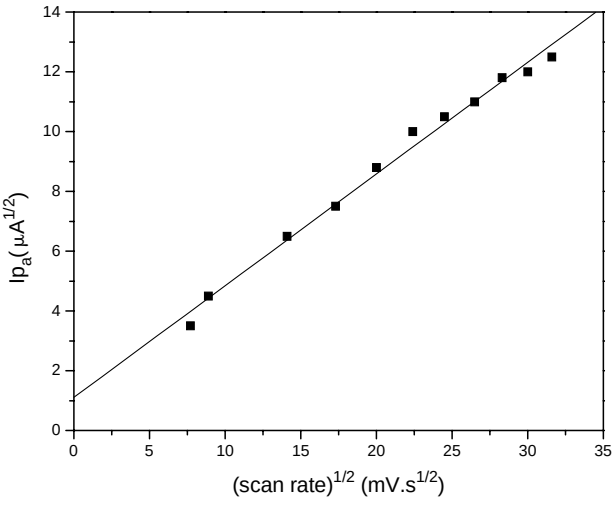

Fig. 5. Square root of anodic peak current vs. square root of the scan rate.

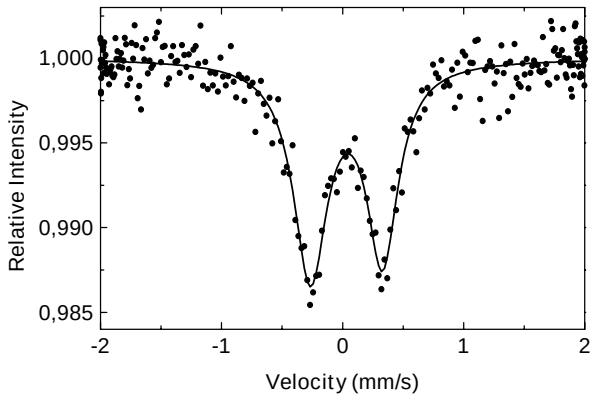

Fig. 6. Mössbauer spectrum of $[4PMCFe(CN)_5]^{3-}$.

interaction between the cyanide of the complex and the hydroxyl of chitosan.

Δ is associated with the nature, symmetry and spatial distribution of the ligands around iron atoms. The observed decrease in Δ for $[4PMCFe(CN)_5]^{3-}$ compared with that for free $[Fe(CN)_5Py]^{3-}$ (0.80 mm s^{-1}) can be attributed to the σ-acceptor decrease of the cyanide group in the attached complex. This may be due to the interactions of the cyanide group of the complexes with the hydroxyl group of the chitosan in a similar manner as observed for the pentacyanoferrate complex attached to the surface of organomodified silica gel (Rodrigues Filho et al., 1994).

4. Conclusion

The amount of pentacyanoferrate in the polymer, as well as the electrochemical properties of the $[4PMCFe(CN)_5]^{3-}$, allow its use in the preparation of a chemically modified electrode, that can be used in sensor and biosensor electrochemistry.

References

Baba, Y., Masaki, K., & Kawano, Y. (1994). *Chemical Letters*, 2389.

Brauer, G. (1965). 2. (pp. 1511). *Handbook of preparative inorganic chemistry, 2*. New York: Academic Press.

Hikima, S., Kakizaki, T., Taga, M., & Hasebe, K. (1993). *Fresenius Journal of Analytical Chemistry*, *345*, 607.

Jinrui, X., & Bin, L. (1994). *Analyst*, *119*, 1599.

Lasko, C. L., Pesic, B. M., & Oliver, D. J. (1993). *Journal of Applied Polymer Science*, *48*, 1565.

Lopes de Alba, P. L., Pacheco, M. A., Orbina, B., & Alvarado, Y. C. (1987). *Bol. Soc. Chil. Qui.*, *32*, 8.

Lorencetti, L. L., & Gushikem, Y. (1993). *Journal of the Brazilian Chemical Society*, *4*, 88.

Macartney, D. H. (1988). *Review of Inorganic Chemistry*, *9*, 101.

Muzzarelli, R. A. A. (1977). *Chitin*, Oxford: Pergamon Press.

Rathke, T. D., & Hudson, S. M. (1994). *J.M.S. Review of Macromolecular Chemistry and Physics*, *C34*, 375.

Rigby, G.W. (1936). US Patent. 2,072,771.

Rodrigues, C. A., Fávere, V. T., Laranjeira, M. C. M., & Stadler, E. (1993). *Journal of the Brazilian Chemical Society*, *4*, 14.

Rodrigues, C. A., Stadler, E., Laranjeira, M. C. M., & Drago, V. (1997). *Journal of the Brazilian Chemical Society*, *8*, 7.

Rodrigues, C. A., Laranjeira, M. C. M., Fávere, V. T., & Stadler, E. (1998). *Polymer*, *39*, 5121.

Rodrigues Filho, U. P., Gushikem, Y., Fujiwara, F. Y., Stadler, E., & Drago, V. (1994). *Structural Chemistry*, *5*, 133.

Tong, P. Y., Baba, Y., Adachi, Y., & Kawazu, K. (1991). *Chemical Letters*, 1529.