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ELECTROCHEMICAL STUDY OF 1 - METHYL - BENZOTRIAZOLE-, BENZIMAIDAZOLE- AND 1,NH_2-BENZIMIDAZOLE - PENTACYANOFERRATE (II) COMPLEXES AT DIFFERENT pH VALUES.

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ABSTRACT

Behaviour of the 1-Methyl-benzotriazole-. Benzimidazole- and 1-NH_2-Benzimidazole-pentacyanoferrate (II), complexes in aqueous solution of 0.5M. $NaClO_4$ at the platinum electrode has been analysed by cyclic voltammetric measurements. The electrode rate constant, k_o, and the transfer coefficient, αn_α of the corresponding complexes have been estimated at different pH values.

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INTRODUCTION

Despite the vigorous development of the chemistry of N-amino derivatives of heteroaromatic systems, including azoles also, data in the principal physicochemical characteristics of these compounds have been almost unavailable up to this time.

Derivatives of benzimidazoles have been extensively used as comertial products (pharmaceuticals, insecticides, fungicides, ...) [1-4]. However, their electrochemical behaviour is still unknown to same extent.

Due the particular behaviour of the pentacianoferrate (II) complexes with these susbtances, same studies have been carried out on the relationship between thermodynamic pKa's azoles and the oxidation potentials of their pentacyanoferrate (II) complexes [5,6]. In this connection in the present research we have determined, by cyclic voltammetric measurements, the electrode rate constant, k_o, and the transfer coefficient, αn_α, of the 1 - methyl - benzotriazole- (1MeBTPCF), benzimidazole- (BPCF) and 1 - NH_2 - benzimidazole - pentacyanoferrate (II) (1NBPCF) complexes at different pH values. The same methods and procedures used in a previous paper [7] has been applied for these substances and they will not described in detail any further. Sodium perchlorate was used as supporting electrolyte. The ligands were prepared by standard methods [8].

RESULTS and ANALYSIS

Cyclic voltammetry (CV) measurements of 1-MeBTPCF, BPCF and 1NBPCF complexes were performed in aqueous solution of $NaClO_4$ 0.5M. at different pH values. The pH of the solution was fixed by adding $HClO_4$ and $NaOH$ [8,9]. Voltammetric curves were obtained by using a platinum rotating electrode. All potentials were refered to the saturated calomel electrode. Measurements were made at 20 mVs^{-1} scan rate.

The experimental values of the half peaks and the separation between anodic and cathodic peaks, ΔE_p, were within a range for which Nicholson's table of values could be utilised. Therefore, the Nicholson method [10] was used to obtain kinetic parameters. For a correct calculation of the function of current, Ψ, we interpolated those values that do not exactly coincide with tabulated ones [7].

1-Methyl-Benzotriazole-Pentacyanoferrate (II) complex

Cyclic voltammetry of this complex was performed in aqueous solution at pH values between 2.2 and 9.7. The i-E curves are given when the electrode is rotating at velocity of 3000 r.p.m. The limiting current and the half peak potential are measured at this velocity. Figure 1 shows a cyclic voltammogram at pH=8.3 with the electrode at rest.

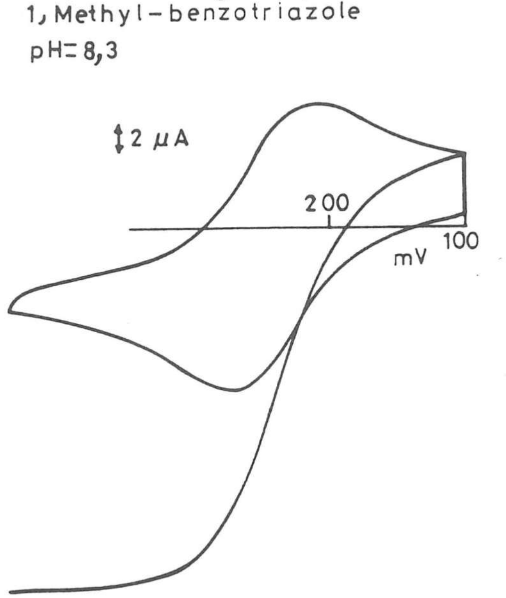

Figure 1.- Voltammogram and polarogram of 1-Methyl-Benzotriazole -pentacyanoferrate (II) complex at pH=8.3. Scan rate = 20 mV/s.

In the studied pH range, the 1MeBTPCF complex displayed only one anodic wave. Voltammetric parameters: the quarter peak potentials, $Ep_{1/4}$, and the three quarter peak potentials, $Ep_{3/4}$, remaining practicaly constant at pH $\geq$ 3.3. In highly acidic media, both parameters increase in 30 mV. On the other land, the obtained values for ΔE_p are $\simeq$ 64 mV for all the pH range. The variation of the half wave potential, $E_{1/2}$, with the pH is shown in Figure 2, whence it follows that $E_{1/2}$ is pH-independent at pH $\geq$ 3.3. However, at pH $<$ 3.3 a value of $\simeq$ 38 mV was found for the slope $dE_{1/2}$/dpH.

TABLE I

Voltammetric and kinetic results from solution at different pH values in presence of 1-Methyl-Benzotriazole - Pentacyanoferrate (II) complex. Scan rate = 20 mV/s.

pH	ΔE_p	k_0	αn_α
	mV.	cms^{-1}	$(n_\alpha = 1)$
9.7	66	0.2×10^{-1}	0.54
8.3	64	0.2×10^{-1}	0.65
7.8	62	0.7×10^{-1}	0.69
7.0	60	0.9×10^{-1}	0.67
5.1	66	0.2×10^{-1}	0.74
4.0	66	0.2×10^{-1}	0.72
3.3	66	0.2×10^{-1}	0.77
2.2	66	0.2×10^{-1}	0.77

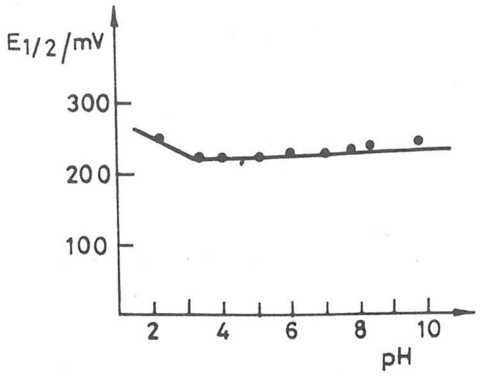

Figure 2.- Variation of the half wave potential, $E_{1/2}$, with pH for 1-Methyl-Bezotriazole -pentacyanoferrate (II) complex in aqueous solution of 0.5N $NaClO_4$.

Kinetic parameters were determined from the Nicholson method and they are given in Table I. Voltammetric and kinetic results obtained at the conditions under which the experiments were made seem to indicate that this complex is a reversible process [11]. However, it is important to remarke that the quantitative kinetic analysis based on peak separation is not very accurate when $\Delta E_p <$ 70mV.

Benzimidazole-Pentacyanoferrate (II) complex

Measurements for this complex were taken in a pH range between 3.3 and 9.9 and only one anodic wave was observed. The CV behaviour of BPCF complex at pH=7.9 is shown in Figure 3. The experimental conditions were the same as for 1MeBTPCF.

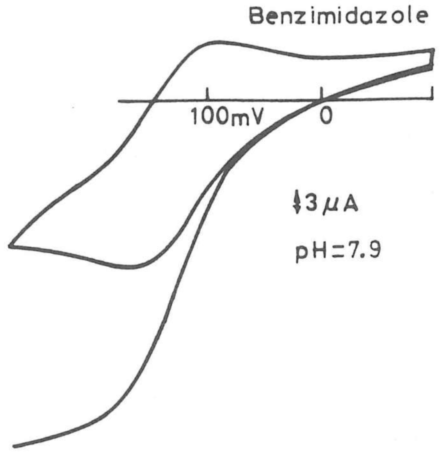

Figure 3.- Voltammogram and polarogram of Benzimidazole -pentacyanoferrate (II) complex at pH=7.9. Scan rate = 20 mV/s.

Dependence of voltammetric parameters on pH was not observed in acidic and neutral media (pH $\geq$ 7.9) where values of $\Delta E_p \simeq$ 84 mv were obtained. However, in higher alkaline media, $Ep_{1/4}$, $Ep_{3/4}$, the anidic, Ep_a, and cathodic, Ep_c, peak potentials are shifted to less positive potentials as pH increases. At the same time, an increase of ΔE_p was found at pH $<$ 7.9.

TABLE II

Voltammetric and kinetic results from solution at different pH values in presence of Benzimidazole - Pentacyanoferrate (II) complex. Scan rate = 20 mV/s.

pH	ΔE_p mV.	k_0 cms^{-1}	αn_α $(n_\alpha = 1)$
9.9	128	1.5×10^{-3}	0.67
9.6	140	0.8×10^{-3}	0.65
7.9	84	5.8×10^{-3}	0.50
7.0	82	6.1×10^{-3}	0.56
6.0	84	5.8×10^{-3}	0.63
4.7	88	4.7×10^{-3}	0.59
3.3	90	3.9×10^{-3}	0.53

The effect of the pH on the electrochemical behaviour of BPCF complex is also observed from the variation of the half wave potentials. Figure 4 shows that $E_{1/2}$ decreases as pH increases but the slope $dE_{1/2}/\mathrm{dpH}$ is only 23 mV at pH < 9.6.

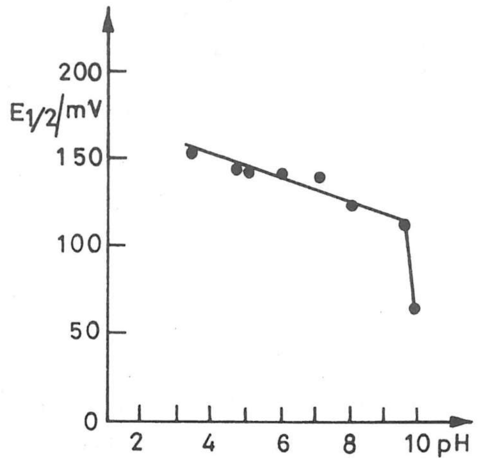

Figure 4.- Variation of the half wave potential, $E_{1/2}$, with pH for Benzimidazole -pentacyanoferrate (II) complex in aqueous solution of 0.5N $NaClO_4$.

Kinetic parameters for BPCF complex are given in Table II. The results obtained for k_o and ΔE_p suggest the process is quasi-reversible but it becomes more irreversible in highly alkaline media.

1-NH_2-Benzimidazole-Pentacyanoferrate (II) complex

The 1NBPCF complex has been studied in a pH range between 2.3 and 9.2. This complex displayed only one well-defined wave but its shape changes with the medium pH.

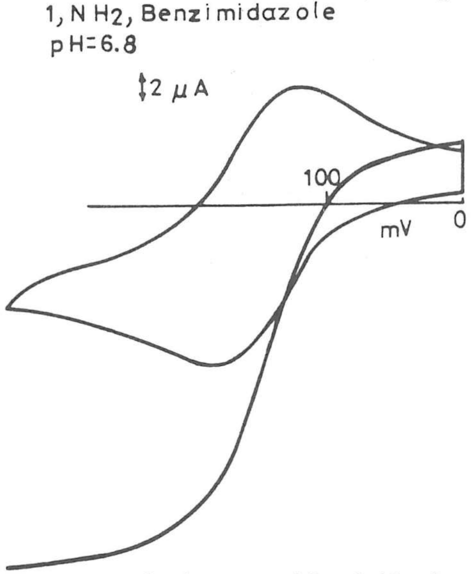

Figure 5.- Voltammogram and polarogram of Benzimidazole -pentacyanoferrate (II) complex at pH=8.3. Scan rate = 20 mV/s.

In Figure 5 is shown voltammograms at pH=6.8 with the electrode at rest, and the same voltammogram at v=3000 r.p.m. As in previous sections, the half peak potential was obtained under this conditions.

TABLE III

Voltammetric and kinetic results from solution at different pH values in presence of 1-NH_2-Benzimidazole - Pentacyanoferrate (II) complex. Scan rate = 20 mV/s.

pH	$E_{1/2}$ mV.	ΔE_p mV.	k_0 cms^{-1}	αn_α $(n_\alpha = 1)$
9.1	126	62	0.60×10^{-1}	0.75
6.8	126	68	0.14×10^{-1}	0.77
5.1	118	66	0.14×10^{-1}	0.75
4.5	116	62	0.60×10^{-1}	0.80
4.0	118	96	0.27×10^{-1}	0.80
2.3	128	100	0.32×10^{-2}	0.69

The influence of pH on the voltammetric parameters is not significative at pH ≥ 4.5. In higher acidic media, anodic peak potentials shift towards more positive values and cathodic peak potentials toward less positive values. Consequently, an increase in ΔE_p was found at pH < 4.5.

The dependence of $E_{1/2}$ on pH is shown in Table III, whence it follows that $E_{1/2}$ is pH-independent at all studied pH range.

The estimation of the corresponding kinetic parameters were made as in the previous sections and they are given in Table III. The results obtained for ΔE_p and k_o show that the classical criteria for reversibility are satisfied for the red-ox process of 1NBPCF complex. However, at pH < 4.5 the system becomes less reversible or close to being quasi-reversible.

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