CYCLIC VOLTAMMETRY OF THE 4,NH_2,1,2,4 TRIAZOLE - , 1,NH_2,1,2,4 TRIAZOLE - AND BENZOTRIAZOLE - PENTACYANOFERRATE (II) COMPLEXES AT DIFFERENT pH VALUES.

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ABSTRACT

The electrochemical study of 4,NH_2,1,2,4,Triazole-pentacyanoferrate (II), 1,NH_2,1,2,4, Triazole-pentacyanoferrate (II) and Benzotriazole-pentacyanoferrate (II) complexes was carried out in a platinum rotating electrode at different pH values. For these complexes, values of the electrode rate constant, k_0, and the transfer coefficient, αn_α have been estimated. The results obtained for these complexes were found to be pH-independent in a wide pH range.

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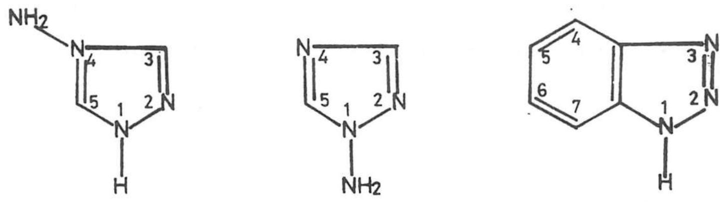
INTRODUCTION

The strong affinity of the pentacyanoferrate (II) ion for unsaturated ligands can be used to make another very interesting series of complexes with imidazole, pyridine, pyrazine [1], sulfoxides [2], CO or NO as the sixth ligand. In this series, the σ-donor and π-acceptor powers of the ligands are expected to vary considerably thus providing large differences in the stability constants for the complexes in their oxidized and reduced forms.

Some kinetic and electrochemical results referring to the imidazole ferrate can be found in a few papers [3-5] but a more general study shows that this family of complexes has a particular behaviour. Spectrophotometric data relevant to some pyrazole are available from the work of Laure [6]. We have studied the cyclic voltammetry of the pyrazole-pentacyanoferrate (II) complexes [7]. As a complement of our study about the behaviour of pentacyanoferrate (II) complexes, the aim of this work was to report an electrochemical study of 4,NH_2,1,2,4,Triazole-pentacyanoferrate (II) (4NTPCF), 1,NH_2,1,2,4,Triazole-pentacyanoferrate (II) (1NTPCF) and Benzotriazole-pentacyanoferrate (II) (BTPCF) complexes (Figure 1 shows the corresponding ligands of these complexes) in order to calculate the kinetic parameters at different pH values.



(a) (b) (c)

Fig. 1.-Labeling of the nitrogen and carbons atoms of: (a) 4,NH_2,1,2,4,Triazole; (b) 1,NH_2,1,2,4 Triazole and (c) Benzotriazole molecules.

EXPERIMENTAL

The complexes were prepared in situ by dissolving solid $Na_3Fe(CN)_5(NH_3)$ and the appropiate ligand : 4,NH_2,1,2,4,Triazole, 1,NH_2,1,2,4,Triazole and Benzotriazole in a ratio close to 1:10 in a 0.5M electrolyte solution of $NaClO_4$. The pH was varied by small additions of strong acid ($HClO_4$) or base (NaOH) and measured inmmediately after recording the voltammetric curves [8-9]. The electrode used for the electrochemical study was a platinum rotating electrode (Methrom 6-1204-010) which was activated before each measurement. The auxiliary electrode was a platinum electrode and the reference electrode was a saturated calomel electrode to which all potentials are referred.

The ligands were prepared by standard methods [9]. Voltammograms have been recorded using an Amel 563 Polarograph coupled to a Hewlett-Packard 7047-A, X-Y recorder.

All the reagents used were of analytical grade. Supporting electrolyte was 0.5M sodium perchlorate. Solutions were prepared using twice-distilled water which had subsequently been passed through a Millipore Mili Q system. All solutions were previously deoxygenated.

RESULTS and DISCUSSION

4,NH_2 1,2,4 Triazole-Pentacyanoferrate (II) complex

Cyclic voltammetric (CV) measurements of 4NTPCF complexes were performed in aqueous solution at pH values between 9.8 and 1.8. Figure 2 shows the CV behaviour of the oxidation of 4NTPCF complex, and represents a voltammogram obtained with the rotating platinum electrode at rest, after it had been activated by passing a nitrogen stream for 30 minutes at pH = 4.8

The i-E curves are given when the electrode is rotating at a velocity v=3000 r.p.m.. It is at this velocity that the limiting current and also the half wave potential are measured. The polarographic behaviour at pH=4.8 is shown in Fig.2. In the studied pH range, this compound displayed only one well-defined polarografic wave. The wave is anodic at pH=9.8 but it is shifted towards the cathodic region when pH $\leq$ 4.8. The small cathodic component increases with decreasing pH. The limiting current is practically pH-independent, although it showed a slight decrease at $pH > 4.8$. The $E_{1/2} - pH$ dependence can be described by two segments of $dE_{1/2}/dpH$ equal to $\approx$ 35 mV below pH 2.7 and practically pH-independent at higher pH values. It should be noted that $E_{p/2}$ value remaining practicaly constant at pH = 9.8 - 2.7. In highly acidic media, an increase in $E_{p/2}$ was found. The quarter peak potentials, $Ep_{1/4}$ and three quarter peak potentials, $Ep_{3/4}$ did not vary appreciably with pH. Only at pH=1.8 these values are 204 and 256 mV respectivly. Voltammetric results are given in Table I.

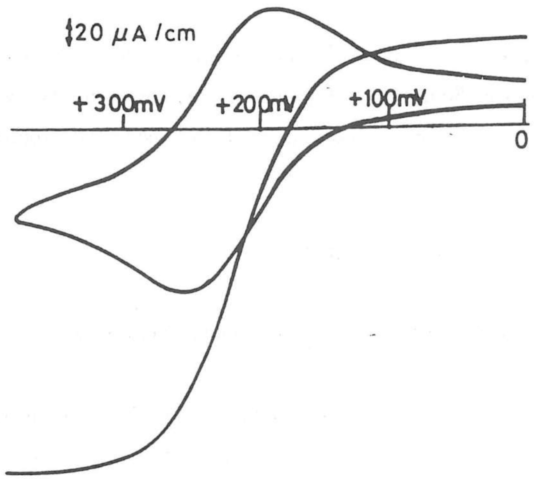


Fig. 2.- Voltammogram and polarogram of 4,NH_2,1,2,4,Triazole-pentacyanoferrate (II) complex at pH=4.8. Scan rate = 20 mV/s.

The experimental values of the half peak potentials, ΔE_p, and the separation between anodic and cathodic peaks, ΔEp, in presence of the studied compounds are within a range for which Nicholson's table of values could be utilised. Therefore, the Nicholson method [10] was used to obtain kinetic parameters. The same procedure used in a previous paper [7] has been applied for these susbtances.

The electrode rate constant, k_0, was calculated from the function of the current, Ψ, which is given by the equation (1):

$$\Psi = (\frac{D_O}{D_R})^{\alpha} k_0 (\frac{\pi n F v D_O}{RT})^{1/2} \tag{1}$$

where v is the scan rate, D is the diffusion coefficient and O and R stand for the oxided and reduced forms respectively. The Ψ values for each experimental ΔE_p were obtained from the Nicholson's tables [10]. For a correct calculation of Ψ we interpolated those values that do not exactly coincide with tabulated one at $\Delta E_p > \Psi$, where Ψ shows a linear dependence on ΔE_p. Then, equation (1) was used by assuming that $D_R = D_O = 0.77 \times 10^{-5} cm^2 s^{-1}$ [11].

The electrode transfer coefficient, αn_α, was calculated from:

$$\alpha n_\alpha = \frac{0.0404}{Ep_{1/4} - Ep_{3/4}} \tag{2}$$

where $Ep_{1/4}$ and $Ep_{3/4}$ are quarter and threee quarter peak potentials respectively.

The obtained values for k_0 and αn_α are given in Table I. However, it is important to remarke that the quantitative kinetic analysis of quasi-reversible cyclic voltammograms based on peak separation is difficult when $\Delta E_p <$ 70mV., since the current function, and thence the electrode rate constant, change very much for small changes of ΔE_p. At an scan rate of 20 mV s^{-1}, it is probably to exist linear sweep effects. Therefore, the kinetics parameters given in Table I must be taken as a rough estimation.

TABLE I

Polarographic, voltammetric and kinetic results from solution at different pH values in presence of 4, NH_2 1,2,4 Triazole-Pentacyanoferrate (II) complex. Scan rate = 20 mV/s.

pH	$E_{1/2}$ mV.	$E_{p/2}$ mV.	$Ep_{1/4}$ mV.	$Ep_{3/4}$ mV.	ΔE_p mV.	k_0 cms^{-1}	αn_α $(n_\alpha = 1)$
7.8	222	190	170	218	86	0.45×10^{-2}	0.80
4.8	216	192	160	214	66	0.19×10^{-1}	0.60
4.2	218	174	162	216	64	0.29×10^{-1}	0.75
3.4	220	186	166	218	66	0.19×10^{-1}	0.72
2.7	226	174	140	190	60	0.98×10^{-1}	0.80
1.8	258	236	204	256	64	0.29×10^{-1}	0.75

* Values estimated from eq.(1).

1, NH_2 1,2,4 Triazole-Pentacyanoferrate (II) complex

Cyclic voltammetry of this complex was performed in aqueous solution at pH values between 9.2 and 1.9. The CV behaviour of the oxidation of 1NTPCF complex at pH = 5.6 is shown in Figure 3. The experimental conditions were the same as for 4NTPCF complex.

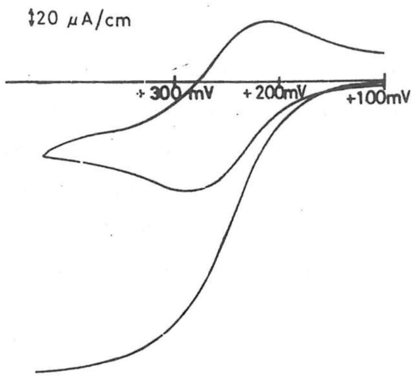


Fig. 3.- Voltammogram and polarogram of 1,NH_2,1,2,4,Triazole-pentacyanoferrate (II) complex at pH=5.6. Scan rate = 20 mV/s.

TABLE II

Polarographic, voltammetric and kinetic results from solution at different pH values in presence of 1, NH_2 1,2,4 Triazole-Pentacyanoferrate (II) complex. Scan rate = 20 mV/s.

pH	$E_{1/2}$ mV.	$E_{p/2}$ mV.	$Ep_{1/4}$ mV.	$Ep_{3/4}$ mV.	ΔE_p mV.	k_0^* cms^{-1}	αn_α $(n_\alpha = 1)$
9.2	246	218	192	224	64	0.29×10^{-1}	0.53
6.6	254	220	164	248	66	0.19×10^{-1}	0.75
5.6	248	216	172	240	68	0.14×10^{-1}	0.72
5.2	242	214	178	240	78	0.73×10^{-1}	0.65
3.3	244	218	180	142	90	0.39×10^{-2}	0.62
1.9	264	244	206	266	82	0.57×10^{-2}	0.96

* Values estimated from eq.(1).

Likewise, the i-E curves are given when the electrode is rotating at velocity v=3000 r.p m. The limiting current and the half peak potential are measured at this velocity.

The 1NTPCF complex displayed only one anodic wave of same height. The dependence of $E_{1/2}$ on pH is indicated in Table II, whence it follows that $E_{1/2}$ is pH-independent at $pH > 3.3$. Similar to the obtained results in presence of 4NTPCF complex, $E_{1/2}$ shifts to more positive values in highly acidic media but, in this case, the $dE_{1/2}/dpH$ value was found to be only 17mV.

Voltammetric results for 1NTPCF complex are shown in Table II. It is observed that in the range between 9.2 and 5.2 there is not change in $E_{p/2}$ remaining data and the peak form for both the cathodic and anodic peaks at pH values lower than 6.6. Values of $Ep_{1/4}$ and $Ep_{3/4}$ did not vary apreciably with an increase in pH. Only at pH=1.9 a small deviation of $Ep_{1/4}$ and $Ep_{3/4}$ toward more positive values is observed. At pH=9.2 there is an increase of 28mV and 24mV respectively. From Table II we can see that ΔEp remains constant at pH 9.2-5.6, reaching 90 mV at pH=3.3. The kinetic parameters estimated from eqs. (1) and (2) are given in Table II.

Benzotriazole-Pentacyanoferrate (II) complex

Measurements for BTPCF complex were taken in a pH range between 7.3 and 2.6.

Figure 4 shows a cyclic voltammograms at pH=4.5 with the electrode at rest, and the same voltammogram at v = 3000 r.p.m. As the previous section, the half peak potential is obtained under these conditions.

In the pH range 2.6-5.4, is observed only one wave of approximatly equal height ($i_L = 10 \mu A$). The value of $E_{1/2} \approx 234$ mV remains practically constant in this pH range (see Table III). At pH=6, two polarografic waves were observed which are not very well-defined. The $E_{1/2}$ values are near to 158 and 250 mV respectively and the limiting currents values are estimated to be 4.2 and 5.1 μA respectively. At pH=7.3, only one wave was found with $E_{1/2}$ and i_L values of 158 mV and 9.8 μA respectively. For this wave, the order of reaction with respect to pH has not been determined because it was observed in a small pH range.

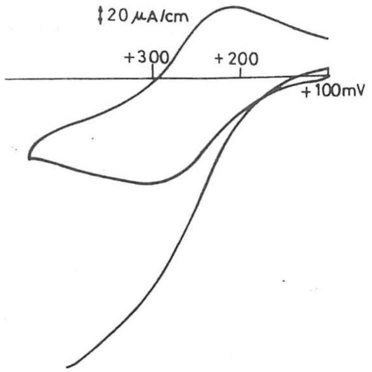


Fig. 4.- Voltammogram and polarogram of Benzotriazole-pentacyanoferrate (II) complex at pH=4.5. Scan rate = 20 mV/s.

TABLE III

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

pH	$E_{1/2}$ mV.	$E_{p/2}$ mV.	$Ep_{1/4}$ mV.	$Ep_{3/4}$ mV.	ΔE_p mV.	k_0^* cms^{-1}	αn_α ($n_\alpha = 1$)
7.3	— 148	—	—	—	-	—	—
6.0	246 158	250	158	226	92	3.8×10^{-3}	0.59
5.5	234 —	226	180	244	104	2.9×10^{-3}	0.63
5.0	246 —	234	190	246	100	3.2×10^{-3}	0.72
4.5	242 —	234	198	246	96	3.5×10^{-3}	0.84
4.1	242 —	234	200	244	86	4.5×10^{-3}	0.90
3.4	246 —	238	202	246	80	6.5×10^{-3}	0.90
2.6	248 —	240	204	246	80	6.5×10^{-3}	0.84

* Values estimated from eq.(1).

Similar behaviour was observed from the voltammetric study. At $pH < 6$ only one wave appears with $E_{p/2}$ value near to 218 mV which is pH-independent. However, ΔEp shows a slight increase with pH. In higher alkaline media, this wave disappears and it is observed with the $E_{p/2}$ shifted about 100 mV. This result seems to indicate that these waves are due to different processes. In Table III are given the corresponding kinetic parameters.

The three studied complexes show an electrochemical behaviour with voltammograms of a single oxidation curve for a given complex. However, analysis of the curves showed some definite differences in the kinetic parameters and in the rate of the corresponding processes.

The results obtained for 4NTPCF, 1NTPCF and BTPCF complexes were found to be pH-independent in a wide pH range where the graph $E_{1/2} vs. pH$ can be represented by a straight horizontal line. Consequently, each complex can be characterized by a value of the plateau potential $E^*_{1/2}$ (a value of $E_{1/2}$ which remains constant in a pH range) of 220 mV, 242mV and 234 mV for 4NTPCF, 1NTPCF and BTPCF respectively. However, in alkaline or highly acidic media, the i vs. E curves showed different values of $E_{1/2}$ compared to $E^*_{1/2}$.

Values of $E^*_{1/2}$ are very close to those obtained for complexes between pentacyanoferrate(II) and pyridine derivatives [12]. In this case, the results were interpreted by attributing the voltammetric curves to the redox reaction:

$$Fe(CN)_5L^{-3} \rightleftharpoons Fe(CN)_5L^{-2} + e^- \tag{3}$$

where L means the corresponding ligand. However, the obtained values for the electrode rate constant and the electrode transfer coefficient show that the classical criteria for reversibility are not fully satisfied for the redox processes of 4NTPCF, 1NTPCF and BTPCF complexes in the studied pH range.

The results obtained for 4NTPCF and 1NTPCF complexes indicate that the possition of the substituent has some effect on the redox process when the pH is changed.

If the NH_2 group is in ^4N, the variation in ΔE_p was found to be only 6 mV in the pH range 1.8 - 4.8. The resulting mean value of 64mV seems to indicate that the process is practically reversible or close to being reversible [13]. This statement is confirmed by the obtained values for the electrode rate constant, k_0, which are around $10^{-1} cm/s$. However, at pH=9.8 a value of 86 mV was obtained for ΔE_p. Although at this pH the constant k_0 is somewhat higher, it is still within the range for quasi-reversible processes. An alternative explanation consists in the attack of OH^- ion at the ligand in a way similar to that observed for the pyrazole ferrates [9].

Different results are obtained when the amine group is in ^1N. In this case the process becomes less reversible with decrease in pH. The classical criteria for reversiblity are verified only at $pH > 5$ where the mean values of ΔE_p and k_0 are 66mV and 2×10^{-2} cm/s respectively. In acidic media, the criteria of reversibility are not fully satisfied and the process becomes quasi-reversible. At pH = 1.9, the i-E curves showed an increase of $E_{1/2}$ compared to $E^*_{1/2}$, which can probably be attributed to the protonation of a CN^- group [12]. The prior protonation of the azo group does not seem to occur because the electrochemical behavior azo compounds [14] was found to be pH-dependent. With increasing pH, the $E_{1/2}$ values were shifted towards negative potentials and the $dE_{1/2}/dpH$ slope was -85 mV. This is not observed for 1NTPCF.

The effect of the molecular structure of the ligand on the reaction rate can be observed from the obtained results for BTPCF complex. The value of ΔE_p varies between 80 mV at pH = 2.6 and 104 mV at pH 5.4. However, at pH=6, the wave splits into two waves. In the studied range of pH, values of k_0 about 10^{-3} cm/s was found. This indicates that the mechanism may be more complex than the expressed in eqn. (1). Studies on the adsorption of organic compounds containing conjugated π - orbitals show specific interaction between the π - orbitals and the electrode surface. Therefore, it is reasonable to assume that an adsorption process could occur in the reaction mechanism and the overall process becomes quasi-reversible.

CONCLUSIONS:

The three studied complexes show an electrochemical behaviour with voltammograms of a single oxidation curve for a given complex. However, analysis of the curves showed some definite differences in the kinetic parameters and in the rate of the corresponding processes.

The kinetic parameters estimated at the conditions under which the experiments were made indicate that these complexes are reversible or quasi-reversible systems with the following k_0 and α values:

4, NH_2 1,2,4 Triazole-Pentacyanoferrate (II):
- pH = 7.8 $k_0 = 0.45 \times 10^{-2} cms^{-1}$

- pH = 4.8 - 1.8 mean value of $k_0 = 0.30 \times 10^{-1} cms^{-1}$
- mean value of $\alpha = 0.74$

$1, NH_2$ 1,2,4 Triazole-Pentacyanoferrate (II):
- pH = 9.2 - 5.2 mean value of $k_0 = 0.34 \times 10^{-1} cms^{-1}$
- pH = 3.3 - 1.9 mean value of $k_0 = 0.48 \times 10^{-2} cms^{-1}$
- mean value of $\alpha = 0.71$

Benzotriazole-Pentacyanoferrate (II):
- pH = 6.0 - 2.6 mean value of $k_0 = 4.41 \times 10^{-3} cms^{-1}$
- mean value of $\alpha = 0.77$

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