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Electroanalytical study of the anodic wave of 5-nitroorotic acid

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Abstract. The electroanalytical behaviour of 5-nitroorotic acid has been studied at several pH values, using DC and differential pulse polarography and cyclic voltammetry techniques. 5-Nitroorotic acid undergoes one oxidation wave in the pH interval considered. The best conditions for determination of the acid are also studied.

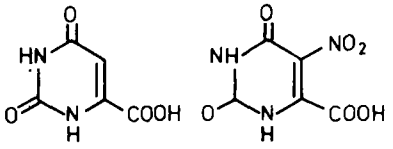
Keywords. 5-nitroorotic acid; polarography; voltammetry; anodic wave.

1. Introduction

Pyrimidine derivatives constitute an important class of compounds because they are components of the biologically important nucleic acids and have been shown to exert a pronounced physiological effect. Since most living systems contain metal ions, which are essential for proper functioning, the question arises as to the effect of such metal ions on nucleic acid.

Orotic acid (I) is a pyrimidine derivative that occurs in nature as an intermediate in the biosynthesis of uridine 5′-monophosphate (UMP), which is also the starting point for the biosyntheses of cytidine and thymidine nucleotides.

Icha (1959) has described orotic acid as polarographically active. 5-Nitroorotic acid (II) is another pyrimidine derivative.



I II

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2. Experimental

2.1 *Apparatus*

A Metrohm Herisau E-506 was used. Dropping time was mechanically kept at 1·0 s, the flow of Hg being $m = 2{\cdot}2\ \text{mgs}^{-1}$, and the remaining experimental conditions were maintained the same as in an earlier paper (Rodriguez *et al* 1988). The reference electrode utilized was Hg/Hg_2SO_4/saturated K_2SO_4 and the auxiliary was a platinum electrode.

A potentiostat VA-Scanner Metrohm E-612 and VA detector Metrohm E-611 were used and voltammograms were recorded on a Linseis LY-XY recorder.

Experimental conditions used were the following: temperature = 25 ± 0·1 °C, pulse amplitude = + 50 mV, potential scan rate = $4\ \text{mVs}^{-1}$.

2.2 *Chemicals and solutions*

Aqueous solutions of 5-nitroorotic acid (5×10^{-3} M) and of Hg(II) (5×10^{-3} M) were used. Britton–Robinson buffers were used. All the reagents used were of analytical grade.

3. Results and discussion

The influence of the pH was studied between the values 2·4 and 9·6 using Britton–Robinson buffers. The anodic wave of the 5-nitroorotic acid was observed throughout this range. Figure 1 shows the recorded polarograms for both DC values at various pH values. In the DC and differential pulse polarography (DPP) techniques, the current does not change with the pH of the solution in the range 4 to 6. E_p moves towards more negative values with increasing pH. A slope of −0·057 V/pH is obtained. The results obtained using the DPP technique are similar. The solutions are polarographically stable at least for the first five hours after preparation.

For the DPP technique, a study has been carried out using various instrumental

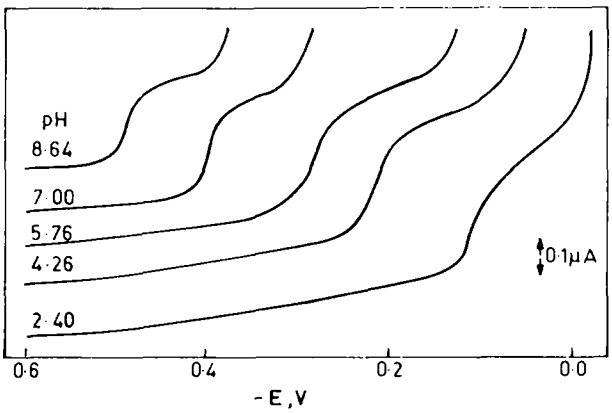

Figure 1. DC polarograms of 5×10^{-5} M 5-nitroorotic acid at various pH values.

variables: drop times (t_d) and pulse amplitudes (ΔE). The optimal values are: $t = 1$ s and $E = +40$ mV.

The influence of temperature was studied in the 10-40 °C range. A temperature coefficient of 1·7% $°C^{-1}$ was obtained. The variation of the mercury column height in the range 40-75 cm provides an increase in I_l. A linear relationship was obtained for I_l versus the square root of the mercury column height ($h^{\frac{1}{2}}$).

The influence of the drop time was studied for DPP. The variation of I_p with $t_d^{2/3}$ was linear.

The effect of the concentration of 5-nitroorotic acid between 5×10^{-6} and 8×10^{-5} M has been studied. A linear relation exists between I_p and concentration. E_p changes slowly with concentration, values larger than 8×10^{-5} M appear ill-defined, and distorted. This indicates a possible adsorption of the reagent.

The number of electrons transferred (n) in the oxidation process was calculated by controlled-potential coulometry using a mercury pool electrode. The value of n obtained for the oxidation process is 2.

The stoichiometry of the complex Hg(II)-5-nitroorotic acid for DC polarography was determined.

The addition of Hg(II) to the 3×10^{-2} M reagent solution produces a decrease in the I_l of the anodic wave and the appearance of a cathodic wave which increases with the addition of Hg(II). The I_{total} remains constant ($I_{total} = I_{cathodic} + I_{anodic}$). The process is supposed to be as follows.

Cathodic process:

$$\text{Hg(II)-5-nitroorotic acid} + 2e^- \rightarrow \text{Hg} + \text{5-nitroorotic acid}$$

Anodic process:

$$\text{Hg}^{\text{electrode}} + \text{5-nitroorotic acid} - 2e^- \rightarrow \text{Hg(II)-5-nitroorotic acid.}$$

The anodic peak current is due to oxidation of the mercury electrode with the formation of the complex Hg(II)-5-nitroorotic acid and the cathodic peak current is due to reduction of the Hg(II) complexed with the reactant.

The application of the molar ratio method (figure 2) showed a ratio of 1:1 between Hg(II) and 5-nitroorotic acid (pH = 4·15).

The anodic sweep was realised first. In this sweep the appearance of an anodic wave corresponding to the oxidation of the Hg (electrode) in the presence of 5-nitroorotic acid was observed.

The anodic sweep was realised first. In this sweep the appearance of an anodic appearance of a cathodic wave corresponding to the reductions of the Hg(II) complexed with the 5-nitroorotic acid (originated in the anodic process) was observed.

In order to check the reversibility of the electrode reactions we have applied the following criteria:

(a) The logarithmic analysis ($\log I/I_l - I$ vs E).
(b) Tomes criteria (Meites 1965).
(c) Birke *et al* (1981) criteria.

In applying both criteria, it has been observed that the process is reversible because in the logarithmic analysis a linear relationship is obtained with a linear correlation coefficient of 0·9955 and a similar result for the Tomes criteria.

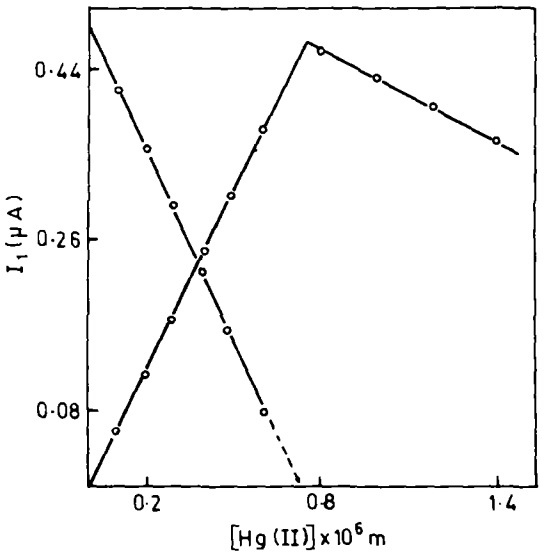

Figure 2. Variation of anodic and cathodic peak current in the DC polarogram of 8×10^{-5} M 5-nitroorotic acid with different concentrations of Hg(II).

The criteria of Birke and co-workers $E_p^c - E_p^a = \Delta E$ and $I_p^a/I_p^c = 1$ for the reversible process are fulfilled.

4. Conclusions

5-Nitroorotic acid at the dropping mercury electrode gives rise to an anodic wave (and five cathodic waves that have been studied in a previous paper, Rodríguez *et al* 1988) which appears at values of pH between 2·40 and 9·60 and has a potential of −0·114 V and −0·526 V respectively.

The wave is diffusion-controlled, taking into account the influence of some variables on its I_p and E_p. Two electrons and two hydrogen ions are involved in the process.

The following mechanism which agrees with the experimental data obtained is proposed.

The electrode reaction is the oxidation of mercury in presence of the reagent which produces a complex Hg(II)-reagent, and this is the basis of a new amperometric method, that is described below.

4.1 *Analytical applications*

The linearity found between I_l or I_p and the concentration of 5-nitroorotic acid has allowed emphasis to be placed on the analytical applicability of the said wave. The possibilities of determining Hg(II) that forms a complex with 5-nitroorotic acid, according to bibliographic data, have been studied.

4.2 *Amperometric determination of Hg(II)*

It was confirmed that the addition of a specific quantity of Hg(II) produces the

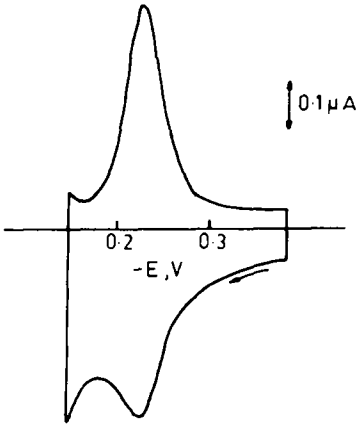

Figure 3. Cyclic voltammogram of anodic wave of 2×10^{-5} M 5-nitroorotic acid (pH = 4·15, $v_b = 200\,\text{mV s}^{-1}$).

expected decrease in the I_l of the anodic part of the wave of 5-nitroorotic acid. The results obtained are shown in figures 2 and 3 in which good linearity for concentrations of Hg(II) between 1×10^{-5} M and 8×10^{-5} M is observed.

References

Birke R, Kimard M H and Strassfeld M 1981 *Anal. Chem.* **53** 852
Icha F 1959 *Pharmazie* **14** 684
Meites L 1965 *Polarographic techniques* 2nd edn (New York and London: Wiley Interscience) p. 224
Rodriguez J, Calvo L, Marin C and Sánchez A 1988 *Proc. Indian Acad. Sci. (Chem. Sci.)* **100** 27