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ELECTROCHEMICAL BEHAVIOR OF 1-HYDROXYPYRIDINE 2-THIONE AND ITS VANADIUM COMPLEX

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Abstract

Electrochemical behavior of 1-hydroxypyridine-2-thione and its vanadium complex is studied using polarographic techniques. Polarograms of ligand and that of the complex is shown with diffusion characteristics of the waves. Cyclic voltagram of thione is investigated which shows that a reversible oxidation reduction of one electron process is taking place. PK_a of the thione is found to be in close agreement with the previous findings.

Introduction

The polarographic behavior of 1-hydoxypyridine-2-thione and some of its metal complexes in 50% ethanol-water solution has been studied at pH values greater than 6.0 [1]. In this study the electrochemical behavior of pure recrystalized ligand and its vanadium complex in aqueous solution of pH=2.0 is reported. This is the optimum pH for the complex formation between vanadium and the ligand which has been explored for spectrophotometric determination of vanadium [2].

Experimental Section

Reagents: A 0.01 M solution of recrystallized 1-hydroxypyridine-2-thione is prepared by dissolving 0.1491 g of thione (Aldrich) in triply distilled water. A buffer solution of pH=2 is prepared using solutions of 0.1 M KCl and 0.01 M HCl. A buffer solution of pH=6.4 is also made by preparing a solution containing 0.01 M CH_3COOH and 0.1 M sodium acetate in 50% ethanol and triply distilled water mixtures. A solution of 0.1 % triton X-100 is used as a maximum suppressor.

Apparatus: An electrochemical unit, model 170 of Princeton Applied Research, is used in this study. A dropping mercury electrode and a saturated calomel electrode are utilized for polarographic measurements. A similar cell equipped with three electrode facility in conjunction with a hanging mercury drop electrode is used for cyclic voltammetric and differential pulse polarographic studies.

Keywords: 1- Hydroxy pyridine- 2- thione Electrochemical
1- hydroxy pyridine- 2- thione

Results and Discussion

The D. C. polarogram, due to the ligand, shows only one wave with $E_{1/2}$=-0.32 V versus SCE. This wave is diffusion controlled as its height is a linear function of concentration of the ligand (Fig. 1-a).

The diffusion characteristic of this wave is further confirmed by the plot of current versus $h_{1/2}$ (Fig. 1-b) and the plot of current versus $t^{1/6}$ (Fig. 1-c).

When vanadium was added to the ligand at pH=2 (0.1M KCl and 0.01 M HCl), the wave, due to the ligand, decreased while another wave appeared on the previous wave (Fig. 2). This post-wave looks like an adsorption wave (Fig. 3), which is probably due to the adsorption of vanadium complex on mercury.

Cyclic voltammogram of the thione in KCl-HCl buffer showed two cathodic waves, one at Ep=-0.14 V and the other at Ep=-0.22 V (Fig.4). The latter peak is due to the electrolyte, as the blank gave the same peak at this voltage.The former peak at-0.14 V is due to the reduction of the ligand. Only one anodic wave, due to the ligand, was observed at -0.08 V. These results show that the reduction and oxidation of thione is a reversible process involving only one electron. The above result confirms what had been obtained previously by other methods [3].

pK_a of the ligand: The pK_a value of thione was measured by changing the pH of the supporting electrolyte and noting the change on the $E_{1/2}$ value of the wave due to thione (Fig. 5).

The results show that the pK_a of this acidic ligand is 4.77 which is close to the value reported in literature by other investigators [3].

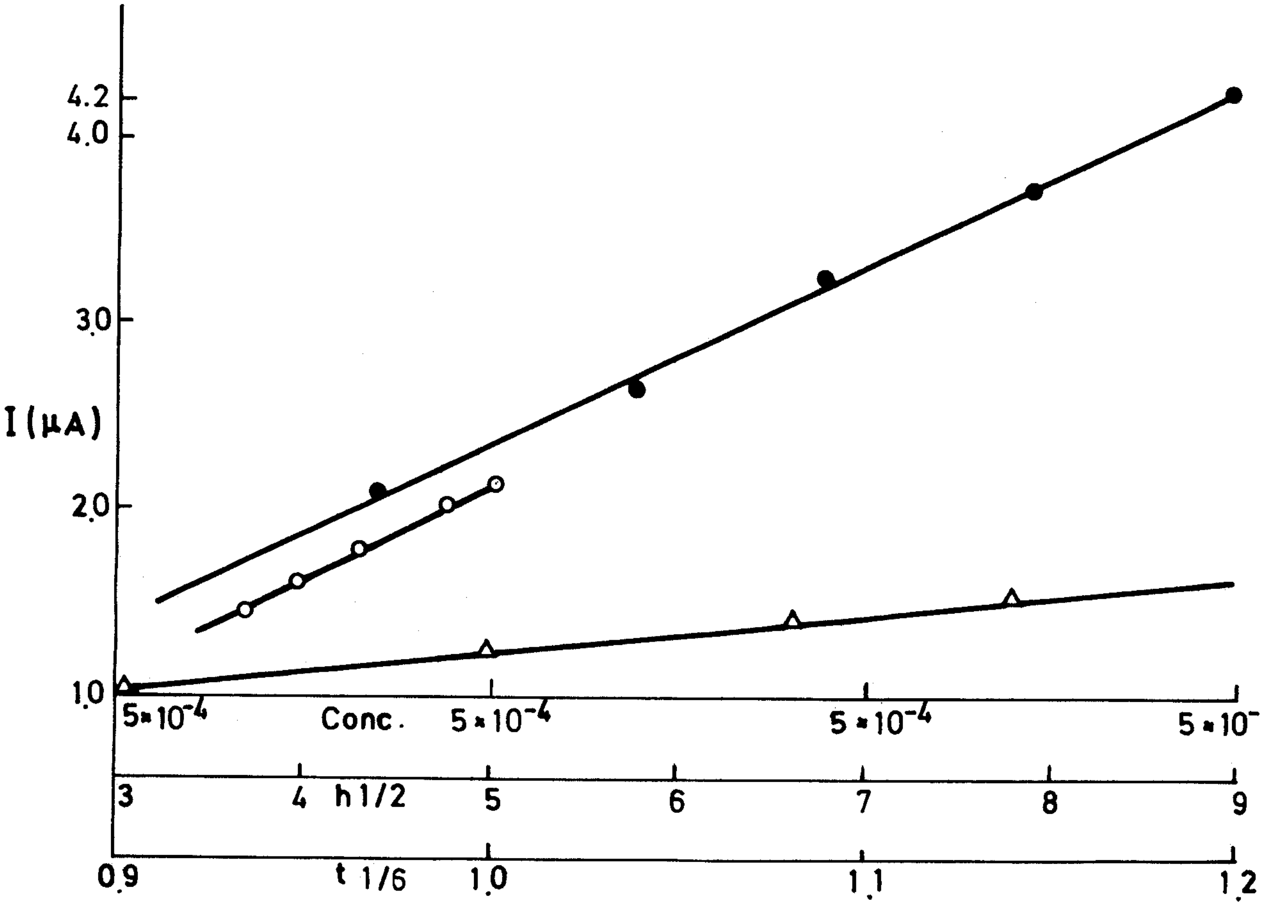

Figure 1. Dependence of current on:

a) Concentration. (full circles)

b) The height of mercury column. (empty circles)

c) Drop time (triangles)

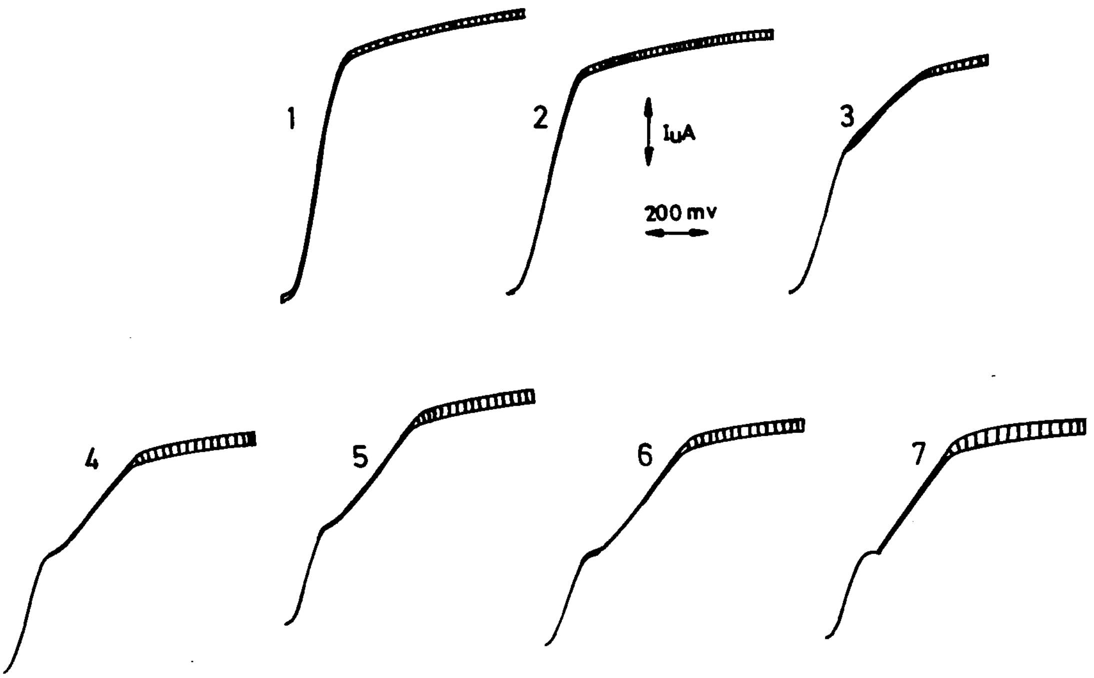

Figure 2. Effect of addition of different Concentrations of Vanadium.

1) (0. conc.) 2)(4.4×10^{-5}M)
3) (8.6×10^{-5} M) 4) (1.26×10^{-4} M)
5) (1.64×10^{-4} M) 6) (2×10^{-4} M)
7) (2.85×10^{-4}M)

Potential sweep was from 0.00 v to more negative potentials.

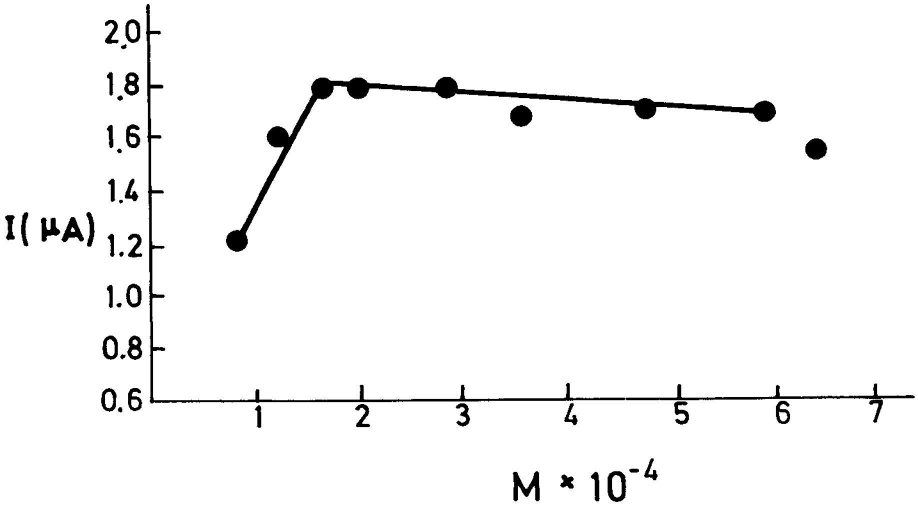

Figure 3. Dependence of current on: A post wave appeared upon addition of metal ion to the ligand.

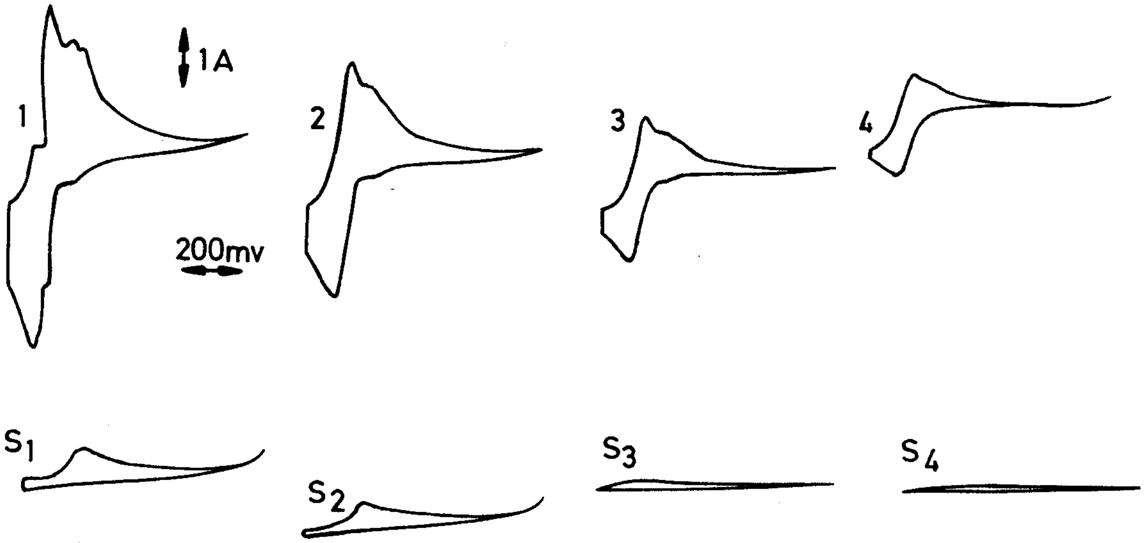

Figure 4. Cyclic voltammograms of thione and the supporting electrolyte (denoted by S) at different scan rates:
1) 100 mv/sec 2)50 mv/sec
3) 20 mv/sec 4) 10 mv/sec
Potential was swept from 0.00 to -0.80 V.

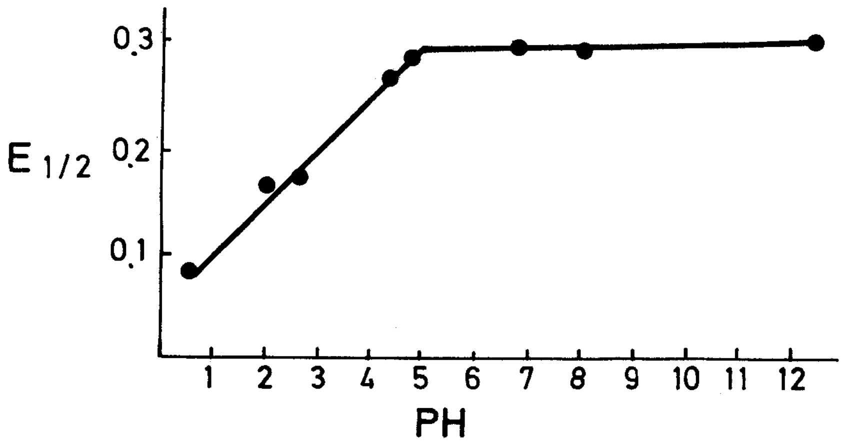

Figure 5. Dependence of half-wave potential of the diffusion current due to the thione on pH.

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