VOLTAMMETRIC BEHAVIOUR OF COPPER IN PRESENCE OF PURINES IN ACID MEDIUM USING GLASSY CARBON ELECTRODES

H. M. Tavares
U. C. E. H. - Universidade do Algarve
8000 FARO - PORTUGAL

ABSTRACT

Cyclic voltammetry (CV) and others voltammetric techniques, with a glassy carbon electrode, have been used to study the interaction of purines with copper in sulphuric medium and others.

If the copper (II) concentration is about 10^{-3} mol dm^{-3} and the purine concentration is equal or higher, is only possible to observe one stage of reduction, but two stages of oxidation are possible. Under these conditions and pH < 2 the copper (I) is stabilised by purine.

The potential variation of each peak of oxidation with increasing purine concentration show processes of electrode of one electron for the observed anodic peaks.

From the shift of the anodic peak potential corresponding to Cu(0) / Cu(I) with increasing ligand concentration the stoichio-metry of the complexes have been determined.

Also the shifts of the anodic peaks potential with increasing pH show processes of one proton.

The aim of this work is to describe the equilibria between purines and copper ions and to propose reactions mechanism on the complexes formation in ours medium conditions.

INTRODUCTION

In aqueous solution purines can exist in a variety of tautomeric and ionic forms.
Under the experimental conditions of pH, purines can exist in one of three forms:

> The neutral XH
> The protonated XH_2^+
> The anionic X^-

But under our conditions of pH (pH 1) purine exist in:

protonated form	96.08%
neutral form	3.91%
anionic form	<0.01%

$$(1)$$

with principal site of protonation (N1) $\qquad (2)$

The voltammetry of copper (II) in complexing solutions indicates that in some complexing solutions reduction proceeds straight to the metal but, in others, *via* the +1 state. Ligands, which sterically or electronically destabilise tetragonal Cu (II) and/or enhance the stabilisation of the Cu (I), can shift the formal Cu (II) - Cu (I) reduction potential to more positive values (3.4), inversely the Cu (I) - Cu (0) reduction potential is shifted to more negative values. This is verified whith copper (II) in purine solutions.

This communication presents a new aproach for elucidating complex stoichiometry and electrochemical complex behaviour of copper ions when purines are

present. The increased resolution afforded by cyclic voltammetry (and other voltammetric techniques) with a glassy carbon electrode is used to elucidate the stepwise formation of complexes.

EXPERIMENTAL

Instrumentation

The voltammograms where obtained using a three-electrode cell and an EG&G PAR model 273 potentiostat with a plotter driven by a minicomputer.

Before recording each voltammogram, the surface of the GCE was polished with alumina paste 0.05 μm and rinsing with deionized water. The potentials were reported *vs* silver/silver chloride.

The pH was measured with a metrohm pH meter, model 654.

Reagents and Solutions

Purines were from Fluka-Garantee puriss. p. a., were used without further purification. Stock solutions 2.0×10^{-1} mol dm^{-3} were prepared in deionized water.

Sulphuric acid (Merck Analitycal-reagent grade) and copper (II) salt (Merck Analitycal-reagent grade). Stock solutions were prepared in deionized water.

Procedure

Prior to the measurements, the samples were deaerated for 10 minutes with argon. The determinations were made at room temperature.
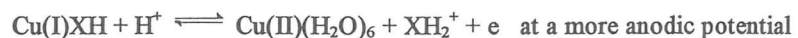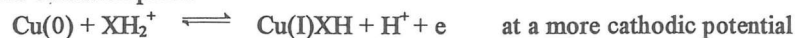
RESULTS AND DISCUSSION

Cyclic voltammograms recorded from 0.1 mol dm^{-3} sulphuric acid and 1.0×10^{-3} mol dm^{-3} copper (II) exhibit only a peak of reduction and a peak of oxidation. But when purines are present at a concentration equal or higher is possible to observe only a peak of reduction and two peaks of oxidation.

The cyclic voltammograms scanned towards negative potentials and scanned in the opposite direction appear identical, which indicates the absence of complicating reactions or acumulation at the electrode surface in the time-scale of the experiments.

The reduction peak may be

$$Cu\,(II)\,(H_2O)_6 + 2e \rightleftharpoons Cu(0) + 6H_2O$$

and the oxidation peaks

$$Cu(0) + XH_2^+ \rightleftharpoons Cu(I)XH + H^+ + e \quad \text{at a more cathodic potential}$$

$$Cu(I)XH + H^+ \rightleftharpoons Cu(II)(H_2O)_6 + XH_2^+ + e \quad \text{at a more anodic potential}$$

This staged oxidation of copper (0) in presence of purines is due to the stabilisation of the copper (I) species by complexation with purines.

The variations of reduction peak potentials of the copper (II), in presence of purine with increasing purine concentration are very small, but your potentials become more anodic.

The variations of oxidation peaks potentials, for the first peak (more cathodic peak Cu(0)/Cu(I)) and second peak (more anodic Cu(I)/Cu(II)) with increasing purine concentration are presented in Fig. 1 and Fig.2, respectively.
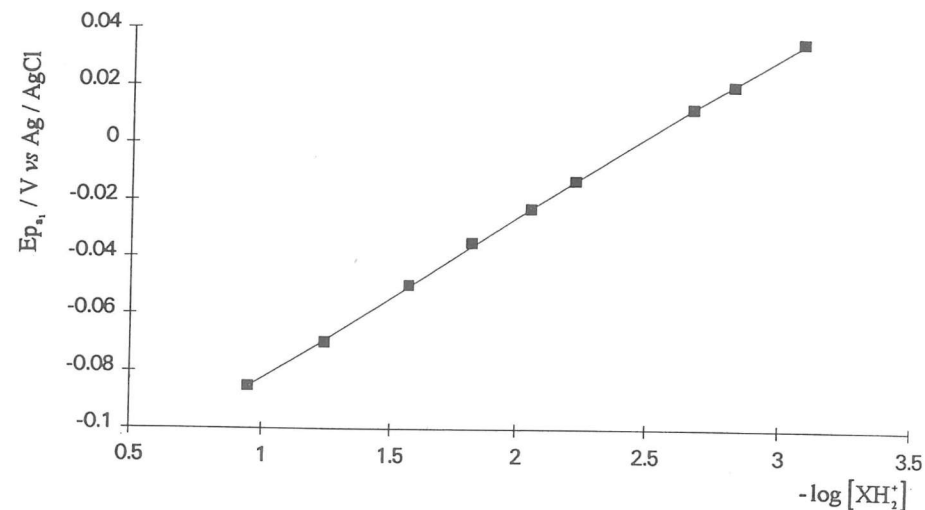

Fig. 1 - Variation of the peak potential (Ep$_{a1}$) Cu (0) /Cu (I) with -log [XH$_2^+$] for the first oxidation.
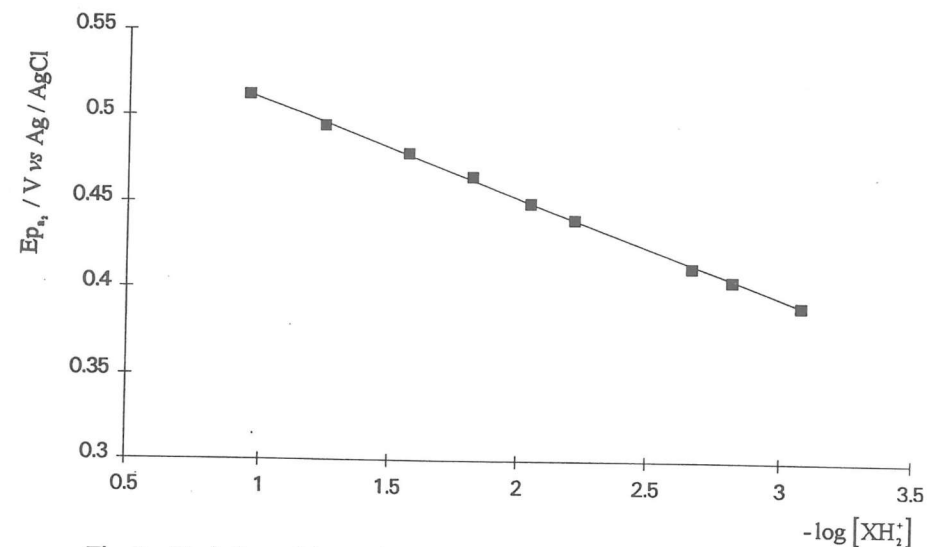

Fig. 2 - Variation of the peak potential (Ep$_{a2}$) Cu (I) / Cu (II) with -log [XH$_2^+$] for the second oxidation.

The cyclic voltammograms recorded at different pH values and the same copper (II) concentration and purine concentration ([XH$_2^+$] > [Cu^{2+}]) give us shifts of peaks with pH in the range 0.5 - 1.1 with slopes dEp/dpH equal to about 60mv. This give us an indication of the processes of one proton and one electron. This can be observed in Fig.3 for oxidation peak Cu(0)/Cu(I) and Fig.4 for oxidation peak Cu(I)/Cu(II).
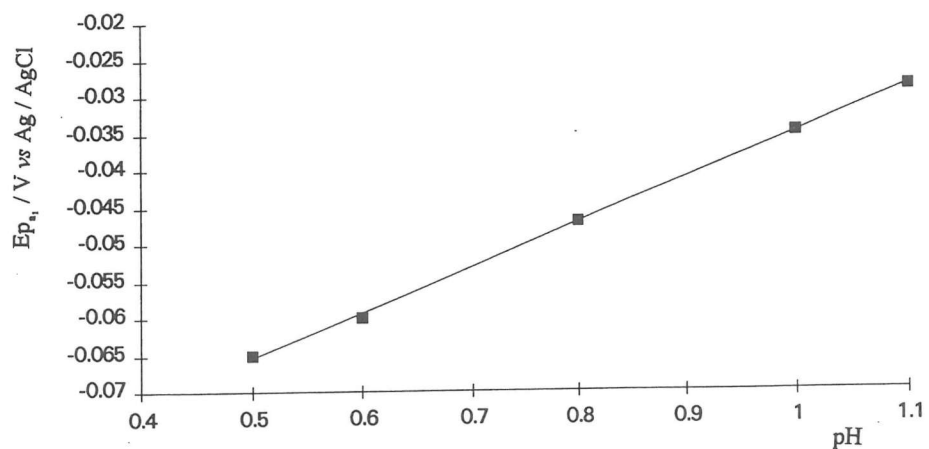
Fig. 3- Dependence of CV oxidation peak potential (Cu (0) / Cu (I)) of 1.0×10^{-3} mol dm^{-3} Cu (II) and purine 1.5×10^{-2} mol dm^{-3} on pH.

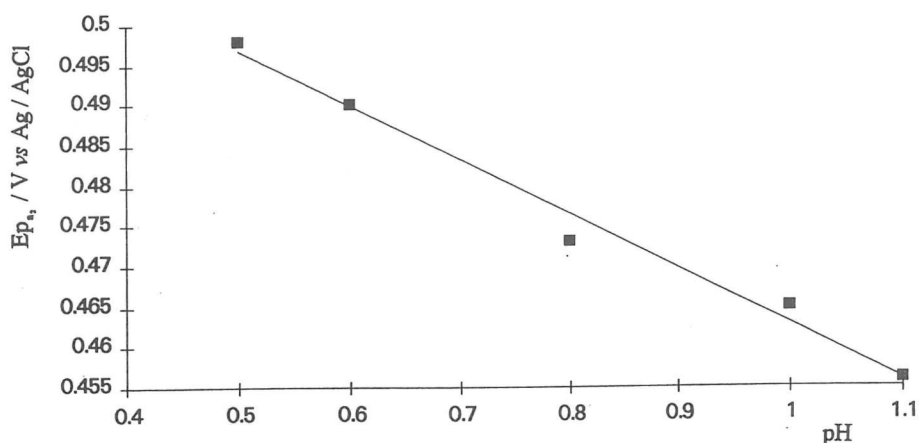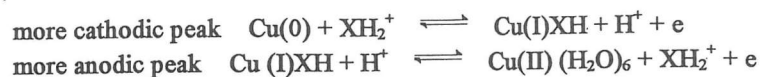Fig. 4- Dependence of CV oxidation peak potential (Cu (I) / Cu (II)) of 1.0×10^{-3} mol dm^{-3} Cu (II) and purine 1.5×10^{-2} mol dm^{-3} on pH.

Having in consideration the slopes of these plots it is possible to admit for each oxidation peak:

more cathodic peak $\quad Cu(0) + XH_2^+ \quad \rightleftharpoons \quad Cu(I)XH + H^+ + e$

more anodic peak $\quad Cu(I)XH + H^+ \quad \rightleftharpoons \quad Cu(II)(H_2O)_6 + XH_2^+ + e$

The results of dependence of the currents for the oxidation peaks on the copper (II) concentration at a constant purine concentration suggested diffusion control of the processes. The Fig.5 shows that the peak current Cu (0) / Cu (I) increases linearly with increasing Cu^{2+} concentration.
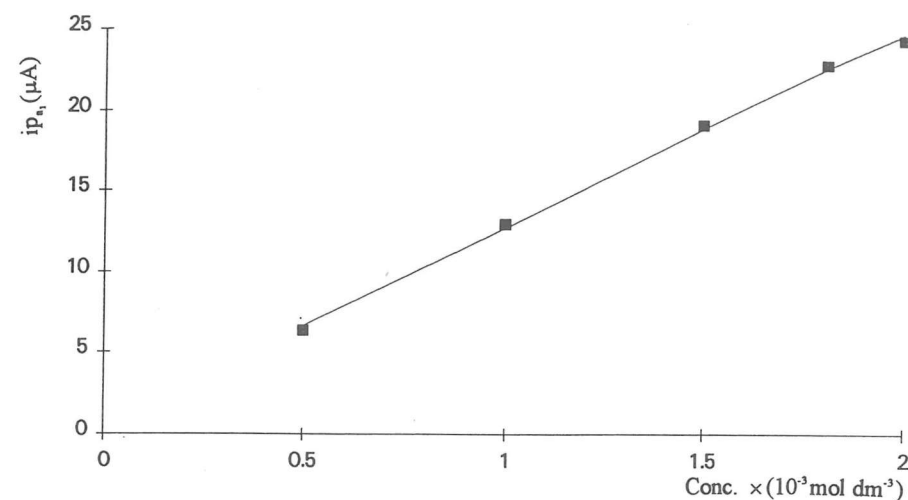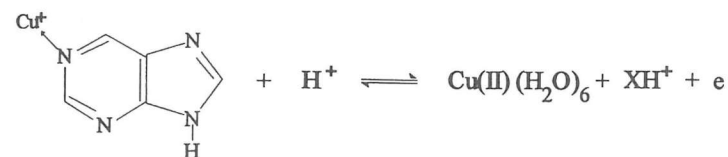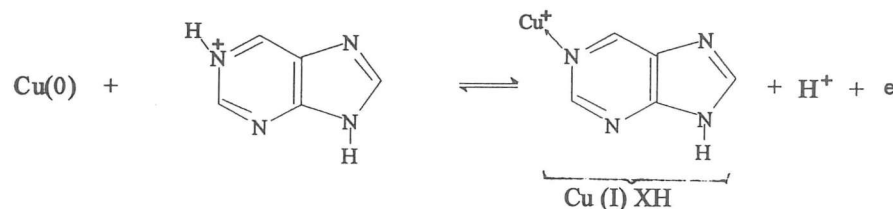

Fig. 5 - Variation of peak current Cu (0) / Cu (I) with Cu^{2+} concentration and 1.5×10^{-2} mol dm^{-3} purine.

Also for a given value of Cu^{2+} concentration and a given value of purine concentration ($[XH_2^+] > [Cu^{2+}]$) and scan rates until 100mV/s, good linear relationships for i_p vs $v^{1/2}$ are obtained.

CONCLUSIONS

The stoichiometry found for cupros complex formed in the first oxidation step is 1:1.

Assuming that the (N7) - H and (N9) - H tautomers are equally predominant in solution (5, 6) and that in the applied conditions the protonated nitrogen is (N1) - the most basic nitrogen in the pyrimidine ring (6, 7 and 8), the following mechanism may be suggested:

for first oxidation peak (with more cathodic potential)

for second oxidation peak (with more anodic potential)

because:

- The variations of the peaks potentials with increasing purine concentration of cyclic voltammograms. The ratios $\Delta Ep/\Delta log\ [XH_2^+]$ determined for purine concentrations varying in the range $(10^{-3} - 10^{-1})$ mol dm^{-3} were close 60 mV, proving that one purine molecule is bound.

- The variations of the peak potentials with pH. The ratios $\Delta Ep/\Delta pH$ determined were close 60 mV, proving processes of one proton and one electron.

REFERENCES

1 - S. F. Mason, *J. Chem. Soc.* 1954, 2071
2 - N. C. Gonella, *et al.* , . *Am. Chem. Soc.,* 105 (1983) 2050
3 - E. R. Deckal, *et al., J. Am. Chem. Soc.,* 98 (1976) 4322
4 - J. O. Gisselbrecht and Maurice Gress, *J. Electroanal. Chem.* , 127 (1981) 127
5 - D. G. Watson, R. M. Sweet and R. E. Marsh, *Acta Cryst.,* 19 (1965) 573
6 - G. Show, "Comprehensive Heterocyclic Chemistry", eds, A. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 5
7 - N. C. Gonella and J. D. Roberts, *J. Am. Chem. Soc.* , 104 (1982) 3162
8 - E. Sletten, J. Sletten and N. A. Fröysteen, XXVI International Conference and Coord. Chem., 1988, Porto, Portugal

ELECTROCATALYTIC BEHAVIOUR OF DIFFERENT SUBSTRATES FOR THE ELECTROOXIDATION OF NaBH4 IN ELECTROLESS METAL DEPOSITION

L. M. Abrantes, A. P. Ricardo

CECUL, Departamento de Quimica, FCUL, R. Ernesto de Vasconcelos, 1700 Lisboa, PORTUGAL.

INTRODUCTION

The catalytic activity of a given substrate for the electroless metal deposition (EMD) is determined by its ability to promote the adsorption of the reductant species and to originate an anionic radical which will be involved in the metal ion reduction; it can be evaluated by measuring the open circuit potential. It is well known that the involved mechanism is highly dependent on the substrate nature, solution pH and composition[1-3].

Sodium borohydride is a reducing agent widely used in industrial electroless plating. It is highly unstable in acid or neutral medium, undergoing fast hydrolysis[4] and if nickel ions are present, nickel boride will be precipitated with consequently bath decomposition; when the pH is maintained above 12, the hydrolysis of borohydride ions can be avoided and good quality Ni-B deposits are produced[5]. However, the mechanism of EMD employing this reductant is not established.

In this work the electrooxidation of borohydride ion (BH_4^-) on Ni and Cu electrodes, in the absence of traditional complexing agents and in metal ions free media, has been studied by cyclic voltammetry and potential time measurements using stationary and rotating electrodes. The results are analysed using the "Intermediate Radical Mechanism"[6] approach.

EXPERIMENTAL

Cyclic voltammetry and potential/time measurements were performed in conventional electrochemical cells. Specpure Nickel and Copper rods have been used to prepare the working electrodes, being a disk of 0.196 and 0.388 cm² area, respectively, exposed to the electrolyte. The electrodes were polished to a mirror finishing and before each experiment a new surface was regenerated by manual polishing with alumina 0,3 μm; as counter electrode a platinum foil was employed and all electrode potentials were controlled with respect to a saturated calomel electrode by an EG & G potentiostat/galvanostat model 273A. Rotating