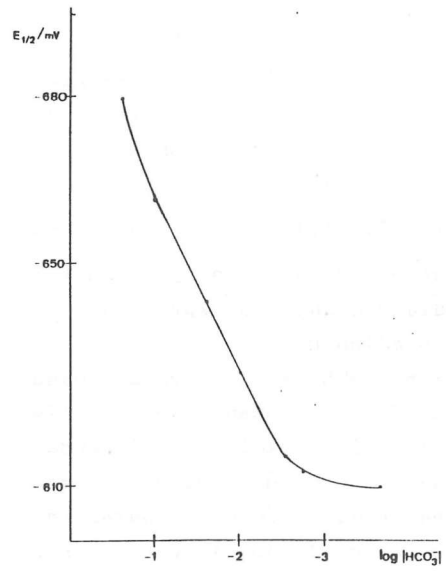
Para la determinación de las constantes de complejamiento se ha procedido mediante un ajuste polinómico por mínimos cuadrados del tipo $y = p(1)x + p(2)x^2 + p(3)x^2 + \ldots$ de la función $F_o(x) - 1 = \exp[-nF/RT\ E_{1/2}] + \ln I_m/I_c = \beta_1 [HCO_3^-] + \beta_2 [HCO_3^-]^2 + \ldots$



considerando como modelo válido aquel que proporciona la mínima suma de cuadrados.

Para el sistema del carbonato básico el modelo adoptado es

$y = p(1)x + p(2)x^2$

dando origen a dos constantes, $\beta'_1 = 129.64$ y $\beta'_2 = 660.36$.

Estas constantes son condicionales, por lo que para la obtención de los valores aparentes es necesario evaluar el coeficiente $\alpha_{Cd(OH)}$. Con ello y mediante la expresión:

$\log \beta = \log \beta' + \log \alpha_{Cd(OH)}$

se han encontrado los valores de la Tabla 2.

Tabla 2

Ligando	Ajuste	Estequiometría	$\beta'_{Cd(L)}$	log β
HCO_3^-	$y = p(1)x + p(2)x^2$	$Cd(HCO_3)^+$	129.64	2.12
		$Cd(HCO_3)_2$	660.36	2.81
HPO_4^-	$y = p(1)x$	$Cd(HPO_4)$	2678.90	3.43
Cl^-	$y = p(1)x + p(2)x^2$	$CdCl^+$	5.74	0.76
		$CdCl_2$	43.28	1.64
SO_4^{2-}	$y = p(2)x^2$	$Cd(SO_4)_2^{2-}$	12.14	1.08

Referencias:

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INTERACTION OF 6-AMINOPURINE (ADENINE) AND OF 6-DIMETHYLAMINOPURINE WITH COPPER IONS IN AQUEOUS MEDIUM. FORMATION OF Cu (I) COMPLEXES

J.E. Simão and H.M. Tavares
Centro de Química Pura e Aplicada - Universidade do Minho
4719 BRAGA CODEX - PORTUGAL

ABSTRACT

Differential pulse polarography (DPP) has been used to elucidate the interaction of adenine with copper and the interaction of 6-dimethyladenine with copper using sulphuric acid 0.1 M as supporting electrolyte.

As has been verified with other purines in this and other media, copper (II) ions are reduced at the mercury electrode in two stages *via* an intermediate valency state, and two reduction peaks may be observed.

Taking into account the variation of the differences (ΔE_p) between the peak potential of each complex and the metal ion with the logarithm of concentration of adenine and the 6-dimethyladenine, respectively, we can conclude that the numbers of the ligands are equal in the two cases and the stability constants are of the same order of magnitude.

INTRODUCTION

In aqueous solution purines can exist in a variety of tautomeric and ionic forms. Information about the species present under particular conditions is of great importance in the interpretation of biochemical processes. Under the experimental conditions of pH adenine and 6-dimethyladenine can exist in one of three forms:

the neutral (AdH and 6-DimAdH)

the protonated (AdH_2^+ and 6-Dim AdH_2^+) or

the anionic (Ad^- and 6-DimAd^-)

Under our experimental conditions 6-aminopurine (adenine) and 6-dimethylaminopurine (6-dimethyladenine) exist in the protonated forms (AdH_2^+ and 6-Dim AdH_2^+) (1) with principal site of protonation (N1) (2).

The voltammetry of the 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 destabilize tetragonal Cu (II) and/or enhance the stabilization 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 (Hg) reduction potential is shifted to more negative values.

This is verified with the copper (II) in adenine solutions or in 6-dimethyladenine solutions.

The normal pulse polarography (NPP) has shown there is no adsorption for the experimental conditions used.

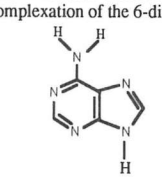
Analysis of the cyclic voltammetric responses with scan rates ≤ 200 mV/s gives evidence for a reversible electron transfer for each reduction step.

$$Cu(II) + XH_2^+ + e = Cu(I)XH + H^+$$

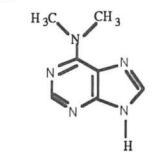
$$Cu(I)XH + H^+ + e = Cu(Hg) + XH_2^+$$

XH_2^+ denotes the protonated form of adenine or 6-dimethyladenine

The aim of this work is to describe the equilibria between purines and copper ions and to determine the stability constants of these complexes. A reaction mechanism has been proposed by comparing the complexation of the adenine with copper ions, with the complexation of the 6-dimethyladenine.



6-aminopurine



6-dimethylaminopurine

EXPERIMENTAL

Instrumentation

Differential pulse polarography and normal pulse polarography were carried out with a PAR 174 A polarographic analyzer coupled to a PAR 303 static mercury dropping electrode (SMDE) assembly. Polarograms were recorded using a Philips 8041 XY recorder. The potentials were reported *vs* silver/silver chloride. A PAR model 175 universal programmer was used for cyclic voltammetry. A three electrode cell was used with the mercury electrode (HMDE) operating as the working electrode, a platinum wire as counter electrode and the potentials were reported *vs* satured calomel electrode.

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

Reagents and Solutions

Adenine and 6-dimethyladenine were of Fluka-Garantie puriss. p.a. grade and were used without further purification. Stock solutions 2.1 x 10^{-3} M of adenine and 2.0 x 10^{-2} M of 6-dimethyladenine were prepared in deionized water.

Sulphuric acid and copper (II) salt of analytical reagent grade were obtained from Merck. Stock solutions were prepared in deionized water.

Procedure

Prior to the measurements, the samples (volume 10 ml) were deareated for 12 minutes with oxygen-free nitrogen. The determinations were made at room temperature. Differential pulse polarography was used with the following parameters: drop time 1s, scan rate 5 mV/s, pulse amplitude 50 mV.

RESULTS AND DISCUSSION

The differential pulse polarography behaviour of adenine in sulphuric acid 0.1 M exhibits one peak centred at potential - 1.38 V *vs* Ag/AgCl. The differential pulse polarography behaviour of 6-dimethyladenine in the same medium, exhibits one peak centred at potential -1.45V *vs* Ag/AgCl. The peaks, result from irreversible two-electron, two-proton transfer for adenine, and from irreversible four-electron, two-proton for 6-dimethyladenine at the pyrimidine ring (5). However, in a solution containing 5.0 x 10^{-5} M copper (II) and higher concentration of adenine or 6-dimethylaminopurine, two reduction peaks were observed corresponding to the reduction

$$Cu\ (II) + XH_2^+ + e = Cu\ (I)\ XH + H^+ \rightarrow \text{at the more positive potential}$$

$$Cu\ (I)\ XH + H^+ + e = Cu\ (Hg) + XH_2^+ \rightarrow \text{at the more negative potential}$$

This staged reduction of copper (II) ions in the presence of adenine or 6-dimethyladenine is due to the stabilization of the copper (I) species by complexation with adenine or with 6-dimethyladenine.

By increasing adenine or 6-dimethyladenine concentration and maintaining copper (II) concentration constant, the peak potential (E_{p_1}) of the copper (II) species shifts to more positive values, while the peak potential (E_{p_2}) of the copper (I) complexed species shifts to more negative values. A simultaneous decrease in the peak height of the copper (II) species was observed in relation to the heigh of copper (II) in the absense of adenine or 6-dimethyladenine.

The variations of peak potentials of the copper (II) in presence of adenine (●) or 6-dimethyladenine (•) ($(E_p)_{Cu^{2+}/Cu^+}$) for the first reduction of the copper (II) ions

$$Cu\ (II) + XH_2^+ + e = Cu\ (I)\ XH + H^+$$

with increasing adenine concentration or 6-dimethyladenine concentration are presented in Fig. 1.

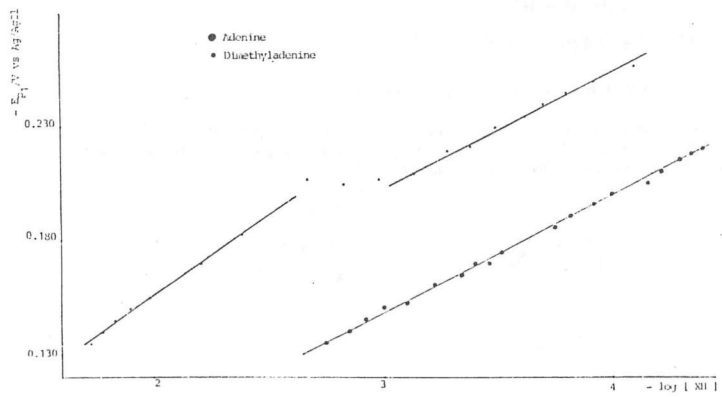


Fig. 1 - Variation of the peak potential $(E_{p_1})_{Cu^{2+}/Cu^+}$ with log [XH] for first reduction.

The variations of peak potentials of the copper (I) complexed ($(E_p)_{c,Cu^+/Cu(Hg)}$) for the second reduction of copper ions

$$Cu(I)\ XH + H^+ + e = Cu\ (Hg) + XH_2^+$$

with increasing adenine concentration and 6-dimethyladenine concentration are presented in Fig. 2.

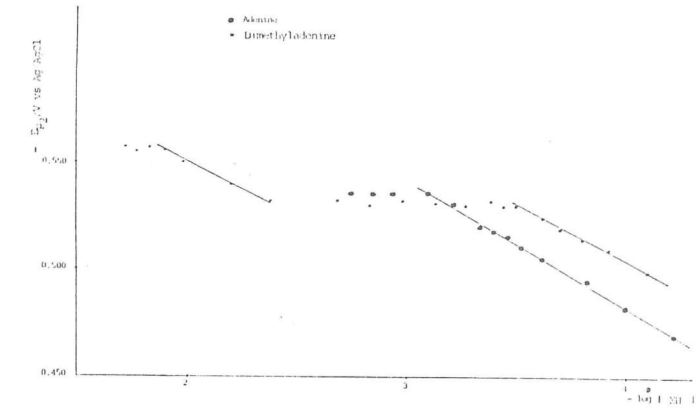


Fig. 2 - Variation of the peak potential $(E_{p_2})_{c,\ Cu^+/Cu}(Hg)$ with log [XH] for the second reduction.

For reversible diffusion controlled processes Parry and Osteryoung (6) have shown that, within the limits of experimental accuracy and in accordance with theory (6, 7, 8), the peak potential of a d.p. polarographic wave (E_p) and the half-wave potential of a d.c. polarographic wave ($E_{1/2}$) are related by the expression.

$$E_p = E_{1/2} - \frac{1}{2}\ \Delta E$$

where ΔE is the pulse amplitude.

It follows from this expression that the shift in the d.p. peak potential on the addition of a complexing agent at a constant pulse amplitude will be the same as the shift in the d.c. half-wave potential. That is:

$$(E_{1/2})_s - (E_{1/2})_c = (E_p)_s - (E_p)_c$$

where the subscripts s and c refer to the simple and complex ions, respectively.

Also, the reversibility of the systems has been determined as previously described by Dillard and Hanck (9) for the calculation of the half-peak width of a differential pulse polarogram using digital simulation. Our results give a value of 95 ± 5 mV, which is in agreement with the predicted value of 99.1 mV for a one-electron process using a 50 mV pulse amplitude.

According to the method of Subrahmanya (10) it is possible to determine the stoichiometry of cupric and cuprous complexes and the stability constants, by means of the relationships:

$$(\Delta E_{p_1}) = (E_p)_{c,Cu^{2+}/Cu^+} - (E_p)_{s,Cu^{2+}/Cu^+} = 0.059\ \log \frac{\beta^+}{\beta^{2+}} - (p - q) \times 0.059 \log [XH]$$

$$(\Delta E_{p_2}) = (E_p)_{c,Cu^+/Cu\ (Hg)} - (E_p)_{s,Cu^+/Cu\ (Hg)} = 0.059 \log \beta^+ - q \times 0.059 \log [XH]$$

XH - denotes adenine or 6-dimethyladenine
$(E_p)_c$ - peak potential of complexed ion
$(E_p)_s$ - peak potential of aqueous ion
β^+ - stability constant of the cuprous complex
β^{2+} - stability constant of the cupric complex
p - ligand number of Cu (II) complex
q - ligand number of Cu (I) complex

The values $(Ep)^{c}_{s,Cu^{2+}/Cu^+}$ and $(E_p)_{s,Cu^+/Cu(Hg)}$ are obtained from the literature (11,12,13).

Applying this method to our experimental data we obtain the results shown in Fig. 3 from the first expression for

adenine (•) and 6-dimethyladenine (•) and the results shown in Fig. 4 from the second expression for adenine (•) and 6-dimethyladenine (•).

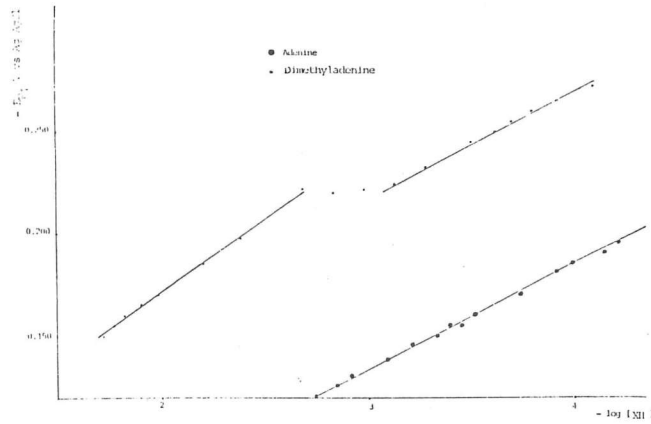


Fig. 3 - Shift in peak potential (ΔE_{p_1}) with log [XH] for Cu(II) + XH_2^+ + e = Cu(I) XH + H^+.

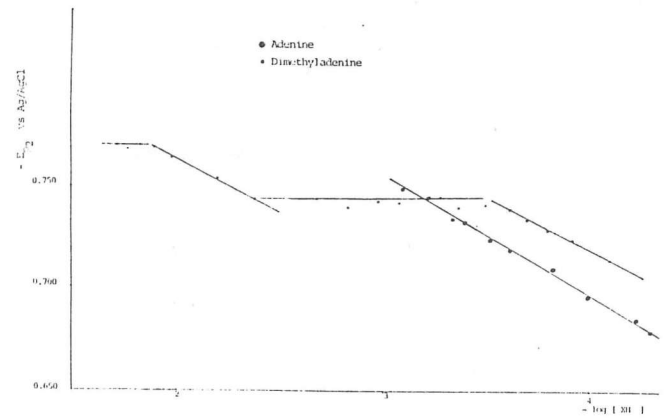


Fig. 4 - Shift in peak potential (ΔE_{p_2}) with log [XH] for Cu(I) complex = Cu (Hg).

The plots of (ΔE_p) as a function of log [XH] allow the stability constants and the ligands numbers (p and q) to be obtained from the intercepts and the slopes of the lines, respectively.

From these data the following values were obtained:

$$\begin{cases} p - q = -1 \\ q = 1 \end{cases} \Rightarrow \quad p = 0$$

As **p** is equal to zero in 0.1 M H_2SO_4 it is not possible for copper (II) ions to complex with these purines. Only copper (I) ions complex.

For adenine $\log \beta^+ = 15.72 \pm 0.02$ $q = 1$

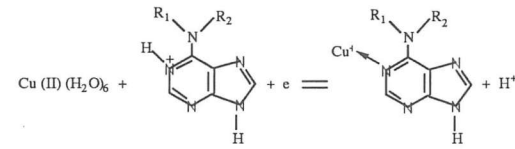
For 6-dimethyladenine $\log \beta^+ = 15.64 \pm 0.03$ $q = 1$

It should be kept in mind that these values of the stability constants and ligand numbers were calculated for adenine concentrations between 5 x 10^{-5} M and about 10^{-3} M and for 6-dimethyladenine concentrations between 8 x 10^{-5} and about 10^{-3} M.

CONCLUSIONS

The stoichiometry found for cuprous complex was 1:1, and is the same for the two purines.

Assuming that the (N7)-H and (N9)-H tautomers are equally predominant in solution (13) and in the applied conditions the protonated nitrogen is (N1), the most basic nitrogen in the pyrimidine ring (14, 15), the following mechanism may be suggested:



First peak (E_{p_1})

Cu (I) XH + H^+ + e = Cu (Hg) + XH_2^+ Second peak (E_{p_2})

$R_1 = R_2 = H$ Adenine

$R_1 = R_2 = CH_3$ 6-dimethyladenine

Taking into account that the stability constant of copper (I) complex of adenine is the same order of magnitude as the stability constant of copper (I) complex of 6-dimethyladenine one is lead to suggested that bonds of the copper (I) - adenine and of the copper (I) -6-dimethyladenine are the same.

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