Conclusions

Our results indicate that it is possible to polymerise aniline on stainless steel substrates, and that PANI films promote the electroless precipitation of silver from aqueous solutions. Electropolymerisation conditions, polymer thickness and surface effective area are important factors for observing good metal recovery efficiencies. The presence of Fe^{3+} in the solution hinders the precipitation process; the interference of Zn^{2+} in silver extraction seems to be complex and deserves further investigation. Results on scaling-up of the process appear to be promising and further work is in progress in this direction.

Acknowledgements

References

1. R. Prakash and K. S. V. Santhanam, *J. Solid State Electrochem.*, **2** (1998) 123 - 125.
2. Q - C. Gu and H - S. Xu, *J. Applied Polymer Science*, **66** (1997) 537 - 531.
3. T. Kobayashi, H. Yoneyama, H. Tamura, *J. Electroanal. Chem.*, **177** (1984) 281 - 291.
4. R. Senthurchelvan, Y. Wang, S. Basak and K. Rajeshwar, *J. Electrochem. Soc.*, **143** (1996) 44 - 51.
5. L. M. Abrantes and A. C. Cascalheira, *1.ᵃˢ Jornadas da Revista Corrosão e Protecção de Materiais*, Lisboa, Portugal, Nov. 98.
6. J. L. Camalet, J. C. Lacroix, S. Aeiyach, P. C. Lacaze, *J. Electroanal. Chem.*, **445** (1998) 117 – 124.
7. E. T. Kang, Y. P. Ting, K. G. Neoh and K. L. Tan, *Synthetic Metals*, **69** (1995) 477 - 478.
8. L. M. Abrantes and J. P. Correia, *Materials Science Forum*, **191** (1995) 235 – 240.
9. S. N. Hoier and S. M. Park, *J. Electrochem. Soc.*, **140** (1993) 2454 - 2463.
10. T. F. Otero and J. Rodrigues, *Electrochimica Acta*, **39** (1994) 245 - 253.
11. David W. DeBerry, *J. Electrochem. Soc*, **132(5)** (1995) 1022 – 1026
12. Pawel J. Kuleza *et al.*, *Electrochimica Acta,* **44** (1999) 2157-2163

SPECIATION OF COPPER IN THE PRESENCE OF BROMAZEPAM

V.Famila*, M.M.Correia dos Santos[a], M.L.Simões Gonçalves

Centro de Química Estrutural, Instituto Superior Técnico, Av Rovisco Pais 1049-001, Lisboa, Portugal.

*Permanent adress: Faculdade de Ciências, Universidade Agostinho Neto, Luanda, Angola.

a) Corresponding autor: e-mail: mcsantos@alfa.ist.utl.pt

ABSTRACT

Complexation of copper with bromazepam is investigated using Differential Pulse Polarography in KNO_3 0.10 $mol.dm^{-3}$ and pH $\approx$ 7. It is apparent from the experimental data that copper in the +1 oxidation state is stabilised by complex formation with bromazepam and so thermodynamic information regarding complexation with Cu(II) and Cu(I) is obtained from the voltammetric results.

**Key words:** Copper, Bromazepam, voltammetry.

INTRODUCTION

Copper is an important trace metal in many biological environmental ecosystems. In oxic conditions Cu(II) is one of the most effective divalent ions for binding to organic molecules. However, Cu(II) can readily undergo one-electron redox reaction producing the π-donor cation Cu(I), in the presence of appropriate ligands for this ion, inducing the oxidation of other species present in the medium.

In the above context, voltammetric methods can give valuable information since Cu(I) species can be electrochemically formed if preferential stabilisation of copper in this oxidation state occurs due to complex formation. In this way thermodynamic data can be computed.

The 1,4-benzodiazepines are a series of drug substances widely studied because of their interesting pharmacological properties and used as sedatives and anti-anxiety agents. These compounds are easily reduced at a mercury electrode through the 2-electron reduction of the 4-5 azometine functional group [1]. In bromazepam, 7-bromo-1,3-dihydro-5(2-pyridyl)-2H-1,4-benzodiazepin-2-one, (scheme 1) the reduction of the azometine group occurs at potentials more positive than the corresponding reductions obtained for non-pyridine containing benzodiazepines. The existence of the -N=CH-CH=N- moiety, similar to that found in $\alpha-\alpha'$ dipyridyl compounds, enables bromazepam to complex some divalent metal ions such as Cu(II), Co(II), Ni(II) and Fe(II) [2-5]. However, the co-ordination chemistry of 1,4-benzodiazepines has mainly concerned synthetic aspects and information regarding the chelating properties in solution is scarce.

In this work we present a study of the interaction of bromazepam with copper(II) at the ionic strength, I, of 0.10 mol.dm^{-3} in KNO$_3$ and at pH = 7. Since both the metal ion and the ligand are reduced at the mercury electrode, copper(II) reduction can be followed while changing the benzodiazepine concentration, and the ligand reduction can be analysed in the presence of various amounts of copper(II) ion. The technique used was Differential Pulse Polarography (DPP) and so the possibility of the stabilisation of the +1 oxidation state was thoroughly investigated in order to obtain information regarding the complexation of Cu(I) and Cu(II) with bromazepam.
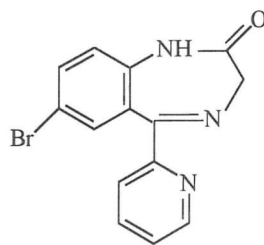
Scheme 1

EXPERIMENTAL

Chemicals and solutions

Stock solutions 10^{-3} mol.dm^{-3} in Bromazepam and 10^{-2} mol.dm^{-3} in Cu(II) were prepared dissolving Bromazepam (from Roche Farmacêutica, Lisboa) in ethanol and Cu(NO$_3$)$_2$ in distilled and deionized water at pH< 2 by the addition of HNO$_3$, respectively.

The supporting electrolyte was KNO$_3$ 0.10 mol.dm^{-3} + PIPES buffer (1,4-piperazinediethanesulfonic acid) (pH= 6.9 ± 0.1).

Instruments

Differential pulse experiments were done with a potentiostat/galvanostat AUTOLAB / PSTAT 10 from Eco Chemie coupled to a Metrohm Stand 663 VA equipped with a dropping mercury electrode, a saturated silver / silver chloride reference electrode and a glassy carbon auxiliary electrode. The following conditions were used: E$_i$ (initial potential) 0.05 V, E$_f$ (final potential) -1.3 V, ΔE (pulse amplitude) 50 mV, t$_p$ (pulse duration) 50 ms and t$_g$ (drop time) 0.5 s and scan rate of 4 mVs^{-1}.

The whole system was controlled by a personal computer also used in the data analysis.

Procedure

Differential Pulse Polarographic (DPP) measurements were done in 50.0 cm^3 of solution (KNO$_3$ 0.10 mol.dm^{-3} and PIPES buffer 10^{-3} mol.dm^{-3}) varying the total ligand [L]$_t$ and total metal [M]$_t$ concentrations between 10^{-7} - 10^{-5} mol.dm^{-3}. The solutions were deaerated with U type nitrogen for 10 minutes.

All experiments were done at least in triplicate and at 20.0 ± 0.2 °C.

RESULTS

The polarographic behaviour of the system Copper(II) + Bromazepam can be observed in fig.1 and in table I, where peak potentials, E_p, and the width of the peaks at half height, $W_{1/2}$, of the polarographic peaks are summarised.
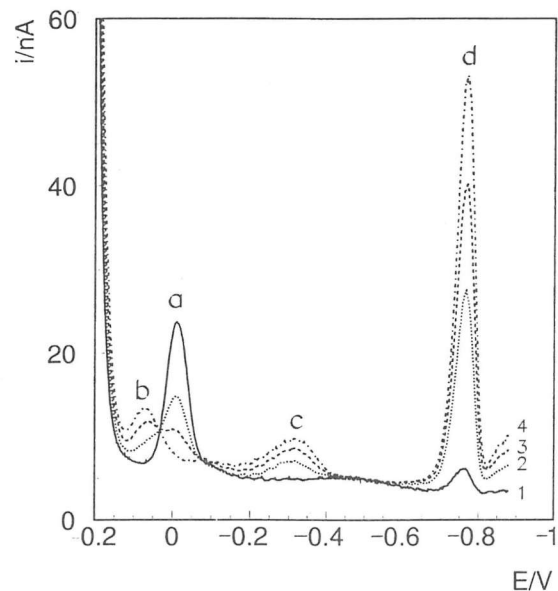

Fig.1: Differential pulse polarography of copper and bromazepam in KNO_3 0.10 mol.dm^{-3} and pH=6.9±0.1 PIPES buffer. Copper concentration 5.0×10^{-6} mol.dm^{-3} and bromazepam concentration (mol.dm^{-3}): 1) 5.00×10^{-7}; 2) 5.01×10^{-6}; 3) 5.99×10^{-6}; 4) 8.00×10^{-6}. Peak a : copper(II) reduction; peak b: copper(II)bromazepam complex reduction; peak c: copper(I)bromazepam complex reduction; peak d: bromazepam reduction

TABLE 1

Peak	E_p/mV	$W_{1/2}$/mV
a	-10±2	61±4
b	59±3	104±4
c	-316±2	102±5
d	-750±2	54±5

As to peaks a and d they can be assigned no doubt to the reductions:

Peak a: $Cu(II) + 2e \Leftrightarrow Cu(Hg)$

Peak d: $L + 2e \Leftrightarrow L_{red}$
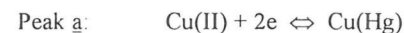
As to peaks b and c taking into account: i) their behaviour with the increasing of the bromazepam concentration (see fig.1); ii) the variation of the peak current associated with peaks a and d shown in fig.2 and iii) E_p and $W_{1/2}$ data presented in table I, one may suggest that the redox reactions responsible for the observed signals may be the following reductions:
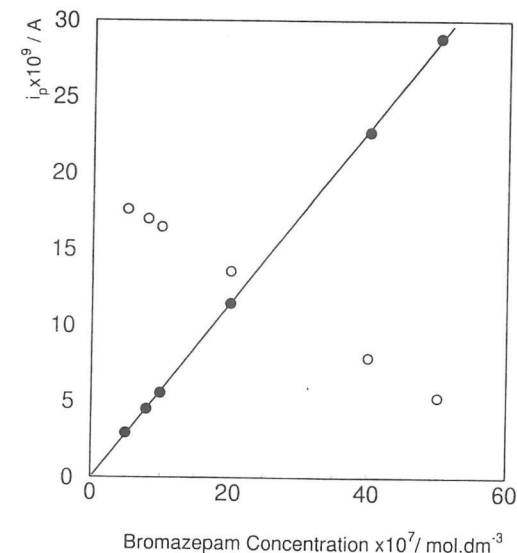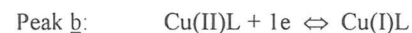
Peak b: $Cu(II)L + 1e \Leftrightarrow Cu(I)L$

Peak c: $Cu(I)L + 1e \Leftrightarrow Cu(Hg)+L$

Fig.2: Titration of copper 5.0×10^{-6} mol.dm^{-3} in KNO_3 0.10 M and pH = 6.9 with bromazepam: (•) bromazepam reduction peak (d); (O) copper(II) reduction peak (a).

This means that copper(II) in solution is progressively complexed by bromazepam being the complex formed inert in the time scale of the electrochemical measurement, i.e., the complex do not dissociate during the electrochemical measurement [6]. The

appearance of two more peaks, b and c, seems to indicate that copper(II) complex can be directly reduced on the electrode being formed copper(I) complex as an intermediate. So, copper in the +1 oxidation state is stabilised in solution due to complex formation and then Cu(II) reduction to Cu(0) takes place *via* two one electron step mechanism [7].

Evidence for the two one electron mechanism can be found comparing the experimental $W_{1/2}$ values of peaks b and c and that of peak a with the theoretical values for a one and a two electron reductions that can be computed using equation (1) [8]:

$$W_{1/2} = 3.52 \, RT \, / \, nF \, (mV) \tag{1}$$

Additional evidence can be obtained by the ratio of the reduction peak currents (of peak a and b or of peak a and c) according to equation (2) [8]:

$$\frac{i_p^a}{i_p^{b(c)}} = \frac{[(1-\sigma)/(1+\sigma)]n}{[(1-\sigma)/(1+\sigma)]n'} \tag{2}$$

This ratio is a function of the number of electrons exchanged, n and n', and of the pulse amplitude: for Δ=50 mV, [(1-σ) / (1+σ)] = 0.453 for n'=1 and [(1-σ) / (1+σ)] = 0.750 for n=2.
In equation 2 similar diffusion coefficients for all the species were assumed which is reasonable according to the molar mass of the ligand.

A summary of the results obtained is presented in table II. As can be seen from this table, the experimental values of $W_{1/2}$ as well as of the ratio of the peak currents compared quite well, within the experimental errors, with the theoretical values assuming that 2 electrons are involved in the reduction responsible for peak a but only one electron is exchanged either in reduction responsible for peak b or for peak c

TABLE II

$W_{1/2}$ comparison		
	Theoretical Value*	Experimental Value
n (electrons)	$W_{1/2}$ (mV)	$W_{1/2}$ (mV)
n = 1	90	102 ± 5 ; 103 ± 4
n = 2	45	63 ± 4 ; 54 ± 5
$\dfrac{i_p^a}{i_p^b}$ or $\dfrac{i_p^a}{i_p^c}$ comparison		
Theoretical value of peak currents ratio With n = 2 and n´ = 1		Experimental value of peak currents ratio
3.4		3.7 ± 0.3

* Limiting value when the pulse amplitude approaches zero; real peaks are larger [8].

In this context peak b has an anodic shift relatively to peak a if the stability constant of Cu(I)L complex is higher than for Cu(II)L species.

The determination of the conditional stability constant K' of the bromazepam complex with copper(II), defined by equation (3), can be computed from the mass balances and the voltammetric data:

$$K' = \frac{[Cu(II)L]}{[Cu(II)]' \, [L]'} \tag{3}$$

The concentration [Cu(II)]', calculated from the current of peak a (fig.1), is composed of hydrated copper ions and of labile complexes formed with OH⁻ that are in rapid equilibrium with hydrated copper ions and all reduced in one common peak. The value obtained for K' is shown in table III.

As to the determination of the stability constant of copper(I) complex with Bromazepam this can be done through the potential value of peak b, as follows [9]:

$$E_{Cu(II)L/Cu(I)L} = E^{o'}_{Cu(II)L/Cu(I)L} + (RT/nF)ln([Cu(II)L]/[Cu(I)L]) - E_{Ag/AgCl} \qquad (4)$$

where $E_{Ag/AgCl}$ is the potential of the reference electrode and

$$E^{o'}_{Cu(II)L/Cu(I)L} = E^{o'}_{Cu(II)/Cu(I)} - (RT/nF)ln(K^{'Cu(II)L}/K^{'Cu(I)L}) \qquad (5)$$

Being $E^{o'}_{Cu(II)/Cu(I)}$ the formal potential of the redox couple Cu(II) /Cu(I) and $K^{'Cu(II)L}$ and $K^{'Cu(I)L}$ are the conditional stability constants of the bromazepam complexes with Cu(II) and Cu(I), respectively.

Since

$$E_p = E_{1/2} - \Delta E/2 \qquad (6)$$

and

$$E_{Cu(II)/Cu(I)} \approx E_{1/2} \qquad (7)$$

using equations (5-7) into equation (4) the following relationship is obtained:

$$E_{Cu(II)L/Cu(I)L} = E_p^{Cu(II)L/Cu(I)L} + (\Delta E/2) = E_p^{b} + (\Delta E/2) =$$
$$E^{o}_{Cu(II)/Cu(I)} + (RT/nF)ln(f_{Cu(II)}/f_{Cu(I)}) - (RT/nF)ln(K^{'Cu(II)L}/K^{'Cu(I)L}) - E_{Ag/AgCl} \qquad (8)$$

In the above equation $E^{o}_{Cu(II)/Cu(I)}$ is the normal potential of the redox couple Cu(II)/Cu(I) and $f_{Cu(II)}$ and $f_{Cu(I)}$ are the activity coefficients of the Cu(II) and Cu(I) ions, respectively, that be can easily estimated for I = 0.10 M through the Davis expression.

So using (8) the ratio of the conditional stability constants was computed:

$$log(K^{'Cu(II)L}/K^{'Cu(I)L}) = -2.4$$

Since $log K^{'Cu(II)L} = 5.9$ (table III) one gets $log K^{'Cu(I)L} = 8.3$. So the formation constant of copper(I) complex is higher then for copper(II) complex as should be.

TABLE III

Conditional formation constants of 1:1 complexes of copper(II) and copper(I) with bromazepam

COMPLEX	log K'	T (ºC)	I (mol.dm^{-3})	METHOD	REFERENCE
Cu(II)L	5.9 ± 0.1	20	0.1	DPP	This work
Cu(II)L	5.81	—	—	Spectral	[2]
Cu(I)L	8.3 ± 0.1	20	0.1	DPP	This work

DISCUSSION

The behaviour now reported show that in solution copper(II) is progressively complexed by bromazepam, being the complexes formed non-labile in the time scale of the electrochemical technique. If the complexes were labile and since we have no excess of ligand, peak a should become broader with the increase of ligand concentration due to the reduction of two metal fractions, the non-complexed and the one from the dissociation of the complex [10]. On the other hand, the appearance of two more peaks, peaks b and c in figure 1, one anodic and the other catodic relatively to non-complexed Cu(II) reduction, indicates that copper in the +1 oxidation state is stabilised in solution due to complex formation and so copper(II) reduction takes place via a two one-electron step mechanism [7].

This behaviour is not so uncommon depending on the composition of the ionic medium. Since copper(I) is a softer cation than copper(II), it shows a stronger affinity to nitrogen binding, being well known that the reduction of Cu(II) in the presence of ammonia occurs via a two step mechanism. The same is true with some monoamines [11] and in the presence of some purine and pyrimidine bases and their nucleosides, as was recently reported [12,13]. The voltammetric behaviour of the redox couple

Cu(II)/Cu(0) in the presence of bromazepam follows a similar pattern as discussed, most probably due to the presence of the bipyridyl moiety. Since complex reduction occurs at potentials more positive than the reduction of the 4-5 azometine group of bromazepam, it is not surprising that this redox reaction should not be affected by complex formation.

References

1. W.F.Smyth, "Voltammetric Determination of Molecules of Biological Significances", John Wiley and Sons, Chichester 1992.
2. M.R.Smyth, T.S.Beng, W.F.Smyth, *Anal.Chim.Acta,* 92 (1977) 129.
3. W.F.Smyth, R.Scannell, T.K.Goggih, D.Lucas-Hernandez, *Anal.Chim.Acta,* 141 (1982) 321.
4. J. Hernandez-Mendez, C.Gonzales-Perez, M.I.Gonzalez-Martin, *Anal.Chim.Acta,* 153 (1983) 331.
5. S. M.Sultan, F.E.Q.Suliman, *Analyst,* 121 (1996) 617.
6. A.M.Mota, M.M.Correia dos Santos, " Trace Metal Speciation of Labile Chemical Species in Natural Waters: Electrochemical Methods" in D. Turner and A.Tessier(eds) "Metal Speciation and Bioavailability", ch.5, p.202, John Wiley and Sons, Chichester 1995.
7. M.L.Simões Gonçalves, L.Sigg, *Electroanalysis,* 3(1991)553.
8. A.J.Bard, L.R.Faulkner, "Electrochemical Methods, Fundamentals and Applications", ch.5, John Wiley and Sons, New York 1980.
9. J.Heyrovsky and J.Kuta, *"Principles of Polarography"*, Publishing House of the Czechoslovak Academy of Sciences, Prague 1965.
10. N.E.Schmith, J.H.Pan, R.H.Philp, Jr, *J.Electroanal. Chem .,* 241 (1988) 281.
11. M.M.Correia dos Santos, M.L.Simões Gonçalves, *Electroanalysis,* 3 (1991) 131.
12. M.M.Correia dos Santos, C.M.L.Freire Lopes, M.L.Simões Gonçalves, *Bioelectrochem. Bioenerg.*, 39 (1996) 55.
13. M.M.Correia dos Santos, P.M.P.Sousa, A.M.M.Modesto, M.L. Simões Gonçalves, *Bioelectrochem. Bioenerg.*, 45 (1998) 267.

DIFFUSIVITY OF NON-ASSOCIATED ELECTROLYTES IN ACRYLAMIDE-BASED HYDROGELS COUPLED WITH A CAPILLARY CELL

Artur J.M. Valente, Victor M.M. Lobo[#][*] and Alexandre Ya. Polishchuk[&]
Department of Management and Industrial Engineering, Lusiada University, 4760 V.N. Famalicão, Portugal; avalente@ave.fam.ulusiada.pt
[#]*Department of Chemistry, University of Coimbra, 3049 Coimbra, Portugal; vlobo@ci.uc.pt*
[&]*Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Street, Moscow 117334, Russia chembio@sky.chph.ras.ru*

Abstract

A technique has been developed to measure the overall diffusion coefficients of KCl and LiCl in acrylamide hydrogels immersed in electrolyte solutions. Once a majority of these kind of polymers are used in connection with electrolyte aqueous solutions, this technique allows the determination of diffusion coefficients representative of systems of aqueous electrolyte solutions normally surrounding polymeric materials. The capillary cell is based on the open-ended capillary conductimetric cell earlier designed to measure diffusion coefficients of electrolytes in aqueous solutions. Polymeric matrices of different hydrophilic character have been studied showing the complex interactions between the different species (water with different structures, polymer and electrolyte). The different thermodynamic effects of cations on the water structure enhance this behaviour. The water structure breaking effect due to potassium ions, when compared with lithium ions, results in the diffusion flux decrease, mainly due to the decrease of water content available as diffusional media inside the matrix.

Keywords

Electrolyte, Diffusion Coefficients, Hydrogels

Introduction

The hydrogels are materials with applications in many fields, such as bio-separation [1] and wastewater treatment [2] among others. In a great number of those applications the hydrogels are in contact with electrolyte solutions. This is the main reason initiating our study of electrolyte behaviour in a hydrogel matrix immersed in aqueous electrolyte solutions.

In a polymer network, water normally exists in a continuum of states between two extremes [3]. They are: water molecules strongly associated with the polymer network through hydrogen bonding (so-called non-freezing water) and much more mobile water molecules unaffected by the polymeric environment (freezing water). However, there is no much information about the electrolyte effect on that water and polymer structure. This results from the assumption that, in the