STUDIA UBB CHEMIA, LVII, 3, 2012 (p. 65 – 72)
(RECOMMENDED CITATION)

DETECTION OF Cu(II) USING ITS REACTION WITH INDIGO CARMINE AND DIFFERENTIAL PULSE VOLTAMMETRY

MARIAME COULIBALY[1], LIANA MARIA MURESAN[2, *], IONEL CĂTĂLIN POPESCU[2]

ABSTRACT. An electrochemical method for Cu(II) determination based on its reaction with indigo carmine (IC) in alkaline medium and differential pulse voltammetry performed at graphite electrode, was elaborated. The experimental parameters affecting the Cu(II) - IC complex formation (reaction time and pH) were optimized. The linear range of the calibration curve, obtaining by representing the IC oxidation current (E_{appl} = 0.175 V *vs.* Ag/AgCl,KCl_{sat}) as function of the Cu(II) concentration (pH 10), was from 10 µM up to 70 µM Cu (II) and the detection limit was 4.74 µM.

Keywords: *Cu(II), indigo carmine, differential pulse voltammetry.*

INTRODUCTION

Copper is an essential trace element in biological systems [1]. Acute copper poisoning occurs when copper salts are ingested. The maximum tolerable daily intake for copper is 0.5 mg Cu / kg body weight [2]. Wilson's disease is a prototypical disease caused by copper toxicosis, affecting first the liver and later the central nervous system, kidneys and eyes. Consequently, monitoring trace of copper in natural environment, biological and other real samples is very important. For this reason, a sufficiently selective and sensitive method for reliable determination of copper would be of great interest.

Among the electrochemical techniques used for the trace analysis of metal ions, differential pulse voltammetry (DPV) is of great interest because of its low cost, easy operation, good sensitivity, high selectivity and accuracy [3].

Indigo carmine is a water soluble aromatic heterocyclic compound, used as redox indicator [4] and as a dye in food and cosmetic industries [5]. The reaction between copper and IC has been used for spectrophotometric determination of Cu(II) in pharmaceutical compounds [6].

---

[1] *Ecole Normale Supérieure, Laboratoire des Sciences Physiques Fondamentales et Appliquées, 08 BP 10 Abidjan, Côte d'Ivoire*

[2] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Physical Chemistry, 11, Arany Janos St., RO-400028 Cluj-Napoca, Romania*

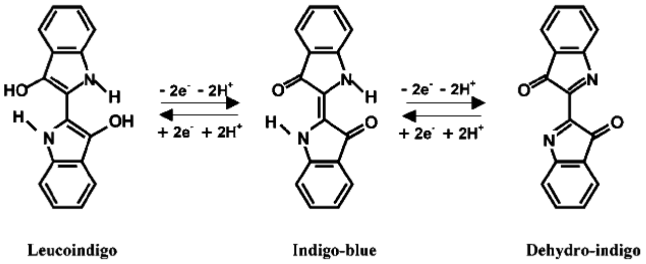
* *Corresponding author: limur@chem.ubbcluj.ro*

In this work, an electrochemical method for copper determination, based on Cu(II) reaction with IC [6] and using DPV measurements performed at graphite electrode, was proposed. The experimental parameters affecting the Cu(II) - IC complex formation (reaction time and pH) were optimized. Due to the electro-inactivity of Cu(II) - IC complex, the decrease of the IC oxidation current measured in alkaline medium (pH 10) at an applied potential of ~150 mV *vs*. Ag/AgCl,KCl$_{sat}$, was used to draw a calibration curve allowing the determination of Cu(II) concentrations.

RESULTS AND DISCUSSION

Electrochemical behavior of indigo carmine

Indigo carmine is an aromatic compound which, similarly to indigo, can be involved in a two steps redox reaction (see Scheme 1) [7-9]:



Scheme 1. Redox reactions involving indigo moiety [8]

As can be seen from Figure 1 and Table 1, the IC voltammetric response shows two well separated peak pairs, in good agreement with the literature data [7, 8, 10]. Taking into account that in alkaline media the A2/C2 peaks pair is better shaped than A1/C1, all further studies were carried out on A2/C2.

Table 1. Electrochemical parameters of the IC voltammetric response recorded at graphite electrode (scan rate 250 mV/s, pH 7).

Peaks pair	$^*E^{0'}$ V *vs.* Ag/AgCl,KCl$_{sat}$	ΔE_p (mV)
A1/C1	-0.062	213
A2/C2	0.717	183

$^*E^{0'} = (E_{pa} + E_{pc})/2$

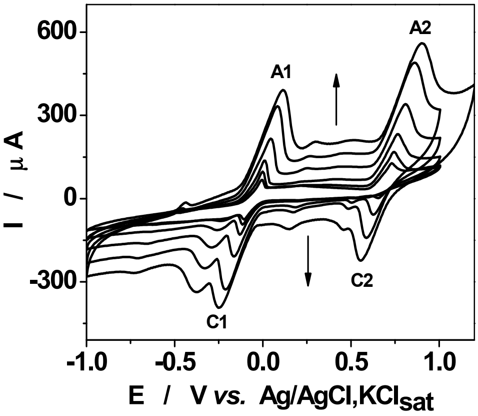


Figure 1. Cyclic voltammograms recorded at graphite electrode for 10^{-3} M IC. Experimental conditions: supporting electrolyte 0.1 M phosphate buffer (pH 7); start potential, -1.0 V *vs.* Ag/AgCl,KCl$_{sat}$; scan rates: 25, 50, 100, 250, 500 and 750 mV/s.

The log-log dependence of the peaks intensities corresponding to the A2/C2 redox couple on the scan rate (Figure 2) revealed that indigo carmine molecules (Scheme 1) are stronger adsorbed on graphite than dehydro-indigo carmine ones. Thus, the slope of this dependence observed for the A2 peak was 0.90 ± 0.02 (R^2 = 0.9939 for N = 10), being close to the theoretical value (1) expected for a surface-confined redox couple. At the same time, the corresponding slope for the C2 peak was 0.74 ± 0.02 (R^2 = 0.9903 for N = 10). This peculiar behavior could be explained by the differences existing between the configurations of IC and dehydro-indigo carmine molecules.

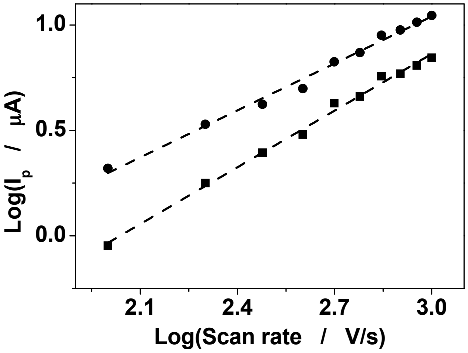


Figure 2. Log(I_p) *vs.* log(scan rate) dependence for A2/C2 peak pair. Experimental conditions: supporting electrolyte 0.1 M phosphate buffer (pH 10); (•) reduction and (▪) oxidation.

PH influence on the IC redox response

Differential pulse voltammetry (DPV) measurements were carried out to investigate the pH effect on the redox couple A2/C2 from Figure 1. As expected for a redox process involving protons and electrons (Scheme 1), the pH increase induces a negative shift of the oxidation peak potential of IC, simultaneously with a monotone decrease of the peak currents (Figure 3).

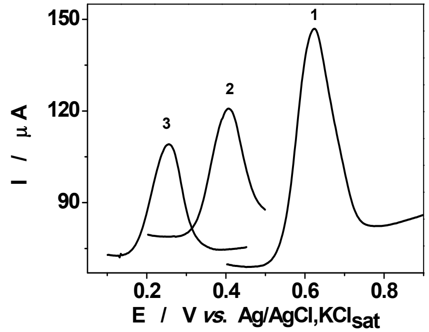


Figure 3. DPV response of IC recorded at graphite electrode. Experimental conditions: scan rate, 0.03 V.s^{-1}; pulse amplitude, 100 mV; supporting electrolytes, (1) acetate buffer (pH 2.5); (2) and (3) phosphate buffer pH 6 and pH 8.5, respectively; IC concentration, 10 µmol.L^{-1}.

Using DPV data for A2/C2 couple, a linear correlation between the anodic peak potential (E_{pa}), and the pH was found (Figure 4). This is described by the equation E_{pa} = 0.750 - 0.061*pH (R^2 =0.9933), which points out to an equal number of protons and electrons participating to this process and confirms once again the Scheme 1 regarding the redox reaction involving IC and dehydro-indigo.

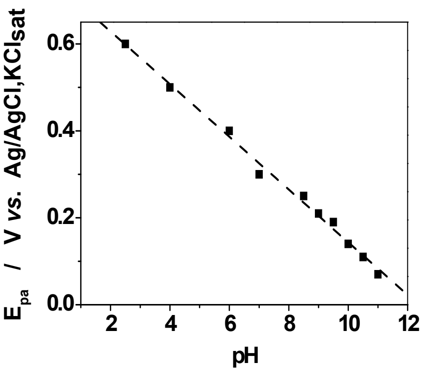


Figure 4. Anodic peak potential (E_{pa}) *vs.* pH dependence for A2/C2 couple.

DPV detection of Cu(II)

When Cu(II) ions are added to an alkaline solution of IC, the Cu_2IC complex is formed [6]. Because at the working potential this complex is electro-inactive, a decrease of the oxidation peak current will appear for A2/C2 redox couple. Moreover, as can be seen from Figure 5, the peak current decrease is depending on Cu(II) concentration in the μM range.

The main parameters influencing the Cu_2IC complex formation (reaction time and pH) were investigated. The influence of the solution pH on the Cu_2IC complex formation was investigated by measuring of the decrease of oxidation peak current (I_{pa}) of A2/C2 redox couple induced by Cu(II) addition at different pH values (results not shown). The maximum decrease of I_{pa} was observed at pH 11 (76%), but pH 10 was chosen as working pH, considering that: (i) at this pH the I_{pa} decrease was still significant (63%) and (ii) at pH 10 the buffering capacity of the carbonate solution is maximum. These results are in agreement with those reported for Cu(II) spectrophotometric determination [6].

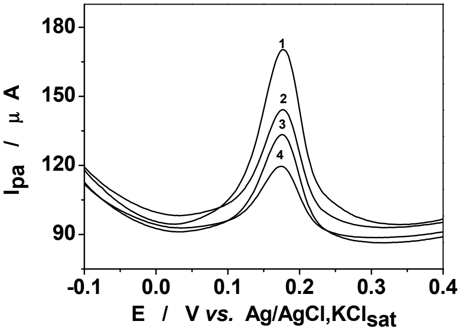


Figure 5. Typical DPV response obtained before (1) and after the addition of different Cu(II) ions concentrations in a solution containing 100 μmol.L^{-1} IC: (2) 40 μmol.L^{-1} Cu(II); (3) 80 μmol.L^{-1} Cu(II); (4) 100 μmol.L^{-1} Cu(II). Experimental conditions: supporting electrolyte, 0.1 M carbonate buffer (pH 10); scan rate 0.03 V/s; pulse amplitude, 100 mV.

Furthermore, in order to estimate the time required for the complex formation, Cu(II) ions were incubated with IC in alkaline medium (pH 10) for various periods of time (5 -120 min). The time evolution of the anodic peak current of A2/C2 redox couple is depicted in figure 6.

Using the data from Figure 6, first-order kinetics [$k = (0.0081 \pm 0.0006)$ min^{-1}] for the free IC concentration decrease due to the complex formation was found ($R^2 = 0.9471$; N = 11). Taking into account the time dependence of the Cu_2IC complex formation, all further measurements

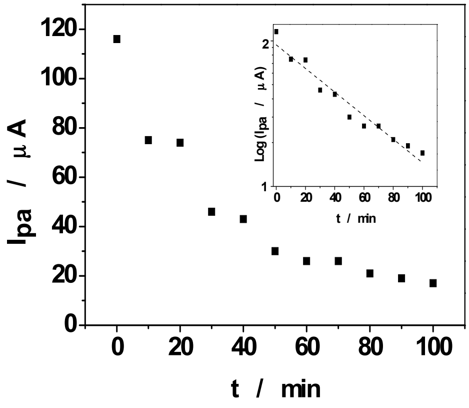


Figure 6. Time evolution of Cu_2IC complex formation. Inset illustrates the first-order kinetic linearization of the free IC concentration decrease. Experimental conditions: IC 10^{-3} mol.L^{-1}; 10^{-3} mol.L^{-1} Cu(II); other conditions as in figure 5.

were performed after a delay of 30 minutes, which was 50% higher than the value recommended by Zanoni *et al* [6] for Cu(II) detection from spectrophotometric measurements.

Under the optimal experimental conditions, the decrease of the oxidation peak current for A2/C2 redox couple due to Cu(II) addition into the alkaline (pH 10) IC solution and as a function of the copper ions concentration is depicted in Figure 7. The linear domain, from 10 up to 70 µM Cu(II), corresponds to the following regression equation: ΔI_{pa} = (1.63 ± 0.99)+ (0, 55 ± 0.03)*[Cu(II)]; R^2 = 0.9853, N = 7. The detection limit (DL) was estimated at 4.7 µM for a signal-to-noise ratio of 3.

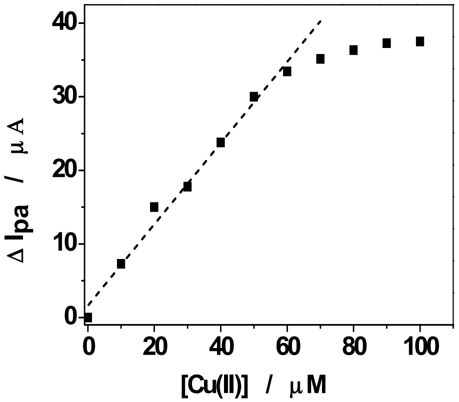


Figure 7. Calibration plot for Cu(II) DPV detection. Experimental conditions: 100 µM IC; electrolyte, 0.1M carbonate buffer (pH 10); reaction time, 30 min.

Conclusions

DPV measurements performed at graphite electrode were successfully used for copper determination, exploiting the Cu(II) reaction with IC in alkaline medium (pH 10). Due to the electro-inactivity of Cu(II) - IC complex, the decrease of the IC oxidation current, measured at an applied potential of ~150 mV *vs.* Ag/AgCl,KCl_{sat}, was used to draw a calibration curve allowing the determination of Cu(II) concentrations.

EXPERIMENTAL SECTION

Reagents

Indigo carmine (3,3 dioxo-2, 2 bis–indolyden-5,5-disulfonic acid disodium salt) was purchased from Sigma Aldrich (St. Louis, MO, USA). A 1 mM Cu (II) stock solution was prepared from $CuSO_4 \cdot 5H_2O$ (Microchim - Romania). All used chemicals were of analytical grade. Aqueous solutions were prepared with distilled water. All experiments were carried out at room temperature.

Electrochemical measurements

Cyclic and differential pulse voltammetric measurements were performed using a computer-controlled potentiostat (Autolab PGSTAT 10, Ecochemie, Utrecht, The Netherlands) and GPES 4.8 software. A conventional three electrodes cell (30 mL) consisting of a graphite electrode as working electrode, a Ag/AgCl,KCl_{sat} as reference electrode and a Pt wire as counter electrode, was used. Before using, the graphite electrode was cleaned by wet polishing with emery paper and filter paper, followed by 2 minutes ultrasonication, in an ultrasonic bath (Elma S10, Elmasonic, Germany). The solutions pH was measured using a digital pH meter (Hanna Instruments, USA). Each individual experiment was performed at least three times and the results were averaged.

ACKNOWLEDGMENTS

M.C. thanks to Agence Universitaire de la Francophonie and Romanian Government for Eugen Ionescu fellowship.

REFERENCES

[1]. G. Barceloux, *Clinical Toxicology*, **1999**, *37*, 217.

[2]. WHO Technical Report Series. *Evaluation of certain food additives and contaminants*, WHO, Geneva, **1982**, 683.

[3]. P.J.S. Barbeira, L.H. Mazo, N.R. Stradiotto, *Analyst*, **1995**, *120*, 1647.

[4]. E.H. Rodd, *Chemistry of carbon compounds*, 4th edition, Elsevier, Amsterdam, IVB, **1960**, 1093.

[5]. J.J. Berzas, J.R. Flores, M.J.V. Llerena, N.R. Farinas, *Anal. Chim. Acta,* **1999**, *391*, 353.

[6]. T.B. Zanoni, A.A. Cardoso, M.V.B. Zanoni, A.A.P. Ferreira, *Brazilian Journal of Pharmaceutical Sciences*, **2010**, *46*, 723.

[7]. M.D. González, C.F. Sánchez, A.C. García, *Electroanalysis,* **2002**, *14*, 665.

[8]. J.B. He, G. Ma, J.C. Chen, Y. Yao, Y. Wang, *Electrochimica Acta*, **2010**, *55*, 4845.

[9]. C.F. Sanchez, A.C. Garcia, *Electrochemistry Communications*, **2000**, *2*, 776.

[10]. P.F. Bolado, D.H. Santos, P.J.L. Ardisana, A.M. Pernia, A.C. Garcia, *Electrochimica Acta*, **2008**, *53*, 3635.