



Study of the electrochemical interaction between Ni (II) and the 1.2-benzodithiole-3-thione on a glassy carbon electrode

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ABSTRACT

In this research, we examined the effect of nickel ions on the electrochemical behaviour of a compound dithiolic. We have noticed that the addition of an increasing quantity of Nickel ions involves the modification of the intensity of the cathodic current of this compound without modifying its potential of reduction. In addition, there is a displacement of the potential of oxidation, which involves an electrochemical signature, which proves the complexation.

Key words: 1.2-benzodithiole-3-thione, Complexation, Ions of nickel, Cyclic voltametry.

INTRODUCTION

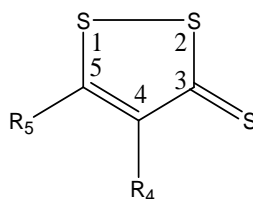
Metals of trace are very important in several biological systems[1]. The interaction of the bivalent ions with the nucleic acids plays a part in the promotion of its functionalities [2,3].

The complexation of the organic compounds with selective metal ions has a large variety of application in medicinal chemistry, chemistry of surface, and analytical chemistry. The formation of a compound is suggested like one of the important mechanisms for certain actions of the drugs [4]. The complexation of a metal is used to reduce the effect of the intoxication.

Among metals which are known as toxic As, Cd, Cr, Cu, Pb, Ni, Ag, Mn and Zn, a sufficient quantity of these compounds in the environment causes risks for the human health [5,7]. Nickel is classified like an intermediate acid according to theory HSAB [8,9]. It is used by the man for various applications, it is essential for health, but when the quantity is important, it becomes very toxic for the majority of the plants, moderately for the mammals and cancerogenic [10]. In the acid earths, it becomes more mobile and can join subterranean water.

The treatment of the intoxication for certain metals of trace appeals to various chelating sulphur, for example it the (BAL) and the (DMPS) for cadmium [11,12]. For lead, the derivatives thiohydroxante [13].

The dithiolethiones which have as a general formula 1 is a series of compounds, which have several therapeutic properties [14], industrialists [15], corrosion inhibitors [16] and antioxidant [17].



1- General formula of 1,2-dithiole-3-thiones

In this work we studied the Nickel electrodeposition to determine its potential of reduction. Then we studied the behavior of the compound dithiolic selected on a vitreous carbon electrode in medium DMF. We then studied the complexation of this compound with Nickel in a mixed medium (DMF/H₂O) by an electrochemical method.

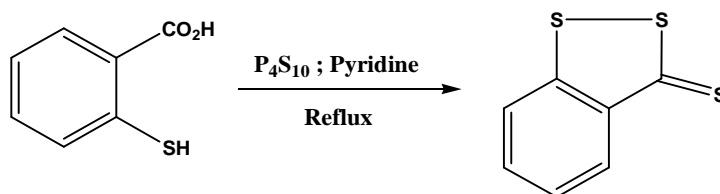
The technique used is the cyclic voltametry. The advantage of using a vitreous carbon electrode is its inertia, and in the electrodeposition, it is possible to study nucleation.

To study the complexation, we examined the effect of Nickel ions on the Redox behaviour of our compound and we obtained an electrochemical signature, which proves the complexation, therefore, we proposed a structure with the compound formed.

EXPERIMENTAL SECTION

2.1. Method and technique:

2.1.1. Synthesis of the 1,2-benzodithiole-3-thione



This dithiolethione was prepared by sulphurization of the -2-mercaptobenzoïque acid using P₄S₁₀, according to the procedure describes by Klingsberg and Schreiber [18].

A solution of acid-2-mercaptobenzoïque (0.13 mol) and P₄S₁₀ (0.05 mol) in pyridine are heated with the reflux during 3 hours. After cooling, the solution is diluted with filtered water then the precipitate is washed with alcohol, and then recrystallized in methanol.

Characterization

1,2-benzodithiole-3-thione

F = 94 °C (Lit. F = 92 °C) [18]

RMN ¹H (89,55 MHz, CDCl₃, δppm/TMS) : 8,15 – 8,27 (m, 4H).

RMN ¹³C (22,50 MHz, CDCl₃, δppm/TMS) : 216,54 C(3) ; 152,72 C(5) ; 140,65 C(4) ; 132,60 C(6) ; 125,90 C(9) ; 124,23 C(8) ; 128,34 C(7).

Materials used

potentiostat-galvanostat PGZ301 models voltalab 40 controlled by a software of work voltamaster4 of the analytical Radiometer, an electrochemical cell made up of a beaker of 50cm³ which contains the electrodes :

1-Electrode of work where the reaction redox is carries out is a microelectrode of glassy carbon of diameter of 3 mm, attached to a stem, washed before each recording with acetone and cleaned by an abrasive paper.

2-Auxiliary electrode is a platinum electrode.

3-Electrode of reference SCE.

The DMF is used for three primary reasons:

- Its high permittivity makes it possible the DMF to dissolve several salts supports.

- It is miscible with water in all proportions and allows us to dissolve interested metal salts.

- Its good electrochemical response with the dithioles and its derivatives.

The electrolyte support nBu₄NBF₄ 0,1M

The nitrogen splashing ensures deoxygenation.

RESULTS AND DISCUSSION

3.1. Electrodeposition of Nickel:

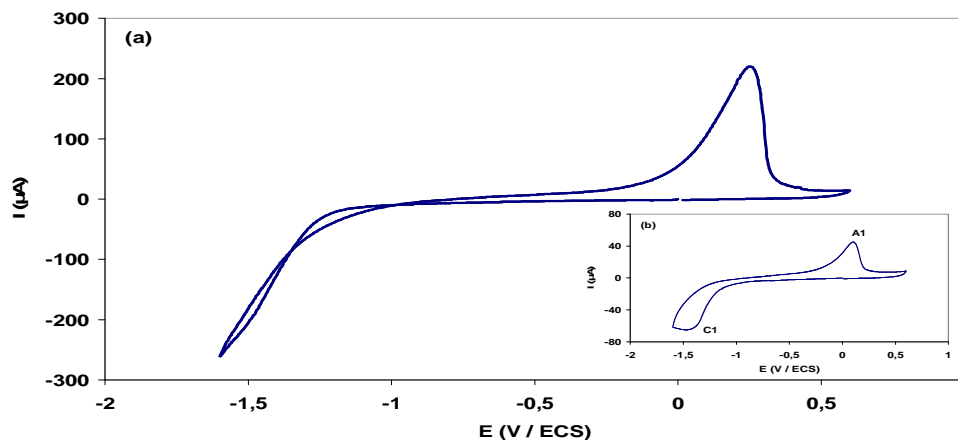


Figure 1. Voltammograms relating to the behavior of nickel in medium DMF/H₂O; 3/1 [Ni(NO₃)₂ 5mM + nBu₄NBF₄ 10⁻¹M] on an electrode of CV ($\Phi = 3$ mm) à 0,1 V.s⁻¹ et 20°C, (a)- revolving electrode ($\omega = 2700$ rpm), (b)- stationary electrode

For not modifying the electrode one uses the electrodeposition of the Nickel, which is used to determine the potential of reduction of this, last thus to avoid its deposit in the following test, when one studies the addition of his ions to our compound.

The CV is used to define the area of the potential of deposition and dissolution of Nickel on ECV. The presence of a crossing between the anodic and cathodic branch is called the phenomenon of nucleation [19].

Figure 1 shows a typical cyclic voltammograms, at the scan rate of 100 mV/s, corresponding to nickel deposition onto GCE from a solution containing 5 mM Ni(NO₃)₂. It is possible to note, at direct scan, a peak at -1.6 V. During the inverse potential scan, it is possible to note two crossovers, E_c and E_{cp}.

The crossover E_c (-1.25 V) is typical of the formation of a new phase involving a nucleation process and it is associated with an electrocatalytic point [19]. The second crossover potential E_{cp} was recorder at -1.1 V and may be related to the conditional equilibrium potential of couple Ni²⁺/Ni⁰. In the anodic zone, it was possible to observe a principal peak at around 0.25 V. The existence of this peak suggests the presence of nickel electrodeposited during the direct scan.

3.2. Study of the electrochemical behaviour of 1.2-benzodithiole-3-thione only:

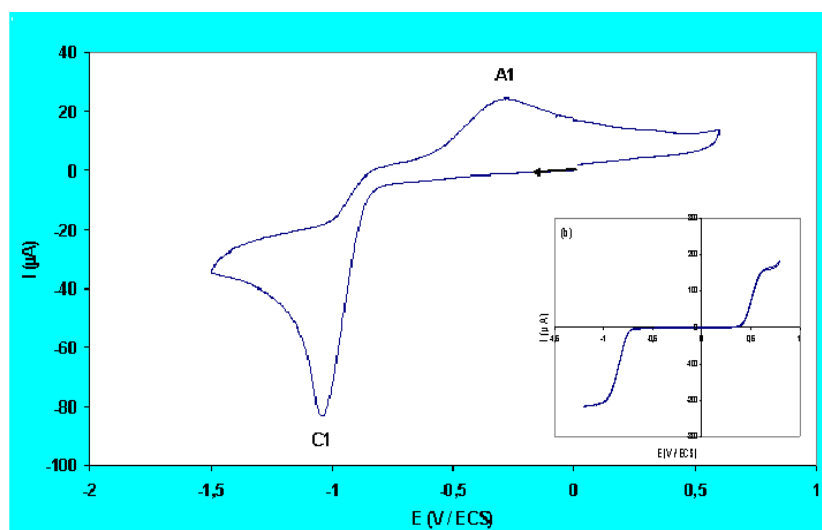
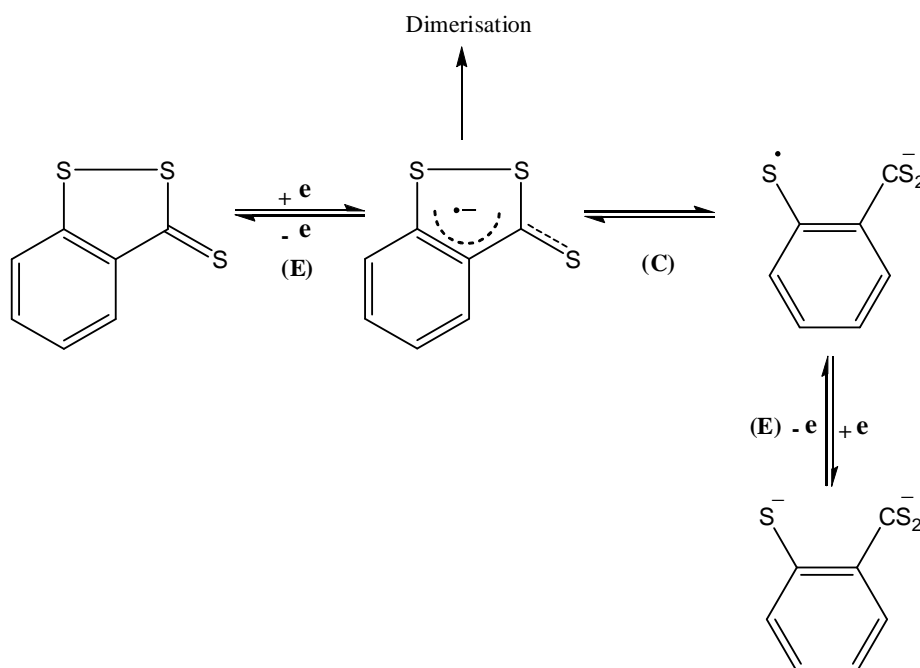


Figure 2. Voltammograms of the compound **1A** (concentration 5mM, medium DMF, nB₄N⁺ BF₄⁻ 0.1 M ; 20 °C ; Electrode CV ; scanning rate 0.1 V.s⁻¹) (a)- stationary electrode, (b)- revolving electrode in the presence of ferrocene ($\omega = 2700$ rpm)

The typical voltammogram shows two peaks and a reversible system, the number of concerned electrons is approximately two; this reduction is carried out in only one bielectronic stage.

Indeed, since what was formulated in the mechanism of the reduction of the dithiolethione [20] the transfer of two electrons to the same potential implies a mechanism (ECE) during which a chemical stage (C) makes possible the transfer of the second electron (E). The chemical stage is necessary to the transfer of the second electron. This stage is reversible so that the oxidation of the species takes back with the initial compounds dithiolic (diagram).



3.3. Study of the electrochemical behaviour of the 1,2-benzodithiole-3-thione in the presence of Nickel ions

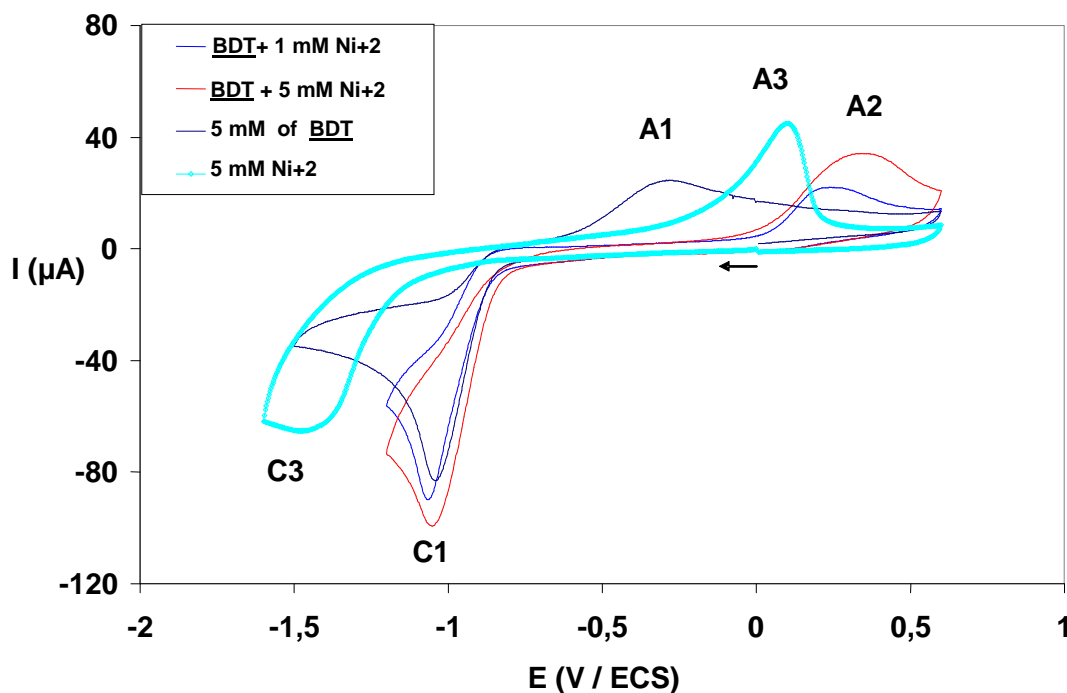


Figure3. Voltammograms of the composes only and in the presence of the Nickel ions

We took the field of the potential between -1.1 V with 0,6 V to avoid the reduction of Nickel and to keep the ions of Nickel.

When one adds a quantity of nickel ions, one observes a modification of the voltammogram, and an increase in the I_{pc} (peak C1), from the following current relation we can deduce the number of electrons involved, and a displacement of E_{pa} (peak A1) as an indication of the formation of a new compound.

$$I_{pc} = -0.269 \cdot 10^5 \cdot n^{3/2} \cdot S \cdot C_{ox} \cdot D_{ox}^{1/2} \cdot v^{1/2}$$

I_{pc} : cathodic intensity of peak is expressed in A to 25°C

n : number of electrons

S : surface electrode in cm^2

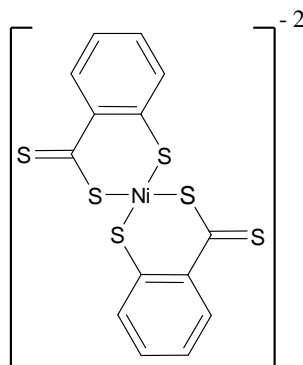
C_{ox} : concentration of electroactive substance in the solution in $mol \cdot cm^{-3}$

D_{ox} : coefficient of diffusion of oxidant is expressed in $cm^2 \cdot s^{-1}$

v : scanning rate of potential (in $V \cdot s^{-1}$)

One notices according to this equation that there is a variation of many electrons and that this number tends towards two.

This addition supports the opening of the cycle and not the dimerisation. We proposed a structure with the compound formed.



CONCLUSION

Electrochemically

complexation is a promising and selective method. It is applicable to easily reducible organic compounds compared to metals ions.

Electrochemical behaviour of the 1,2-benzodithiole was studied in presence and absence of Nickel ions. The presence of Nickel ions involves a change of the pace of the voltammogram, the increase in peak I_{pc} due to an increase in the number of electrons, a displacement of the peak of oxidation towards oxidations that are most difficult, hence the formation of a complex and the disappearance of the reversibility of the studied compound.

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