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Study of the electrochemical oxidation of 2-Thiazolamine and 2-Oxazolamine on a platinum wire as working electrode.

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Abstract. The electrochemical oxidation of 2-aminothiazole (2AT) and 2-aminoxazole (2AO) was studied by means of the cyclic voltammetry technique (VC), on a Pt wire as working electrode. An anodic wide peak centred at 0.79V was observed and 0.98V (Ia wave) caused by the oxidation of the 2AT and 2AO compounds and the formation of cationic radicals on the clean surface of the electrode, respectively. During the studies of (VC) in a small range of exploration speeds, the oxidation signal increased with the increase in speed and moved to more positive potential values. This dependence of the potential with respect to the potential sweep speed indicated a controlled diffusion of the system of an irreversible nature. At T=298K, from the electrochemical oxidation of 2 AT, a thin coating film with a light brown color was obtained on the surface of the Pt wire. However, in the electrooxidation of 2 AO, that result was not evident. While the 2AT electrooxidation product loses conductivity, in the case of the 2AO compound, the electrogenerated product on the surface of the platinum wire maintains the conductive properties.

1. Introduction

Oxazoles and thiazoles are useful organic compounds in the pharmaceutical industry and agricultural chemistry. For example, the aminothiazole heterocycle system is a useful structural element in medical chemistry and has found wide applications in the development of drugs such as antiallergenic [1], antihypertensive [2], anti-inflammatory [3], antibacterial [4] and anti-HIV agents [5]. Different thiazole compounds are used as agrochemicals [6-9]. Among them, Ritonavir is a known anti-HIV drug and Imidacloprid is an important insecticide. Substituted oxazole derivatives are found to be associated with several biological activities such as antibacterial [10], antifungal [11], antituberculous and anti-inflammatory activities [12], and recently antiprotozoal activity in vitro against pathogenic protozoa *Giardia lamblia* and *Trichomonas vaginalis* [13].

The first observation, from the undertaken analysis of literature data is that while ring heterocyclic is the basis for thiazole classification, its influence on their redox behavior is reduced. The electroactivity of 2-aminothiazole and its derivatives regards on primary amine group dictates the electrochemical profile. The electrochemical profile of 2-aminothiazole akin to their redox behavior is mainly driven by the stability of electro generated amino cation radicals, which as a consequence determines the overall electrode reactions.

2-Aminothiazole and its derivatives are reported to have anticorrosive properties [14]. The inhibitory property has been attributed to their molecular structure. The planarity and the pairs of free



electrons in the heteroatoms are important characteristics to determine the adsorption of these molecules on the surface of the metal, the strength of the adsorbed layer is related to the functional groups linked to the aromatic ring [15]. The manipulation of these compounds has been able to provide useful information for the study and design of drugs although this does not lead to obtaining an analogously more effective than the reference compound; likewise, as the analysis of the results obtained can lead to the establishment of structure-activity relationships that can serve as a basis for the synthesis of new active compounds that offer new treatment alternatives to emerging diseases. It is a subject matter of research in order to be used as a useful moiety in the design of potent molecular architectures which containing low or more bioactive pharmacophore [16-19].

Due to the conjugated structure and high sulfur and nitrogen atom molar ratio (30%) in 2AT molecules, electrochemical oxidation of 2AT has been previously addressed to synthesize a conducting polymer and promising adsorbent for heavy metal ions. Dubrovskii y Aksiment'eva studied electrooxidative polymerization of 2-aminothiazole in aqueous and organic media using the cyclic voltammetry method [20]. In this study the results allowed them to assume that the formation of a π -conjugated system involves the amino group and the positions in the thiazole ring activated for the electrophilic substitution. In 2011 the electrochemical polymerization of 2-aminothiazole (AT) was studied in acetonitrile with tetrabutylammonium tetrafluoroborate (TBAFB) as the supporting electrolyte via constant potential electrolysis (CPE) [21]. Structural analyses indicated that AT polymerizes via oxidation of -NH₂ group and formation of -N(H)- linkages between the AT rings. It was also shown that acetonitrile may participate in the polymerization reactions and enter into the structure of the polymer. Solmaz and Kardas, studied the electrochemical oxidation of 2-aminothiazole on a platinum sheet [22]. A high quality and electrochemically stable pAT film with light-brownish color was obtained. It was concluded that the polymer formation proceeds by the autocatalytic mechanism for the reaction of electrochemical coupling of 2AT molecules over carbon and nitrogen atoms including the steps of monomer oxidation over amino group with cation-radical formation and coupling of cation radicals accompanied by deprotonation. Two years later 2-AT was electrochemically polymerized on a mild steel (MS) specimen from 0.3 M aqueous ammonium oxalate solution containing 0.01 M 2-aminothiazole (2-AT) using cyclic voltammetry technique [23]. It was found that the obtained coatings were adherent to the steel surface. The corrosion protection performance of the polymer film was enhanced by the deposition of Ni and Zn on top of the polymer surface and as a result exhibiting an improved barrier effect against the attack of a corrosive environment [23].

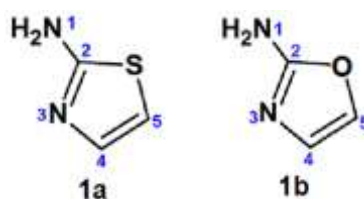


Figure 1. 1a. Structure of the derivatives 2-aminothiazole (2AT) and **1b.** 2-aminoxazole (2AO)

On the other hand, oxazoles are a class of heterocyclic compounds, composed of a five-membered ring with an oxygen atom and a nitrogen atom, which are particularly important in pharmaceutical chemistry. The interest in 2-aminoxazoles is associated with the high biological activity and broad spectrum of the action of some of their derivatives. Due to its wide range of biological activities, the study of its redox behavior is important because of its relationship with antioxidant properties. However, probably due to the similarity with the primary aromatic amines, the electrochemical oxidation of 2-aminoxazole has not been reported. Considering the above, in this work, we report a preliminary study of the electrochemical oxidation in aqueous medium of 2-aminothiazole and 2-aminoxazole on platinum wire electrode by cyclic voltammetry.

2. Experimental

The 2-aminothiazole and 2-aminoxazole (Aldrich Chemical Co., 90%) were analytical reagent grade and used as received.

The solutions were prepared with bi-distilled water. The electrochemical measurements were carried out using an AUTOLAB 128N electrochemical analyser under a computer control. A double-wall one compartment cell with a three-electrode configuration was used. A platinum wire (active surface $d = 0.3$ mm, $l = 0.7$ cm), platinum gauze and Ag/AgCl electrodes were used as the working, auxiliary and the reference electrodes, respectively and all potentials given in this paper were referred to this reference electrode. Prior to an experiment, the working electrode surface was cleaned by short-term polarization in concentrated sulfuric acid. The cyclic voltammetry measurements were made in anodic sweep, from -0.2 to 1.7 V. In addition, experiments were carried out at different sweep speeds ($0.03 < v < 0.15$ Vs^{-1}). A study of 25 potential sweeping cycles was carried out at $v = 0.05$ Vs^{-1} .

3. Results and discussions

3.1. Electrochemical behavior of 2-aminothiazole 1a and 2-aminoxazole 1b derivatives

The cyclic voltammograms obtained in 0.01M 2-aminothiazole 1a and 2-aminoxazole 1b, containing 0.3M ammonium oxalate solution is presented.

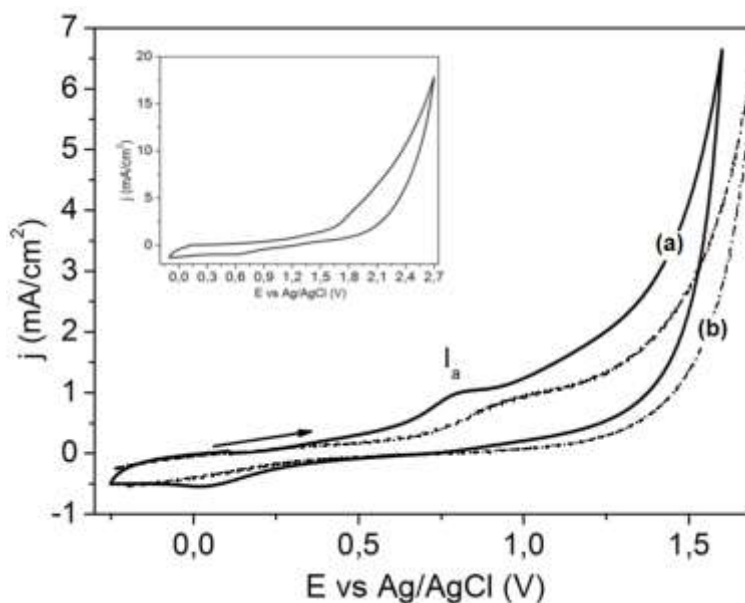


Figure 2. The cyclic voltammograms recorded on the platinum (Pt) wire electrode for (a) 0.01M 2-aminothiazole + 0.3M ammonium oxalate and (b) 0.01M 2-aminoxazole + 0.3M ammonium oxalate. Insert: cyclic voltammogram recorded for Pt wire electrode in 0.3M ammonium oxalate, scan rate: 100 mVs^{-1} .

In Fig. 2 Insert shows the cyclic voltammogram recorded for the Pt wire electrode in 0.3M ammonium oxalate solution in the absence of compounds (1a and 1b).

At the forward scan, the current is constant around zero between 0.00 and 1.60 V potential ranges. After 1.60 V, the anodic current is gradually increased up to 1.75 V. At the reverse scan, similar behavior was observed for the Pt electrode.

As seen from Fig. 2 in the first scan, during the forward scan a broad anodic peak centered at 0.79 V and 0.98 V caused by the oxidation of compounds (1a and 1b) and formation of 2-aminothiazole

and 2-aminooxazole cation radical onto the clean electrode surface respectively. In general, the chemical properties of 2-aminothiazole **1a** and 2-aminooxazole **1b** are determined by the character of the thiazole and oxazole ring and the amino group respectively. The presence of an amino group leads to the development of new properties that are associated with the manifestation of basicity and, in addition to this, changes the properties of the thiazole and oxazole ring.

The carbon atom in the 2 position has a relatively high partial positive charge, and this leads to a decrease in the basicity of the amino group bonded to this atom. With that in mind, compound **1a** is easier to oxidize than compound **1b**. This is due to the greater basicity that the amino group has in **1a** than in **1b**. The strong electronegativity character of the oxygen atom in **1b** in relation to the sulfur atom in **1a** was observed in the energy level that was required to oxidize each compound.

A study of the electrochemical oxidation of both compounds at different potential scanning speeds showed irreversible nature of **1a** wave. The cyclic voltammograms of (a) 0.01M 2-aminothiazole (b) 0.01M 2-aminooxazole in 0.3M ammonium oxalate solution at different scan rates were recorded and obtained data are shown in Fig. 3.

In a small range of scanning speeds, the oxidation signal **1a** increases with increasing speed and moves to more positive potential values. The influence of the square root of the scan rate on the peak current showed a linear relationship with a non-zero intercept, this may be due to the electron transfer process complicated by the associated adsorption between 0.025 and 0.1 Vs⁻¹ [24].

The peak current values are higher for compound **1a** than **1b**. This behavior is very interesting since, as we know, the current is dependent on the number of electrons, concentration and diffusion coefficient of the compound, since the other parameters are constant. Therefore, a possible explanation for this result is that the diffusional parameter for compound **1a** was higher. This can be inferred from the Randles-Sevcik equation [25]; from this equation, the diffusion coefficient value is obtained for **1a** and **1b** derivatives, Table 1.

$$I_p = 2,68 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (1)$$

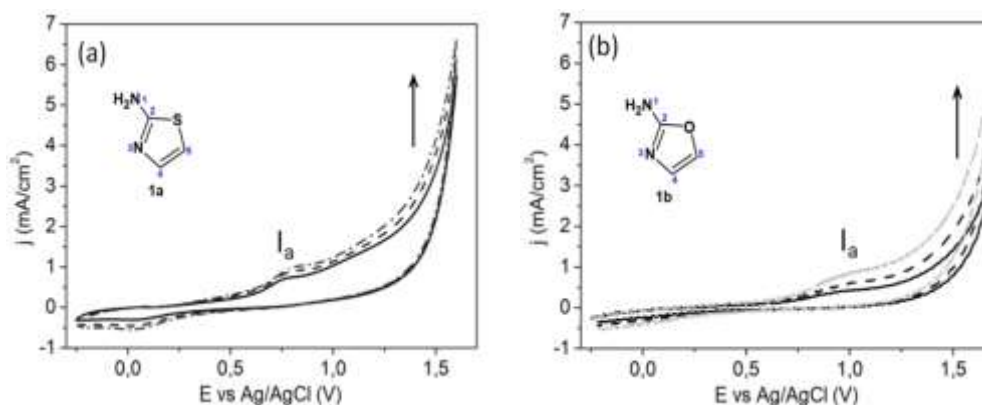


Figure 3. The cyclic voltammograms recorded on the platinum (Pt) wire electrode for (a) 0.01M 2-aminothiazole (b) 0.01M 2-aminooxazole in 0.3M ammonium oxalate, at different scan rates: 50, 80 and 100 mVs⁻¹

Table 1 Voltammetric Data Obtained from the electrochemical oxidation of the Studied **1a**, 2-aminothiazole (2AT) and **1b**, 2-aminooxazole (2AO).

Compounds	E_{p1a}/V^a	$I_{p1a}/\mu A$	$D \times 10^{-6}$	αn_α	k^0/s^{-1}	$\left(\frac{\Delta I_p}{\Delta \sqrt{v}}\right)$	$\left(\frac{\Delta \log(I_p)}{\Delta \log(v)}\right)$	$\left(\frac{\Delta E_p}{\Delta \log(v)}\right)$	pK_a^*
1a	0.79	32,8	4.21	0,52	12.1	32,2	0,67	0,011	16
1b	0.98	30,1	3.26	0,50	4.9	21,3	0,54	0,010	14

*Stauss, U. et al 1973 [26], ^a v = 0.1 Vs⁻¹

The adsorptive character of 2-aminothiazole **1a** and 2-aminoxazole **1b** on the Pt wire electrode was identified from the peak current's (i_p) dependence on the scan rate (v). Plots of $\log i_p$ vs. $\log v$ is a straight line and its slope is 0.67 and 0.54 for (wave Ia) respectively, which is less than the theoretical value of 1.0 that is expected for an ideal reaction of surface species.

The lower experimental slope than the theoretical one may be attributed to the partial involvement of **1a** and **1b** molecules in the electrode reaction of the adsorbed ones. The overall electrode process may thus be suggested as mainly diffusion-controlled with adsorption of **1a** and **1b** molecules at the electrode surface.

An analysis of the dependence of the peak potential of the Ia wave with respect to the variation of the potential sweep speed a linear relationship was observed in the range 0.025 to 0.3 Vs^{-1} , where the potential was given by:

$$E_p = E^o - \left(\frac{RT}{\alpha n_\alpha F} \right) \left[0.78 - \ln \frac{k^o}{D^{\frac{1}{2}}} + \ln \left(\frac{\alpha n_\alpha F v}{RT} \right)^{\frac{1}{2}} \right] \quad (2)$$

Where α is the cathodic charge transfer coefficient, n_α is the number of electrons involved in the speed determining step, D is the diffusion coefficient and k^o is the standard rate constant of the electrochemical reaction. In Table 1, the data obtained from E_{pIa} vs. $\log v$ for derivatives **1a** and **1b**, which was linear where the potential change was observed towards more positive values with increasing scanning speeds of potential, indicated a controlled diffusion of the system of irreversible nature [27]. The α_n value was calculated from the slope of the graph between E_{pIc} and $\log v$. In most irreversible cases, α is in the range of 0.30 to 0.70, so it is likely that the number of electrons transferred in the Ic wave is 1. The D values for **1a** and **1b** could be determined from the slope of pIc vs $v^{1/2}$ plot, after careful substitution and unit analysis. The values of diffusion coefficients (D) are found to be $4.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $3.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for 1st and 2nd peak respectively. The value of k^o can be determined from the intercept of the previous plot if the value of E^o is known. The value of E^o can be obtained from the intercept of E_p vs. v curve by extrapolating to the vertical axis at $v = 0$. In our system the intercept for E_p vs. $\log v$ plot was 0.575 V and 0.748 V for **1a** and **1b** respectively. The E^o was obtained to be 0.657 V and 0.911 V for 1a and 1b compounds. The k^o was calculated to be 12.1 s^{-1} and 4.9 s^{-1} respectively.

In order to investigate the electrochemical behavior of compounds **1a** and **1b**, a cyclic voltammetry study of potential scan segments was developed. The cyclic voltammogram of compounds **1a** was recorded in 0.3M ammonium oxalate solution and the obtained voltammogram is given in Fig. 4. As seen from Fig. 4, the anodic current value started to increase from 0.60 V and an anodic peak around 0.85 V was observed. This peak can be assigned to the oxidation of compound **1a**.

When the potential sweep was related in the cathodic sense, a reduction wave was observed around 0.00V. It is clear from Fig. 4 that in the second cycle, monomer oxidation is accompanied by the formation of a film on the electrode surface. As the sweep segments increased, a decrease in oxidation process was observed indicating the formation of products with low conductivity. When the cycle numbers increased, a yellow-green colored film was formed on the Pt wire surface whose color was changed to light brown after further segments. The peak current increased with the increasing cycle numbers and becomes stable after 15 cycles. It can be seen from Fig. 4, the subsequent cycling (cycle 25) of the Pt wire electrode does not alter the voltammogram profile. The modified Pt wire electrode surface can be cycled between the oxidized and neutral states without significant without decreasing modified surface activity, indicating high stability of the deposited products on Pt wire electrode surface.

The Fig 5 showed the electrochemical behavior of compounds **1b**. The cyclic voltammogram of compounds **1a** was recorded in 0.3M ammonium oxalate solution and the obtained voltammogram is given in Fig. 5.

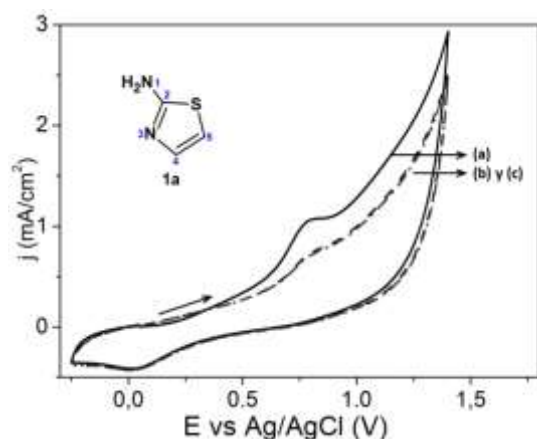


Figure 4. The voltammograms (a) 1 cycle, (b) 15 cycles and (c) 25 cycles recorded on the platinum (Pt) wire electrode for 0.01M 2-aminothiazole in 0.3M ammonium oxalate solution, scan rate: 50 mVs⁻¹.

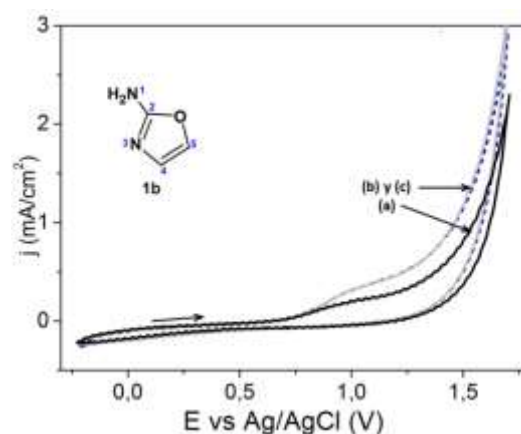


Figure 5. The voltammograms (a) 1 cycle, (b) 15 cycles and (c) 25 cycles recorded on the platinum (Pt) wire electrode for 0.01M 2-aminooxazole in 0.3M ammonium oxalate solution, scan rate: 50 mVs⁻¹.

As seen from Fig. 5, an anodic peak around 0.95 V was observed. This peak can be assigned to the oxidation of compound **1b**. When the potential sweep was related in the cathodic sense, no reduction wave was observed. From Fig. 5, as the scan segments increased, an increase in the oxidation process was observed indicating the formation of products with good conductivity. When the number of cycles increased, the formation of a colored film on the surface of the Pt wire was not evident. The peak current increased with the increasing cycle numbers and becomes stable after 15 cycles. It can be seen from Fig. 5, the subsequent cycling (cycle 25) of the Pt wire electrode does not alter the voltammogram profile.

4. Conclusions

The electroactivity of 2-aminothiazole and 2-aminooxazole derivatives resides on the primary amine group in C-2 position in thiazolic and oxazole ring respectively and the electron donor ability is mainly governed by 2-aminothiazole and 2-aminooxazole chemistry. While the electrogenerated product during the electrochemical oxidation of 2-aminothiazole loses conductive properties, the product obtained from the electrooxidation of 2-aminooxazole is electroactively increased the anodic current in each cycle of potential sweep until its value is stabilized. The redox behavior varies according to the heteroatom type and to changes in the basic or acid properties of the amino group. From literature, the dissociation constants (K_a) of 2-aminooxazole **1b** ($K_a \sim 10^{-14}$) and 2-aminothiazole **1a** ($K_a \sim 10^{-16}$) showed that the latter is stronger base. Consequently, the potential required for oxidation is reduced as the stability of cation radicals is improved. Knowing that the electrochemical oxidation of 2-aminothiazole takes place through the formation cation radical, for the case of 2-aminooxazole, the probable mechanism of near-electrode reactions can be described from one-electron oxidation of 2-aminooxazole with the formation of a radical cation capable of taking part in the oxidative coupling of the head-to-tail type as in the case of primary arylamines, to afford the target polyaminooxazole. As an alternative reaction route, one can suggest the deprotonation of radical cations with participation of the monomer as the proton acceptor to form radicals. We have assumed that in the first electron transfer the derivatives 2-aminooxazole is converted into their respective radical cations, further investigations being necessary in order to fully understand the studied anodic process of electron transfer.

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