



Studying the Electrochemical Behavior of 2-amino-4-methylphenol in the Presence of Penicillin Amine Using Cyclic Voltammetry Technique

Davood Kaviani¹*, Majid Saghi², Maryam Agha Mohammadi², Mohammad Hosein Bigtan²

¹ Young Researchers and Elite Club, East Tehran Branch, Islamic Azad University, Tehran, Iran

² Department of chemistry, Faculty of science, Arak branch, Islamic Azad University, Arak, Iran

Abstract

The studies performed about electrochemical oxidation 2-amino-4-methylphenol indicate that ortho-quinone yielded through oxidation of this chemical compound was unstable and it could be used as Michael acceptor under solvent influences, carrier electrolyte, additives and could be transformed into the various compounds in the form of 1-4 addition Michael reaction. Based on this, in the paper firstly electrochemical oxidation of 2-amino-4-methylphenol in the water has been studied. Then the electrochemical behavior of the compound has been assessed in the presence of nucleophile Penicillin amine under different conditions. The studies indicate that the above compounds could be transformed to new derivatives in the presence of Penicillin amine and phosphate buffer with concentration of 0.2 M and pH=7 during the EC mechanism. Using electrochemical data obtained by performing studies, electrolysis of 2-amino-4-methylphenol has been made in the presence of Penicillin amine, which is served as nucleophile and the product has been yielded with suitable practical efficiency. In all cases in order to optimize the electrolysis conditions and to determine the mechanism, cyclic voltammetry (CV) and Controlled Potential Coulometer (CPC) were utilized.

Keywords: 2-amino-4-methylphenol, Electrochemical, Penicillin amine, Voltammetry technique

1. Introduction

2-amino-4-methylphenol which chemical structure has been shown in the Fig. 1, is one of vital organic compounds in series of aromatic compounds. As it has been shown in the Fig. 1, in the structure of the compound two important functional groups including hydroxyl functional group and being amine functional group have positioned

on the benzene ring. Type of chemical structure and adjacent of these two functional groups have given the unique characteristics of the compound so that it takes part in the electrochemical reactions [1]. Amino phenols such as 2-amino-4-methylphenol or Poly (2-amino-4-methylphenol) are interesting electrochemical materials since, unlike aniline and other substituted anilines, they have two groups ($-NH_2$ and $-OH$), which could be oxidized [2].

*Corresponding Author

E-mail address: davood.kaviani@gmail.com

In the paper, the electrochemical behavior of 2-amino-4-methylphenol has been studied in the presence of Penicillin amine, which its chemical structure has been illustrated in the Fig. 2. Penicillin amine is a pharmaceutical of the chelator class [3]. It has been sold under the trade names of Cuprimine and Depen. The pharmaceutical form is D-penicillamine, as L-penicillamine is toxic (it inhibits the action of pyridoxine) [4]. It is an α -amino acid metabolite of penicillin, although it has no antibiotic properties [5]. In the paper, the electrochemical behavior of 2-amino-4-methylphenol has been studied in the presence of Penicillin amine using cyclic voltammetry (CV) procedure. Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as desired.

The current at the working electrode is plotted versus the applied voltage (i.e., the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution [6-8]. Orthoquinone yielded of electrochemical oxidation of 2-amino-4-methylphenol was unstable and could be used as Michael acceptor under solvent influences, carrier electrolyte, additives and could be transformed into the various compounds in the form of 1-4 addition Michael reaction. In the paper firstly electrochemical oxidation of 2-amino-4-methylphenol in the water has been studied and then the electrochemical

behavior of this material has been investigated under different conditions in the presence of Penicillin amine nucleophile.

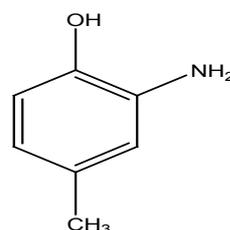


Fig. 1. Molecular structure of 2-Amino-4-methylphenol.

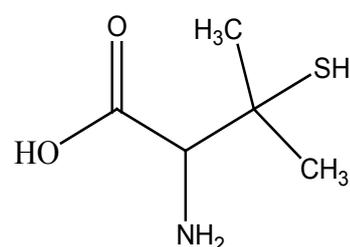


Fig. 2. Molecular structure of Penicillin amine.

2. Materials, apparatuses and methods

The chemical compound used as nucleophile, Penicillin amine and substrates was 2-amino-4-methylphenol which has been utilized with no purification. In order to make different buffers from chemical materials such as phosphoric acid 1 M, acetic acid 1 M and NaOH 20% all of which were purchased from Merck Company, have been used. Also, Alumina (made by Merck Ltd.) was used in order to polish GC electrode. Potentiostat/galvanostat device (SAMA 500, Electroanalyzer system, I. R. Iran) was utilized in order to perform cyclic voltammetric measurements, to record and graph cyclic voltammograms.

Also this Potentiostat/galvanostat device was used for potential-controlled electrolysis. A triple electrode system was used to reduce ohmic losses in all performed voltammetric measurements and glassy carbon (G.C)

electrode with 2mm diameter was used to graph the cyclic voltammogram which was as working electrode (W.E). Platinum-wire electrode was utilized as counter electrode (C.E) and the Saturated Calomel Electrode (SCE) was used as reference electrode in all studies. All above electrodes were made by Azar Electrode ltd (Iran).

3. Results and discussion

The results of studying the electrochemical behavior of 2-amino-4-methylphenol in the absence of Penicillin amine indicate that voltammograms have one anode peak and one cathode peak related to current ratio (I_{pc}/I_{pa}) which approximately equals to 1 and this indicate the semi-reversible redox process related to a redox couple of substrate 2-amino-4-methylphenol. In other words due to the low rate of hydroxylation reaction or other coupling reactions, nothing was found in the time scale of the used technique. The results of voltammograms indicate that as the residence time increases, cathode current decreases from one side and ΔE_p increases from other side.

This result could be considered as related to polymer formation on electrode surface. Anion forms of 2-amino-4-methylphenol could react to iminoquinone as one nucleophile. Increasing the concentration of 2-amino-4-methylphenol caused to increase the reaction speed so that the reaction speed and the time scale of cyclic voltammograms become comparable. The electrochemical behavior of 2-amino-4-methylphenol has been studied in the presence of Penicillin amine and at different pHs. The results of these voltammograms indicate that 2-amino-4-methylphenol in the presence of Penicillin amine at relatively acidic to slightly alkaline pHs exhibit best reversible behavior [9].

Also at about neutral pHs, best results are obtained because 2-amino-4-methylphenol keep the its reversible behavior solely but in the presence of Penicillin amine, back cathodic peak has highly decreased. This is indicative of involving the 2-amino-4-methylphenol reaction in the presence of Penicillin amine. Therefore, all experiments were carried out in the presence of Penicillin amine at pH=7 and in Phosphate buffer (Fig. 3).

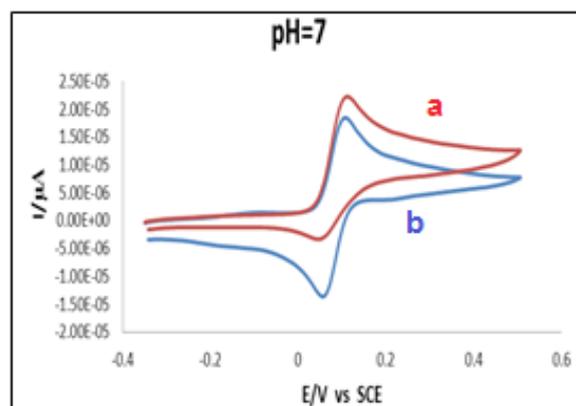


Fig. 3. cyclic voltammograms of 2-amino-4-methylphenol solely (a) and in the presence of nucleophile (b) at pH=7

3.1. The electrochemical behavior of 2-amino-4-methylphenol in the presence of Penicillin amine and buffer

The electrochemical behavior of 2-amino-4-methylphenol in the presence of Penicillin amine with the same concentration in water and in the presence of phosphoric acid 0.1 M buffer as the carrier electrolyte have been studied and their cyclic voltammograms have been plotted. The results indicate the chemical reaction among the iminoquinone form of 2-amino-4-methylphenol and Penicillin amine, because the cathode peak height has been decreased.

Comparing the cyclic voltammograms of Penicillin amine in the absence of 2-amino-4-methylphenol indicate that Penicillin amine is not electroactive at range of applied potential. The back cathodic peak of those compounds

shows more considerable reduction, which has electron withdrawing groups and this can support that existing these electron withdrawing groups lead to accelerate the addition reactions of Quinone obtained by electrochemical reaction with Penicillin amine. The reason is that the positive charge density increases and because of more readiness for accepting the nucleophile and Michael addition. Also increasing the ratio of IP_{c1}/IP_{a1} along with increasing scan rate of potential supports reactivity of iminoquinone with Penicillin amine so that as scan rate increases and scan aperture decreases, then the required opportunity for performing the Michael addition reaction among iminoquinone and Penicillin amine is lost. In other words, plotting the current function curve $IP_{\alpha}/V^{1/2}$ by scan decreasing rate along with increasing scan rate of potential show that such behavior is a measure of EC mechanism[10]. In one general trend with pH increasing, IP_c/IP_{α} decreases, which it indicates the higher reaction rate at highest pHs.

3.2. Electrochemical behavior of 2-amino-4-methylphenol at various scan rates

After determining the optimal pH, the material voltammogram was studied in the presence of and in the absence of nucleophile Penicillin amine at various scan rates. The cyclic voltammograms of the two materials indicated the reaction among stock and nucleophile and it revealed that as scan rate of the potential increase, the cathodic peak decreases because the formed iminoquinone loses the opportunity to react with Penicillin amine. Now if we plot the current changes curve by the scan rate of the potential, it will be found that as the scan rate of potential increases, then current ratio's potential will increase and approach to one (Fig. 4).

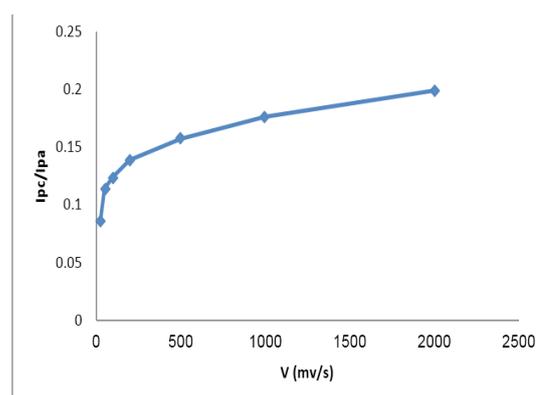


Fig. 4. IP_c/IP_{α} current ratio change curve by the scan rate of potential.

From other side, plotting the curve of current function $IP_{\alpha}/V^{1/2}$ by scan rate show that as scan rate of potential increases, decreasing trend will be obtained which such behavior is one measure of EC mechanism (Fig. 5).

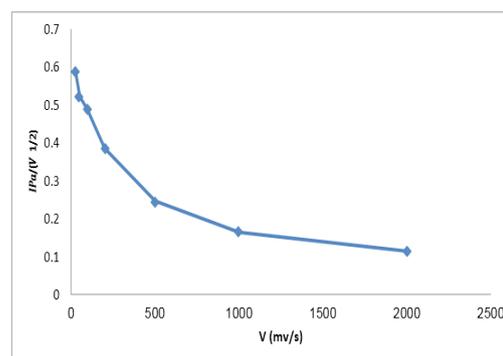


Fig. 5. $IP_{\alpha}/V^{1/2}$ current ratio change curve by the scan rate of potential.

3.3. Plotting the multiple cyclic voltammograms

Fig. 6 shows the cyclic voltammogram of 2-amino-4-methylphenol (5 M) in the presence of Penicillin amine (5 M) and the buffer (1 M) as the carrier electrolyte at GC electrode surface. As it is found that at second and third cycles, new peak is not found which is because of EC mechanism. The reason of anodic current reduction and its movement to more positive potential is due to contaminate

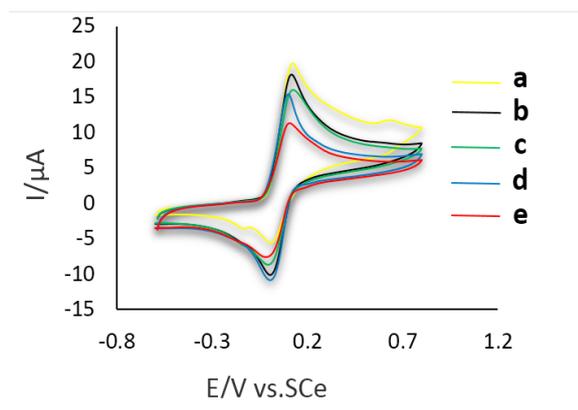


Fig. 6. The cyclic voltammogram of 2-amino-4-methylphenol (5 M) in the presence of Penicillin amine (5 M) and the buffer (1 M) as the carrier electrolyte at GC electrode surface ($\Phi=2\text{mm}$). The dominated conditions: The potential of 0.36 V respectively after consuming 0 (a), 8 (b), 10 (c), 16 (d), 24 (e), coulomb electricity, scan rate of potential 100 mV/s.

the work electrode surface into the generated product which from one side, it cause to decrease the surface and as a result cause to decrease the current and from other side, the resistance against current increased therefore the anode current moves to the positive side. As it is found in Fig. 6, the anode current decrease with the progress of electrolysis, which is due to the product sequestration and because of forming polymeric layers during electrolysis on the carbon electrode surface and cause to decrease its efficiency. Also plotting the current changes of anodic peak during coulometry by the consumed coulomb support the consumption two electrons as per each molecule of 2-amino-4-methylphenol which it confirms the EC mechanism (see Fig. 7).

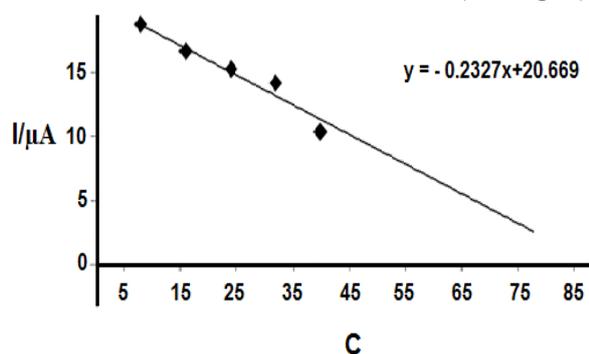


Fig. 7. The chart of the anodic peak current changes by the consumed coulomb.

According to date from the cyclic voltammogram and coulometry and spectral information about electrooxidation of 2-amino-4-methylphenol, the following mechanism (Fig. 8) could be suggested for electrooxidation in the presence of Penicillin amine [11].

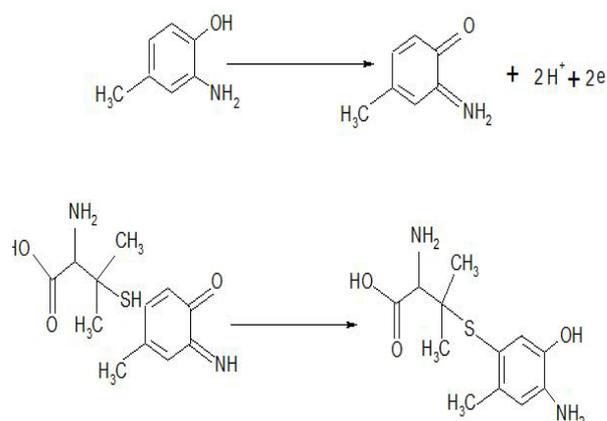


Fig. 8. The proposed mechanism of electrooxidation in the presence of Penicillin amine.

4. Conclusion

In the paper, electrochemical oxidation of 2-amino-4-methylphenol was studied in water and the electrochemical behavior of the above compound has been investigated in the presence of Penicillin amine at various conditions. The results show that the above compounds could be transformed to new derivatives in the presence of Penicillin amine and phosphate buffer with concentration of 0.2 M and pH=7 during EC mechanism. Also electrolysis of 2-amino-4-methylphenol was carried out in the presence of Penicillin amine which has the role of nucleophile and the product was yielded with suitable practical response. In all cases, cyclic voltammetry (CV) and controlled potential coulometry (CPC) were used for optimization of electrolysis conditions and for determining the mechanism.

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