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Electrochemical Behavior and the Detection Limit of Ascorbic Acid on a Pt Modified Electrode

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The electrochemical behavior of ascorbic acid (AA) at the DL-Alanine (DL-Ala) polymer film modified platinum electrode (DL-Ala/Pt electrode) had been studied by using cyclic voltammetry. The main proposition of the research is also to indicate the detection limit of AA on the used modified electrode. The modified electrode shows an excellent electrocatalytical effect on oxidation of AA in 0.1 M KH_2PO_4 using cyclic voltammetry. The effect of DL-Ala/Pt modified electrode increases clear by the anodic current peak about 13.67 µA while the peak potential shifts to negative values as compared to the bare Pt electrode. The anodic current increased with an increase in AA concentration from 2 mM to 7.5 mM and with increasing scan rate from 20-200 mV/s and it is potential shifted to more positive values. The detection limit of this modified electrode with AA was calculated to be $9.24\text{x}10^{\mathbf{-6}}$ M. Chronoamperometric measurements were used to find the diffusion coefficient of AA with a value of 6.92 x 10^{-6} cm^2s^{-1}.

Keywords: Electrochemical behavior; Ascorbic acid; Cyclic voltammetry; DL-Ala/Pt modified electrode; Chronoamperometric

1. INTRODUCTION

Ascorbic acid (AA) is the water-soluble type of organic acid, which is also known widely as vitamin C. AA is essential in the human body due to its importance in antioxidant property. Besides, AA plays an important role in metabolisms include collagen synthesis, amino acid metabolism, adrenaline, anti-inflammatory steroids, certain hormones and neurotransmitters synthesis [1, 2]. In some cases, excessive quantities of AA may result in inhibition natural processes occurring in food and can give to taste deterioration; added to apple pulp (250 mg/kg), vitamin C inhibits oxidation processes responsible for apple juice aroma [3].

Applications of modified electrodes in electrocatalysis and sensors have been enriched by the specific properties of conducting polymers. These properties - such as good stability, reproducibility, selectivity, activity and large service area – lead to decrease the normally large overpotential and raise the current encountered in the electrooxidation of materials.

It is very difficult to determine AA directly at ordinary (carbon or metal) electrodes, because of its high overpotential and consequent fouling by oxidation products [4]. Therefore, some chemically modified electrodes with various active mediators immobilized on the electrode surface have been used as the catalyst of electrooxidation of AA [5-7]. These include a glassy carbon electrode (GCE) and a carbon paste electrode with complexes and organic compounds, such as cobalt hexacyanoferrate [8] ruthenium (III) diphenyldithiocarbamat [9], cobalt pentacyanonitrosylferrate [10], ferrocene with *b*-cyclodextrin [11], norepinephrine [12], Ni[$Me_2(CH_3CO)$], tetraeno N_4 complex [13] and aniline [14].

Fabrication of chemically modified electrode (CME) has been widely reported to improve sensitivity and selectivity in determining amino acids, vitamins, DNA and etc. in recent years [15-18]. Many studies have indicated that a polymer film modified electrodes show an enhanced response for determination of various important biological and clinical species [19]. It was found that some amino acids such as cysteine and alanine have been used for electrocatalysis of AA, UA and DA [20,21]. But the electrochemical oxidation of AA at the DL-alanine polymer film in the service of platinum electrode has been not reported yet. On the other hand the electropolymerization of L-alanine on smooth electrodes such as platinum and glassy carbon electrodes was studied in literature [22].

Many analytical methods used for AA determination. Classic (conventional) techniques are represented by volumetric methods titration with an oxidizing solution such as potassium iodate [23], or bromate [24]. Volumetric techniques can suffer from lack of specificity [14] which limits their use to samples not containing other reducing agents. Square-wave voltammetry was used to determine AA based on its oxidation at a zeolite modified carbon paste electrode [25], and the method was applied to the AA determination in citrus juice. Cyclic and differential pulse voltammetries were used for AA electrocatalytical determination at a carbon paste electrode modified by 2, 7-bis (ferrocenylethynyl) fluoren-9-one [26].

The present study aims to investigate the electrochemical behavior and detection limit of AA at a DL-Ala/Pt modified electrode by using cyclic voltammetry. Also study the influence of AA concentration and scan rate on the oxidation behavior of AA. Moreover, find the diffusion coefficient of AA by using chronoamperometric technique.

2. EXPERIMENTAL

2.1. Reagents and solutions

All chemicals were of analytical reagent grade unless otherwise specified and were used as received without further purification. Double distilled water was used to prepare buffer and reagent solutions. The supporting electrolyte used in all the experiments was 0.1 M KH_2PO_4 solutions.

Stock solution of 0.1M KH_2PO_4 (Cablo Erba Co. Code No. 455100) was prepared by dissolving 3.4 gm in 250 mL double distilled Water. While stock solution of 0.01 M AA was ready by dissolving 0.44 gm in 250 mL of double distilled water at room temperature.

2.2. Electrochemical equipment

The apparatus used in these experiments is EG&G PRINCETON APPLIED RESEARCH POTENTIOSTAT/GALVANOSTAT MODEL 263 (made in USA). The cell consists of three electrodes (model K0264 micro-cell), the working and counter (model K0266) electrodes were of high purity platinum wire, while an Ag/AgCl saturated KCl (model K0265) electrode was used as the reference electrode and chemically modified Pt electrode as working electrode.

2.3. Preparation of the DL-alanine polymer film modified Pt Electrode

A platinum electrode (2 mm in diameter) was polished to a mirror finished with polish paper, followed by washing in nitric acid, ethanol and distilled water. Then, a Pt electrode was electrochemically cleaned by cycling the electrode potential between −1 to 1 V in 1 M H_2SO_4 (pH = 0.61) [27,28], until a stable voltammogram was obtained. After that it was washed with doubly distilled water and dried, the electropolymerization of DL-Alanine on a platinum electrode was carried out in 0.1 M Na_2HPO_4 containing 0.01 M DL-Alanine with potential cycling between −0.6 to 2.0 V. After 20 cycles the surface of the film modified electrode was washed with doubly distilled water to remove the physically adsorbed material and for drying, it was heated for 5 min. at 55ºC in oven. Then, the film electrode was transferred to an electrochemical cell.

All experiments have been carried out in duplicate; the measurements have shown good reproducibility.

2.4. Electrochemical measurement

Unless otherwise mentioned, all electrochemical measurements were performed with 6 mM AA in 0.1 M potassium dihydrogen phosphate KH_2PO_4 as a supporting electrolyte at DL-Ala/Pt modified electrode. Cyclic voltammetry was used to detect the electrochemical response of AA. A potential cycling between -0.3 to 1.1 V, was applied to the working electrode at room temperature.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of AA

Figure 1 shows the cyclic voltammograms obtained with the platinum electrode at scan rate 100 mV/s under different conditions: curve A is the cycling performed with the bare Pt electrode in

0.1M KH_2PO_4; curve B is obtained in 0.1M KH_2PO_4 containing 6 mM of AA; curve C represents the electrode containing the polymer film of DL-Alanine in 0.1M KH_2PO_4 without AA and curve D refers to the electrode with the polymer film of DL-Alanine in 0.1M KH_2PO_4 containing 6 mM of AA.

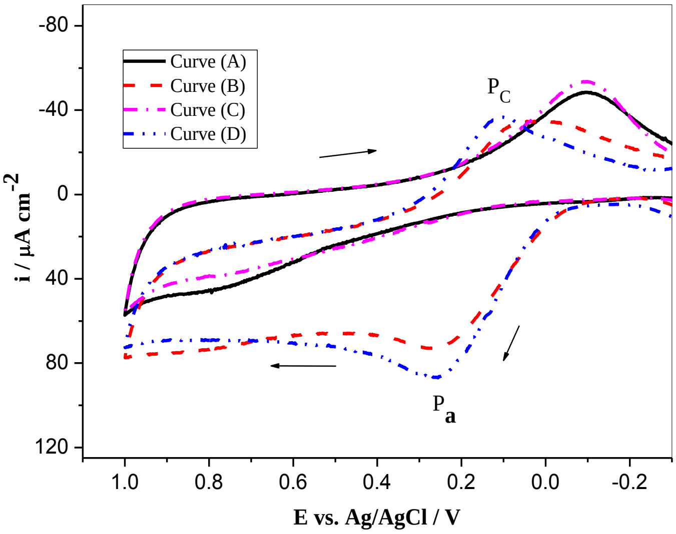

Figure 1. Cyclic voltammograms obtained with the platinum electrode in 0.1 M KH_2PO_4 at scan rate 100 mV/s under different conditions: curve (A) electrode without polymer film and without AA; curve (B) electrode without polymer film and with AA; curve (C) electrode with polymer film and without AA, and curve (D) electrode with polymer film and with AA.

As can be seen from Figure 1, for the bare Pt electrode in 0.1M KH_2PO_4 in absence AA (curve A), only one cathodic peak appears at about -0.1 V, corresponding to reduction of water. After addition, AA to the solution curve B is obtained and an anodic peak of current appears around +0.26 V, which in a good agreement with the reported data [29-31], about oxidation of AA at a bare platinum electrode. The return sweeping shows only the water reduction peak. This means that the process is not reversible. In addition, the cathodic peak associated with water reduction and shifted to more positive potential in presence AA. This may be related to adsorption of molecules of AA on the surface of the electrode, preventing the interaction between platinum and the solvent molecules. In the potential sweeping of the platinum electrode containing the polymer film of DL-Alanine without ascorbic AA (curve C), no anodic current peak appears. Absence of an anodic peak was expected due to absence of AA.

The last voltammogram of Figure 1, curve D, corresponds to the electrode with the polymeric film in presence AA. As observed, the anodic current peak increases about 13.67 µA while the peak potential shifts to negative values. This means that the electrode containing the polymer film of DL-Alanine presents electro-catalytic activity to AA. The increase of current peak indicates that a higher amount of species was oxidized, while the shift in potential shows higher facility in oxidizing these species.

The overall reaction of AA oxidation expressed by the following reaction [32]:

$$C_6H_8O_6 \text{ (Ascorbic acid)} \longrightarrow C_6H_6O_6 \text{ (Dehydroascorbate)} + 2\,H^+ + 2\,e^- \quad (1)$$

Reaction of AA oxidation revealed that AA electrochemical oxidation reactions (eq. 1), is diffusion controlled-two electrons and two protons-process. Moreover, also during the cathodic potential scans no significant currents were detected, this oxidation process is irreversible [31].

3.2. Effect of AA concentration

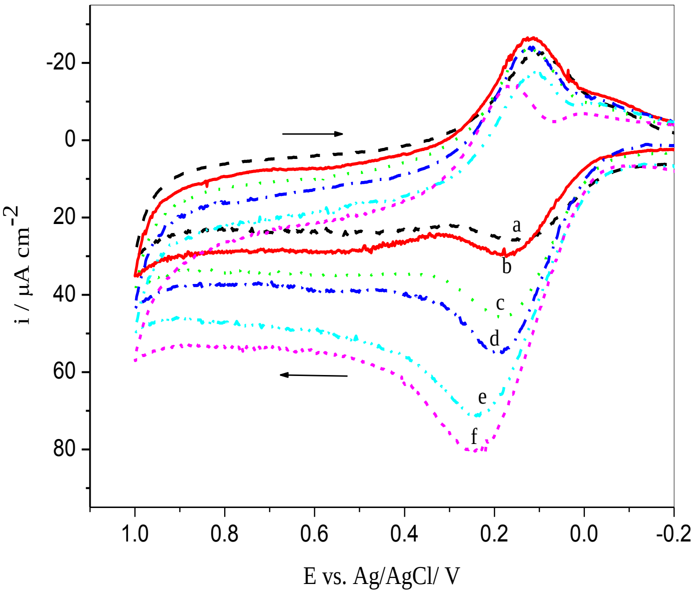

Figure 2. Cyclic voltammograms of DL-Ala/Pt modified electrode in 0.1 M KH_2PO_4 at scan rate 50 mV/s with increasing AA concentration as (a) 2, (b) 3.33, (c) 4, (d) 5, (e) 6 and (f) 7.5 mM.

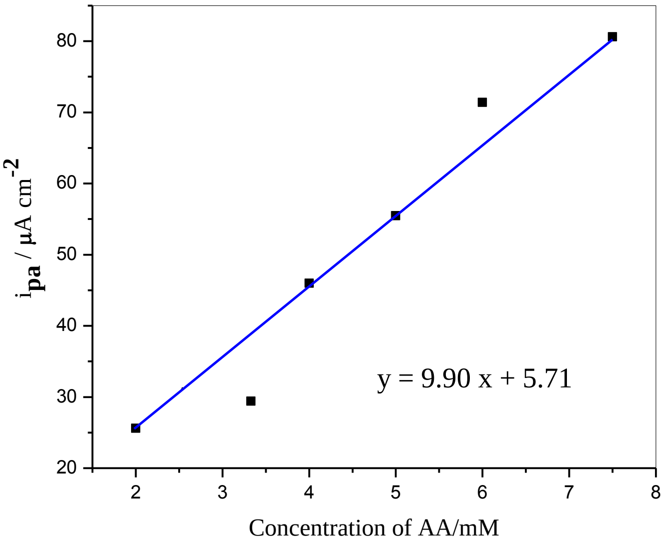

Figure 3. Calibration graph for different concentrations of AA in 0.1 M KH_2PO_4 using a DL-Ala/Pt modified electrode at scan rate 50 mV/s.

Concentration of AA was determined using DL-Ala/Pt modified electrode as shown in Figure 2. The anodic current increased with an increase concentration of AA from 2 mM to 7.5 mM, and it is potential shifted to more positive values.

The calibration graph of AA in different concentrations was obtained by using a DL-Ala/Pt modified electrode shows in Figure 3. A linear response was achieved in the concentration range of 2 to 7.5 mM, with a sensitivity response of 9.90 mA/M obtained from the linear equation slope, which is in the same order of size with previously reported value of 13.7 µA/mM [33].

Table 1. The data used to calculate the value of SD taken from figure 3

X	i_J	I_J
4	45.73	45.31
5	54.97	55.21
6	71.46	65.11
6.92	78.74	74.22

Table 1 shows the data used to calculate the value of standard deviation of the mean current applying on Figure 3. This value calculated according to equation 2 [34]:

$SD = 1 / (n-2) \sum (i_j - I_j)^2$ …………………………………………..(2)

Where SD is the standard deviation which is the square root of the variance, i_j is the experimental value of the experiment number j and I_j is the corresponding recalculated value, at the same concentration using the regression line equation 3:

$Y = 9.90\,x + 5.71$ ……….………………………………………….(3)

The calculated SD was used in determining the detection limit (DL, 3 x SD / slope). From these values, the detection limit of determination of AA by using a DL-Ala/Pt modified electrode was calculated to be 9.24×10^{-6} M. This value is very clothing to the value reported in literature [33].

3.3. Effect of scan rate

The effect of a varying scan rate in the oxidation process of AA was studied. Cyclic voltammograms of 6 mM AA in 0.1 M KH_2PO_4 supporting electrode using a DL-Ala/Pt modified electrode was obtained for the scan rate from 20-200 mV/s (Figure 4). It noted from Figure 4 that, with an increasing scan rate, the anodic current peak for the electrooxidation of AA increases due to more molecules of AA are oxidized and it is potential shifts to more positive values.

Figure 5 shows the plot of log I_{pa} (peak current) vs. log *v* (scan rate). The linear correlation coefficient (r) was calculated and being equal 0.97, and the linear relationship given by equation 4:

$Y = 0.41\,X + 1.1$ ……………………………………………… (4)

The observed increase in the oxidative current of AA is due to heterogeneous kinetics. The obtained slope (0.48) is in a good agreement with the theoretical slope (0.5) for a diffusion controlled process [30]. Good linearity between the anodic peak current and the square root of scan rate (Figure 6) which obtained by the equation 5:

Y = 7.51 X + 47.42……………………………………………… (5)

This supports the idea that the electrode reactions of AA were under diffusion control [33].

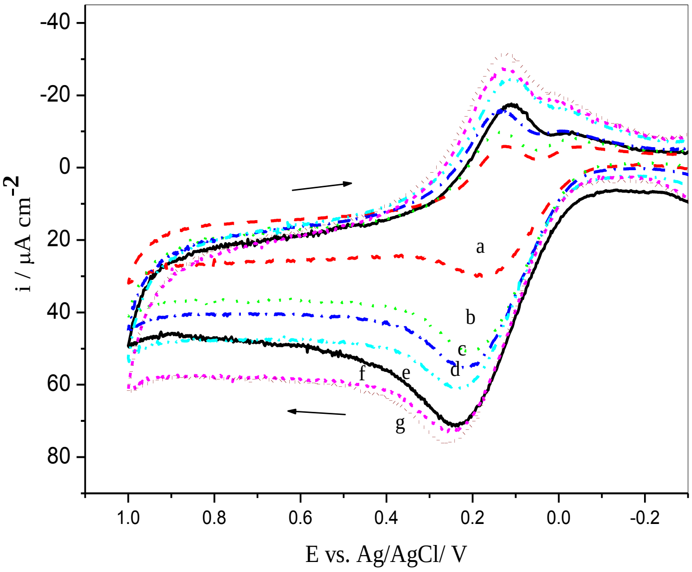

Figure 4. Cyclic voltammograms of 6 mM AA in 0.1 M KH2PO4 at a DL-Ala/Pt modified electrode, at scan rates (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70 and (m) 80 mV/s.

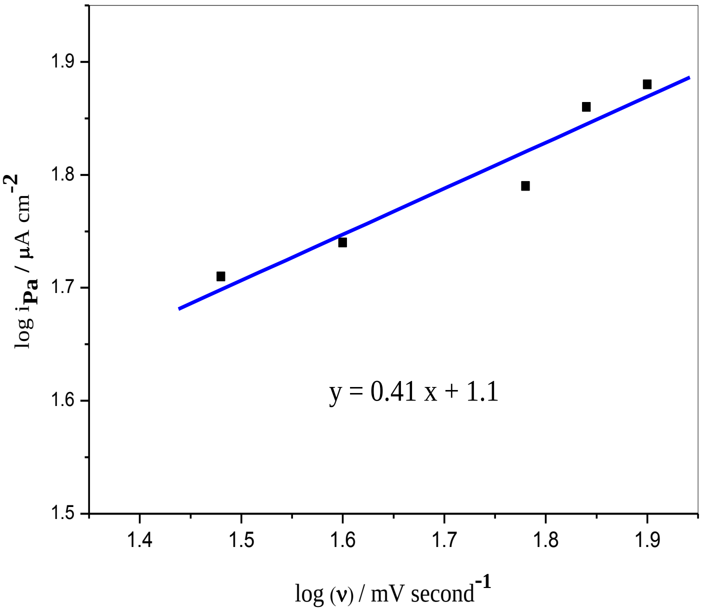

Figure 5. Plot of log I_{pa} vs. log v., other parameters same as in figure 4.

3.4. Chronoamperometric measurements

The chronoamperometry was employed along with other electrochemical methods for the investigation of electrode processes at chemically modified electrodes. Figure 7 shows chronoamperometric measurements of AA at a DL-Ala/Pt obtained by setting the working electrode potential at -0.6 V (first potential step) and at +1 V (second potential step) for the various concentrations of AA in 0.1 M KH_2PO_4.

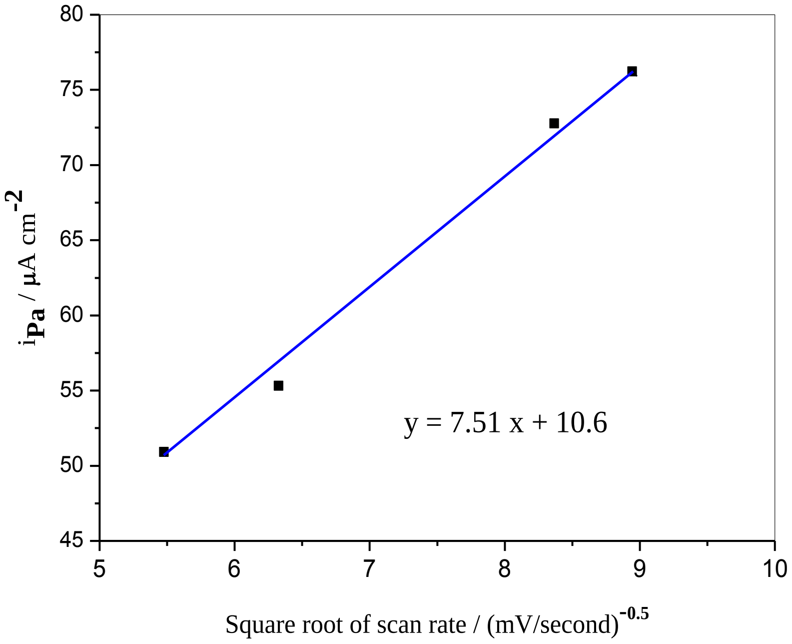

Figure 6. Plot of peak current vs. square root of v., other parameters same as in figure 4.

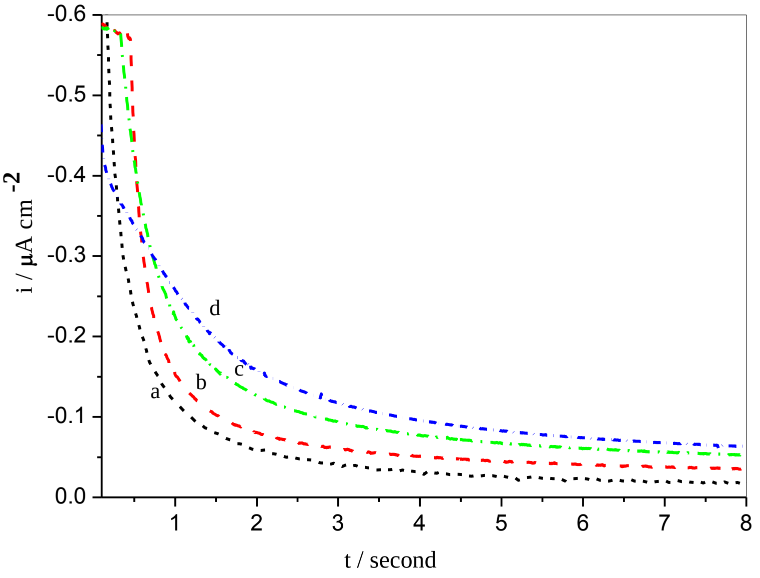

Figure 7. Chronoamperometric response at a DL-Ala/Pt modified electrode in 0.1 M KH_2PO_4 for different concentrations of AA ((a) 2, (b) 5, (c) 8.33, and (d) 9.52 mM) First and second potential steps were -0.6 and +1 V vs. Ag/AgCl respectively.

In chronoamperometric studies, we have determined the diffusion coefficient of AA for a DL-Ala/Pt modified electrode. For an electroactive material (AA in this case) with a diffusion coefficient of D, the current for the electrochemical reaction (at a mass transport limited rate) is described by Cottrell equation 6 [35].

$I = n\,F\,A\,D^{1/2}\,C_b\,\pi^{-1/2}\,t^{-1/2}$ ……………………………………… (6)

Where, D and C_b are the diffusion coefficient ($cm^2\,s^{-1}$) and the bulk concentration (mM). Under diffusion control, a plot of I vs. $t^{-1/2}$ will be linear (Figure 8), and from the slope the value of D obtained. The mean value of the D of AA was found to be 6.92 x 10^{-6} $cm^2\,s^{-1}$; this value is compared with the values obtained by other literature [30].

3.5. Stability of DL-Ala/Pt modified electrode

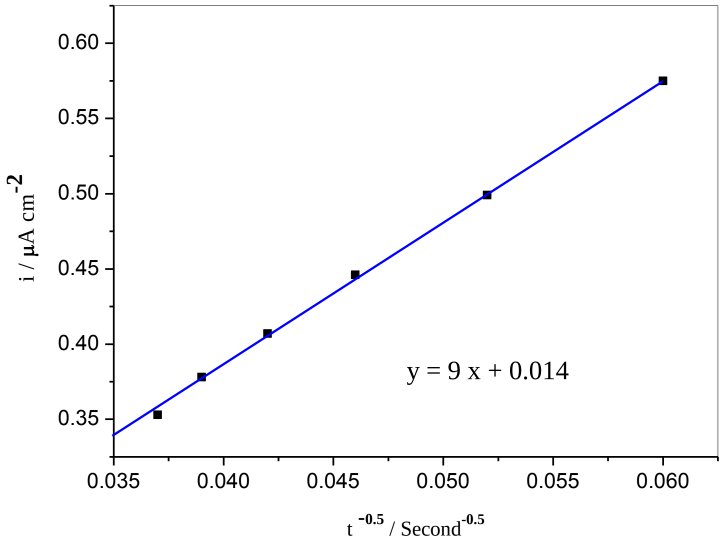

Figure 8. Cottrell's plot for potential step chronoamperometry of 5 mM AA acid in 0.1 M KH_2PO_4.

The DL-Ala/Pt modified electrode has high stability while kept in double distilled water at room temperature. Where there is no clear change in values of oxidation peak currents of AA with using this electrode after two weeks.

4. CONCLUSION

The DL-Ala/Pt modified electrode was successfully fabricated and enhanced the anodic current of AA. Both anodic current and sensitivity improved when a DL-Ala/Pt modified electrode was used instead of a bare Pt electrode. The electrocatalytic reaction of AA was irreversible and the anodic current obtained was under diffusion control. The anodic current peak was dependent on concentration of AA and scan rate. The detection limit of this modified electrode with AA was calculated to be

9.24×10^{-6} M. From the chronoamperometric measurements, the value of diffusion coefficient of AA was found to be 6.92×10^{-6} cm^2 s^{-1} using a DL-Ala/Pt modified electrode.

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