

# **Electrochemical Study of Catechol in Presence of Sulfanilic Acid and Diethylamine at Different pH**

by

**Md. Alim Uddin**

A thesis submitted in partial fulfillment of the requirements for the degree of  
Master of Science in Chemistry



**Khulna University of Engineering & Technology**

**Khulna 9203, Bangladesh.**

**December 2015**

# **Dedicated**

To My Parents

**Sabia Begum and Late Md. Abdul Khalek Biswas**  
who have desired underprivileged life to continue my smile.



## Declaration

This is to certify that the thesis work entitled "Electrochemical Study of Catechol in Presence of Sulfanilic acid and Diethylamine at Different pH" has been carried out by Md. Alim Uddin in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work has not been submitted anywhere for the award of any degree or diploma.

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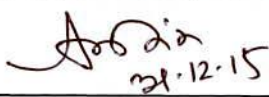
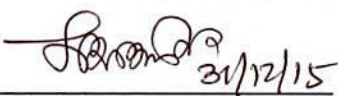
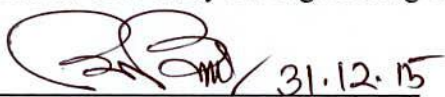
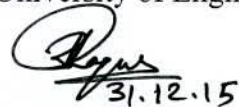
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## Approval

This is to certify that the thesis work submitted by Md. Alim Uddin entitled "Electrochemical Study of Catechol in Presence of Sulfanilic Acid and Diethylamine at Different pH" has been approved by the board of examiners for the partial fulfillment of the requirements for the Degree of Master of Science in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh in December 2015.

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**Md. Alim Uddin**



## Abstract

The electrochemical behavior of catechol in presence of diethylamine and sulfanilic acid & catechol in presence of sulfanilic acid + diethylamine have been studied by cyclic voltammetry, controlled potential coulometry, differential pulse voltammetry and chronoamperometry techniques using Glassy carbon (GC), Gold (Au) and Platinum (Pt) electrodes. The voltammetric studies have been carried out in variation of catechol, diethylamine and sulfanilic acid concentration, buffer solution of different pH, different electrodes and scan rate.

Upon addition of diethylamine and sulfanilic acid in catechol solution at the second scan of potential a new anodic peak appeared at the negative potential and the reduction peak shifted with respect of pure catechol. Also the anodic and cathodic peak current decreases significantly compared with the pure catechol that indicates the participation of reaction of *o*-benzoquinone with diethylamine, sulfanilic acid and their mixtures. The products generated from the reaction of catechol with diethylamine and sulfanilic acid are assumed to be 4-(diethylamino)-benzene-1,2-diol, and 4-(bis(3,4-dihydroxyphenyl)amino) benzenesulfonic acid, respectively that undergo electron transfer at more negative potentials than the catechol. The electro-synthesized products originated from catechol with diethylamine and sulfanilic acid were isolated. The formation of new products was also confirmed by FTIR spectra.

The effect of pH of catechol in presence of diethylamine and sulfanilic acid were studied by varying pH from 3 to 11 except sulfanilic acid 2-9. For diethylamine, it is seen that at pH 3-5, no new anodic peak appeared after repetitive cycling. In the pH 7-11, the *o*-benzoquinone undergoes nucleophilic attack by the amines that voltammetric new anodic peak  $A_0$  appeared after repetitive cycling. In contrast, for sulfanilic acid at pH 9 no new anodic peak appeared after repetitive cycling. Whereas in pH 7, the voltammogram shows a small peak. For diethylamine, the maximum peak current is obtained at pH 7 but the maximum peak current of sulfanilic acid is obtained at pH 3. The slopes of the peak potential,  $E_p$  vs pH plot was determined graphically as the anodic peaks of catechol-diethylamine (69 mV/pH for first anodic peak  $A_1$  or 55 mV/pH for appeared peak  $A_0$ ) and

catechol-sulfanilic acid (36 mV/pH for first anodic peak  $A_1$  or 38 mV/pH for appeared peak  $A_0$ ) at 0.1 V/s. This indicates that the oxidation reaction of catechol-diethylamine adduct proceeded via the  $1e^-/1H^+$  process whereas catechol-sulfanilic acid adduct proceeded via the  $2e^-/2H^+$  processes. This also suggests that during the reaction not only electron but also proton are released from the catechol-amine adduct.

The reaction was strongly influenced by the pH as well as concentration of diethylamine and sulfanilic acid. The reaction was mostly favorable in 250 mM of diethylamine with fixed 2 mM of catechol at pH 7. The reaction of catechol in presence of sulfanilic acid was favorable in 2 mM sulfanilic acid, 2 mM catechol at pH 3. The electro-oxidation of catechol-diethylamine adduct are facilitated in neutral media whereas catechol-sulfanilic acid in acid media.

The scan rate effect on cyclic voltammogram of catechol in presence of diethylamine and sulfanilic acid were also studied. The peak current of both the anodic and the corresponding cathodic peaks increases with the increase of scan rate. The nearly proportionality of the anodic and corresponding cathodic peak suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process. The current function for anodic peak  $A_0$ , ( $I_p/v^{1/2}$ ) of catechol-diethylamine derivative was found to be decreased exponentially with increasing scan rate. Catechol-diethylamine derivatives have been found to undergo electrochemical reaction with ECE (electron transfer-chemical reaction- electron transfer) type mechanism. But, the current function for the anodic peak  $A_0$ , ( $I_p/v^{1/2}$ ) of catechol-sulfanilic acid derivative was found to be decreased with increasing scan rate and such a behavior is adopted as indicative of an ECECE type mechanism.

## Contents

|                                                        | PAGE |
|--------------------------------------------------------|------|
| Title page                                             | i    |
| Dedication                                             | ii   |
| Declaration                                            | iii  |
| Certificate of Research                                | iv   |
| Acknowledgement                                        | v    |
| Abstract                                               | vi   |
| Contents                                               | viii |
| List of Tables                                         | xi   |
| List of Figures                                        | xv   |
| <br><b>CHAPTER I</b>                                   |      |
| Introduction                                           | 1-8  |
| 1.1 General                                            | 1    |
| 1.2.1 Catechol (Cate)                                  | 3    |
| 1.2.2 Natural occurrence of Catechol                   | 4    |
| 1.2.3 Use of Catechol                                  | 4    |
| 1.2.4 Diethylamine                                     | 4    |
| 1.2.5 Use of Diethylamine                              | 5    |
| 1.2.6 Sulfanilic acid                                  | 5    |
| 1.2.7 Use of Sulfanilic acid                           | 6    |
| 1.3 Electrochemical properties of Catechol derivatives | 6    |
| 1.4 Objectives of the Thesis                           | 7    |
| <br><b>CHAPTER II</b>                                  |      |
| Theoretical Background                                 | 9-23 |
| 2.1 Mass transfer process in voltammetry               | 9    |
| 2.1.1 Migration                                        | 9    |
| 2.1.2 Diffusion                                        | 10   |
| 2.1.3 Convection                                       | 10   |
| 2.2 Cyclic voltammetry                                 | 11   |
| 2.2.1 Single electron transfer process                 | 14   |
| 2.2.1(a) Reversible processes                          | 15   |
| 2.2.1(b) Irreversible processes                        | 16   |



|                    |                                                                       |              |
|--------------------|-----------------------------------------------------------------------|--------------|
|                    | 2.2.1(c) Quasi-reversible process                                     | 17           |
|                    | 2.2.2 Multi electron transfer processes                               | 18           |
|                    | 2.3 Pulse techniques                                                  | 21           |
|                    | 2.3.1 Differential pulse voltammetry (DPV)                            | 21           |
|                    | 2.4 Chronoamperometry (CA)                                            | 22           |
| <b>CHAPTER III</b> | <b>Experimental</b>                                                   | <b>24-33</b> |
|                    | 3.1 Chemicals                                                         | 24           |
|                    | 3.2 Equipment's                                                       | 25           |
|                    | 3.3 Cyclic voltammetry (CV)                                           | 25           |
|                    | 3.4 Important features of CV                                          | 26           |
|                    | 3.5 Differential pulse voltammetry (DPV)                              | 29           |
|                    | 3.6 Important Features of DPV                                         | 29           |
|                    | 3.7 Chronoamperometry (CA)                                            | 30           |
|                    | 3.8 Computer controlled potentiostats (for CV, DPV and CA experiment) | 30           |
|                    | 3.9 Electrochemical cell                                              | 30           |
|                    | 3.10 Electrodes                                                       | 31           |
|                    | 3.11 Preparation of electrode                                         | 31           |
|                    | 3.12 Removing dissolved Oxygen from solution                          | 31           |
|                    | 3.13 Electrode polishing                                              | 32           |
|                    | 3.14 Experimental procedure                                           | 32           |
|                    | 3.15 Preparation of buffer solutions                                  | 32           |
| <b>CHAPTER IV</b>  | <b>Results and Discussion</b>                                         | <b>34-63</b> |
|                    | 4.1.1 Electrochemical behavior of Catechol                            | 34           |
|                    | 4.1.2 Electrochemical behavior of Catechol + Diethylamine             | 35           |
|                    | 4.1.3 Effect of scan rate of Catechol + Diethylamine                  | 37           |
|                    | 4.1.4 Effect of pH of Catechol + Diethylamine                         | 40           |
|                    | 4.1.5 Concentration effect of Diethylamine                            | 43           |
|                    | 4.1.6 Concentration effect of Catechol                                | 44           |
|                    | 4.1.7 Effect of electrode materials                                   | 44           |

|        |                                                                       |    |
|--------|-----------------------------------------------------------------------|----|
| 4.1.8  | Subsequent cycles of CV of Catechol + Diethylamine                    | 45 |
| 4.1.9  | Controlled-potential coulometry of Catechol + Diethylamine            | 46 |
| 4.1.10 | pH effect of DPV of Catechol + Diethylamine                           | 47 |
| 4.1.11 | Effect of deposition time change on DPV of Catechol + Diethylamine    | 48 |
| 4.1.12 | Effect of concentration of DPV of Catechol + Diethylamine             | 48 |
| 4.1.13 | Spectral analysis of Catechol + Diethylamine                          | 50 |
| 4.1.14 | Chronoamperometry of Catechol + Diethylamine                          | 50 |
| 4.2.1  | Electrochemical behavior of Catechol + Sulfanilic acid                | 51 |
| 4.2.2  | Subsequent cycles of CV of Catechol + Sulfanilic acid                 | 52 |
| 4.2.3  | Scan rate effect of Catechol + Sulfanilic acid                        | 53 |
| 4.2.4  | Effect of pH of Catechol + Sulfanilic acid                            | 56 |
| 4.2.5  | Concentration effect of Sulfanilic acid                               | 58 |
| 4.2.6  | Concentration effect of Catechol composition                          | 59 |
| 4.2.7  | Controlled-potential coulometry of Catechol + Sulfanilic acid         | 59 |
| 4.2.8  | Effect of electrode materials                                         | 60 |
| 4.2.9  | pH effect of DPV of Catechol + Sulfanilic acid                        | 60 |
| 4.2.10 | Effect of deposition time change of DPV of Catechol + Sulfanilic acid | 61 |
| 4.2.11 | Effect of concentration of DPV of Catechol + Sulfanilic acid          | 62 |
| 4.2.12 | Spectral analysis of Catechol+ Sulfanilic acid                        | 62 |
| 4.2.13 | Chronoamperometry of Catechol+ Sulfanilic acid                        | 63 |
| 4.2.14 | CV of Sulfanilic acid + Diethylamine mixture with Catechol            | 63 |

|                  |                    |            |
|------------------|--------------------|------------|
| <b>CHAPTER V</b> | <b>Conclusions</b> | <b>183</b> |
|                  | <b>References</b>  | <b>185</b> |



## LIST OF TABLES

| Table No | Description                                                                                                                                                                                                                                                                                                                                | Page |
|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.1      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM catechol in aqueous buffer solution (pH 7) at different scan rate                                                              | 64   |
| 4.2      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current $I_p$ ( $\mu A$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1 <sup>st</sup> cycle) | 64   |
| 4.3      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ), of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)        | 65   |
| 4.4      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate (1 <sup>st</sup> cycle)         | 65   |
| 4.5      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)         | 66   |
| 4.6      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) of GC electrode at different scan rate (1 <sup>st</sup> cycle)         | 66   |
| 4.7      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)         | 67   |
| 4.8      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) of GC electrode at different scan rate (1 <sup>st</sup> cycle)         | 67   |

| Table No | Description                                                                                                                                                                                                                                                                                                                           | Page |
|----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.9      | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine and 2mM catechol in buffer solution (pH 9) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)  | 68   |
| 4.10     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 11) of GC electrode at different scan rate (1 <sup>st</sup> cycle)   | 68   |
| 4.11     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine and 2mM catechol in buffer solution (pH 11) of GC electrode at different scan rate (2 <sup>nd</sup> cycle) | 69   |
| 4.12     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1 <sup>st</sup> cycle)    | 69   |
| 4.13     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)    | 70   |
| 4.14     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1 <sup>st</sup> cycle)    | 70   |
| 4.15     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)    | 71   |
| 4.16     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1 <sup>st</sup> cycle)    | 71   |



| Table No | Description                                                                                                                                                                                                                                                                                                                    | Page |
|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.17     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate ( $2^{nd}$ cycle)   | 72   |
| 4.18     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate ( $1^{st}$ cycle)   | 72   |
| 4.19     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate ( $2^{nd}$ cycle)   | 73   |
| 4.20     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Gold electrode at different scan rate ( $1^{st}$ cycle) | 73   |
| 4.21     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Au electrode at different scan rate ( $2^{nd}$ cycle)   | 74   |
| 4.22     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode at different scan rate ( $1^{st}$ cycle)   | 74   |
| 4.23     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode at different scan rate ( $2^{nd}$ cycle)   | 75   |
| 4.24     | Peak Current $I_p$ ( $\mu A$ ), peak potential $E_p$ (V), of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s and different pH media ( $1^{st}$ cycle)                                                                                                                                                    | 75   |
| 4.25     | Peak Current $I_p$ ( $\mu A$ ), peak potential $E_p$ (V), of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s and different pH media ( $2^{nd}$ cycle)                                                                                                                                                    | 76   |

| Table No | Description                                                                                                                                                                                                                                                                                                                   | Page |
|----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.26     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate ( $2^{nd}$ cycle) | 76   |
| 4.27     | Peak current $I_p$ ( $\mu A$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Au electrode at different scan rate ( $2^{nd}$ cycle)                                                                                                                 | 77   |
| 4.28     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Au electrode at different scan rate ( $2^{nd}$ cycle)                                                                               | 77   |
| 4.29     | Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Pt electrode at different scan rate ( $2^{nd}$ cycle) | 78   |
| 4.30     | Peak Current $I_p$ ( $\mu A$ ) and Peak potential $E_p$ (V) of pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s ( $2^{nd}$ cycle), $A_0$ = appeared anodic peak and $A_1$ = $1^{st}$ anodic peak                                                                               | 78   |
| 4.31     | Peak Current $I_p$ ( $\mu A$ ) and Peak potential $E_p$ (V) of pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s ( $2^{nd}$ cycle), $A_2$ = $2^{nd}$ anodic peak                                                                                                                | 79   |
| 4.32     | Peak Current $I_p$ ( $\mu A$ ) and Peak potential $E_p$ (V) of pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s ( $2^{nd}$ cycle)                                                                                                                                              | 79   |



## LIST OF FIGURES

| Figure No | Description                                                                                                                                                                                                                                                                                                                                               | Page |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.1       | Cyclic voltammogram (CV) of 5 cycles of 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s                                                                                                                                                                                                                                        | 80   |
| 4.2       | Cyclic voltammogram of 5 cycles of 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s                                                                                                                                                                                                                                       | 80   |
| 4.3       | Comparison of cyclic voltammogram of only 2mM catechol, 250mM diethylamine and 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (1 <sup>st</sup> cycle) (Where A <sub>1</sub> = 1 <sup>st</sup> oxidation peak, C <sub>0</sub> = Appeared reduction peak, C <sub>1</sub> = 1 <sup>st</sup> reduction peak) | 81   |
| 4.4       | Comparison of cyclic voltammogram of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (2 <sup>nd</sup> cycle) (A <sub>0</sub> = Appeared oxidation peak)                                                                                                    | 81   |
| 4.5       | Comparison of cyclic voltammogram of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                                                                                                                               | 82   |
| 4.6       | Comparison of cyclic voltammogram of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                               | 82   |
| 4.7       | Comparison of cyclic voltammogram of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                                                                                                                               | 83   |
| 4.8       | Comparison of cyclic voltammogram of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                               | 83   |
| 4.9       | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1 <sup>st</sup> cycle) (Where A <sub>1</sub> = 1 <sup>st</sup> oxidation peak, C <sub>0</sub> = Appeared reduction peak, C <sub>1</sub> = 1 <sup>st</sup> reduction peak)                                                      | 84   |
| 4.10      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2 <sup>nd</sup> cycle), A <sub>0</sub> = Appeared oxidation peak                                                                                                                                                               | 84   |

| Figure No | Description                                                                                                                                                                                                                                                               | Page |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.11      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)                                                                                      | 85   |
| 4.12      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle)                                                                                      | 85   |
| 4.13      | Variation of peak current ratio of corresponding peak ( $I_{pa1}/I_{pc1}$ ) and anodic peak ( $I_{pa0}/I_{pa1}$ ) vs scan rate ( $v$ ) of 2mM catechol + 250mM diethylamine in the second scan of potential of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s | 86   |
| 4.14      | Plots of current function ( $I_p/v^{1/2}$ ) versus scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode in Appeared anodic peak                                                                                               | 86   |
| 4.15      | Plots of peak potential ( $E_p$ ) versus scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)                                                                                                         | 87   |
| 4.16      | Plots of peak potential ( $E_p$ ) versus scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) of 2 <sup>nd</sup> cycle                                                                                                        | 87   |
| 4.17      | Cyclic voltammogram of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 3) at different scan rate (1 <sup>st</sup> cycle)                                                                                                                         | 88   |
| 4.18      | Cyclic voltammogram of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 3) at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                         | 88   |
| 4.19      | Cyclic voltammogram of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 5) at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                         | 89   |
| 4.20      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 9) at different scan rate (1 <sup>st</sup> cycle)                                                                                                                         | 89   |
| 4.21      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 9) at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                         | 90   |
| 4.22      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) at different scan rate (1 <sup>st</sup> cycle)                                                                                                                        | 90   |



| Figure No | Description                                                                                                                                                                           | Page |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.23      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) at different scan rate (2 <sup>nd</sup> cycle)                                    | 91   |
| 4.24      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 3) at 1 <sup>st</sup> cycle | 91   |
| 4.25      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 3) at 2 <sup>nd</sup> cycle | 92   |
| 4.26      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 5) at 2 <sup>nd</sup> cycle | 92   |
| 4.27      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 9) (1 <sup>st</sup> cycle)  | 93   |
| 4.28      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 9) (2 <sup>nd</sup> cycle)  | 93   |
| 4.29      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) (1 <sup>st</sup> cycle) | 94   |
| 4.30      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) (2 <sup>nd</sup> cycle) | 94   |
| 4.31      | Cyclic voltammogram of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1 <sup>st</sup> cycle)                                     | 95   |
| 4.32      | Cyclic voltammogram of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2 <sup>nd</sup> cycle)                                     | 95   |
| 4.33      | Cyclic voltammogram of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1 <sup>st</sup> cycle)                                     | 96   |
| 4.34      | Cyclic voltammogram of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2 <sup>nd</sup> cycle)                                     | 96   |



| Figure No | Description                                                                                                                                                                           | Page |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.35      | Cyclic voltammogram of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1 <sup>st</sup> cycle)                                     | 97   |
| 4.36      | Cyclic voltammogram of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2 <sup>nd</sup> cycle)                                     | 97   |
| 4.37      | Cyclic voltammogram of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1 <sup>st</sup> cycle)                                     | 98   |
| 4.38      | Cyclic voltammogram of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2 <sup>nd</sup> cycle)                                     | 98   |
| 4.39      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)  | 99   |
| 4.40      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle)  | 99   |
| 4.41      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 1 <sup>st</sup> cycle | 100  |
| 4.42      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle)  | 100  |
| 4.43      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)  | 101  |
| 4.44      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle)  | 101  |
| 4.45      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)  | 102  |
| 4.46      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle)  | 102  |

| Figure No | Description                                                                                                                                                                                                                                                                                                                                                                                            | Page |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.47      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at different scan rate (1 <sup>st</sup> cycle) (Where A <sub>1</sub> = 1 <sup>st</sup> oxidation peak, A <sub>2</sub> = 2 <sup>nd</sup> oxidation peak, C <sub>0</sub> = Appeared reduction peak, C <sub>1</sub> = 1 <sup>st</sup> reduction peak, C <sub>2</sub> = 2 <sup>nd</sup> reduction peak) | 103  |
| 4.48      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at different scan rate (2 <sup>nd</sup> cycle), A <sub>0</sub> = Appeared oxidation peak                                                                                                                                                                                                            | 103  |
| 4.49      | Plots of peak current (I <sub>p</sub> ) versus square root of scan rate (v <sup>1/2</sup> ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)                                                                                                                                                                                                     | 104  |
| 4.50      | Plots of peak current (I <sub>p</sub> ) versus square root of scan rate (v <sup>1/2</sup> ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle)                                                                                                                                                                                                     | 104  |
| 4.51      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) at different scan rate (1 <sup>st</sup> cycle)                                                                                                                                                                                                                                                      | 105  |
| 4.52      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                                                                                                                                                      | 105  |
| 4.53      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 9) at different scan rate (1 <sup>st</sup> cycle)                                                                                                                                                                                                                                                      | 106  |
| 4.54      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 9) at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                                                                                                                                                      | 106  |
| 4.55      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 11) at different scan rate (1 <sup>st</sup> cycle)                                                                                                                                                                                                                                                     | 107  |
| 4.56      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 11) at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                                                                                                                                                     | 107  |
| 4.57      | Plots of peak current (I <sub>p</sub> ) versus square root of scan rate (v <sup>1/2</sup> ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) (1 <sup>st</sup> cycle)                                                                                                                                                                                                     | 108  |
| 4.58      | Plots of peak current (I <sub>p</sub> ) versus square root of scan rate (v <sup>1/2</sup> ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) (2 <sup>nd</sup> cycle)                                                                                                                                                                                                     | 108  |



| Figure No | Description                                                                                                                                                                           | Page |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.59      | Plots of peak current ( $I_p$ ) versus square root of Scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol at Au electrode in buffer solution (pH 9) (1 <sup>st</sup> cycle)  | 109  |
| 4.60      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol at Au electrode in buffer solution (pH 9) (2 <sup>nd</sup> cycle)  | 109  |
| 4.61      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol at Au electrode in buffer solution (pH 11) (1 <sup>st</sup> cycle) | 110  |
| 4.62      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol at Au electrode in buffer solution (pH 11) (2 <sup>nd</sup> cycle) | 110  |
| 4.63      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                     | 111  |
| 4.64      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                     | 111  |
| 4.65      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at Pt electrode (1 <sup>st</sup> cycle)  | 112  |
| 4.66      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at Pt electrode (2 <sup>nd</sup> cycle)  | 112  |
| 4.67      | Plots of peak potential ( $E_p$ ) versus different scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at Pt electrode (1 <sup>st</sup> cycle)           | 113  |
| 4.68      | Plots of peak potential ( $E_p$ ) versus different scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at Pt electrode (2 <sup>nd</sup> cycle)           | 113  |
| 4.69      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                     | 114  |
| 4.70      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                     | 114  |



| Figure No | Description                                                                                                                                                                          | Page |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.71      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) at different scan rate at Pt electrode (1 <sup>st</sup> cycle)                                    | 115  |
| 4.72      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                    | 115  |
| 4.73      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                    | 116  |
| 4.74      | Cyclic voltammogram of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                    | 116  |
| 4.75      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) at Pt electrode (1 <sup>st</sup> cycle) | 117  |
| 4.76      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) at Pt electrode (2 <sup>nd</sup> cycle) | 117  |
| 4.77      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) at Pt electrode (1 <sup>st</sup> cycle) | 118  |
| 4.78      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) of Pt electrode (2 <sup>nd</sup> cycle) | 118  |
| 4.79      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) at Pt electrode (1 <sup>st</sup> cycle) | 119  |
| 4.80      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) at Pt electrode (2 <sup>nd</sup> cycle) | 119  |
| 4.81      | Cyclic voltammogram of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                    | 120  |
| 4.82      | Cyclic voltammogram of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                    | 120  |
| 4.83      | Cyclic voltammogram of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                    | 121  |

| Figure No | Description                                                                                                                                                                          | Page |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.84      | Cyclic voltammogram of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                    | 121  |
| 4.85      | Cyclic voltammogram of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                    | 122  |
| 4.86      | Cyclic voltammogram of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate Pt electrode (2 <sup>nd</sup> cycle)                                       | 122  |
| 4.87      | Cyclic voltammogram of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (1 <sup>st</sup> cycle)                                    | 123  |
| 4.88      | Cyclic voltammogram of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) at different scan rate of Pt electrode (2 <sup>nd</sup> cycle)                                    | 123  |
| 4.89      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode (1 <sup>st</sup> cycle) | 124  |
| 4.90      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode (2 <sup>nd</sup> cycle) | 124  |
| 4.91      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode (1 <sup>st</sup> cycle) | 125  |
| 4.92      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) Pt electrode (2 <sup>nd</sup> cycle)    | 125  |
| 4.93      | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode (1 <sup>st</sup> cycle) | 126  |
| 4.94      | Plots of peak current versus square root of scan rate of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) Pt electrode (2 <sup>nd</sup> cycle)                            | 126  |
| 4.95      | Plots of peak current versus square root of scan rate of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode (1 <sup>st</sup> cycle)                         | 127  |



| <b>Figure No</b> | <b>Description</b>                                                                                                                                               | <b>Page</b> |
|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 4.96             | Plots of peak current versus square root of scan rate of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode (2 <sup>nd</sup> cycle)     | 127         |
| 4.97             | Comparison of cyclic voltammogram of pH (3, 5, 7, 9, 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1 <sup>st</sup> cycle)        | 128         |
| 4.98             | Comparison of cyclic voltammogram of pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)     | 128         |
| 4.99             | Plots of peak current ( $I_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1 <sup>st</sup> cycle)   | 129         |
| 4.100            | Plots of peak current ( $I_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)   | 129         |
| 4.101            | Plots of peak potential ( $E_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1 <sup>st</sup> cycle) | 130         |
| 4.102            | Plots of peak potential ( $E_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle) | 130         |
| 4.103            | Cyclic voltammogram of pH comparison (3, 7, 9 and 11) of 250mM diethylamine + 2mM catechol at Au electrode and at scan rate 0.1V/s (1 <sup>st</sup> cycle)       | 131         |
| 4.104            | Cyclic voltammogram of pH comparison (3, 7, 9 and 11) of 250mM diethylamine + 2mM catechol at Au electrode and at scan rate 0.1V/s (2 <sup>nd</sup> cycle)       | 131         |
| 4.105            | Plots of peak current ( $I_p$ ) versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (1 <sup>st</sup> cycle)                       | 132         |
| 4.106            | Plots of peak ( $I_p$ ) current versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                       | 132         |
| 4.107            | Plots of peak potential ( $E_p$ ) versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                     | 133         |



| <b>Figure No</b> | <b>Description</b>                                                                                                                                                                                           | <b>Page</b> |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 4.108            | Cyclic voltammogram of pH comparison (3, 5, 7 and 9) of 250mM diethylamine + 2mM catechol at 0.1V/s scan rate of Pt electrode (1 <sup>st</sup> cycle)                                                        | 133         |
| 4.109            | Cyclic voltammogram of pH comparison (3, 5, 7 and 9) of 250mM diethylamine + 2mM catechol at scan rate 0.1V/s of Pt electrode (2 <sup>nd</sup> cycle)                                                        | 134         |
| 4.110            | Plots of peak ( $I_p$ ) current versus pH of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                   | 134         |
| 4.111            | Plots of peak potential ( $E_p$ ) versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                 | 135         |
| 4.112            | Comparison of cyclic voltammogram of different concentration (150, 200, 250, 300, 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) (1 <sup>st</sup> cycle)              | 135         |
| 4.113            | Comparison of cyclic voltammogram of different concentration (100, 150, 200, 250, 300, 350 and 400mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) (2 <sup>nd</sup> cycle) | 136         |
| 4.114            | Plots of peak current ( $I_p$ ) versus concentration (C) (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol at GC electrode in buffer solution (pH 7) 1 <sup>st</sup> cycle                 | 136         |
| 4.115            | Plots of peak current ( $I_p$ ) versus different concentration (C) of diethylamine + fixed 2mM catechol at GC electrode in buffer solution (pH 7) 2 <sup>nd</sup> cycle                                      | 137         |
| 4.116            | CV of concentration comparison (150, 250, 300 and 350mM) of diethylamine + 2mM catechol at Au electrode in buffer solution (pH 7) and at scan rate 0.1V/s (1 <sup>st</sup> cycle)                            | 137         |
| 4.117            | CV of concentration comparison (150, 250, 300 and 350mM) of diethylamine + 2mM catechol at Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                | 138         |
| 4.118            | Concentration comparison of (150, 200, 250, 300 and 350mM) diethylamine + 2mM catechol in buffer solution (pH 7) at scan rate 0.1V/s of Pt electrode (1 <sup>st</sup> cycle)                                 | 138         |
| 4.119            | Concentration comparison of (150, 200, 250, 300 and 350mM) diethylamine + 2mM catechol in buffer solution (pH 7) at scan rate 0.1V/s of Pt electrode (2 <sup>nd</sup> cycle)                                 | 139         |

| Figure No | Description                                                                                                                                                                                                                                  | Page |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.120     | CV of composition change of catechol (2, 5, 10 and 15 mM) + the fixed composition (250 mM) of diethylamine of GC (3mm) electrode at pH7 and scan rate $0.1\text{Vs}^{-1}$ (2 <sup>nd</sup> cycle)                                            | 139  |
| 4.121     | Plots of appeared anodic peak ( $A_0$ ) and anodic peak ( $A_1$ ) current, $I_p$ vs concentration, $C$ of catechol (fixed 250mM diethylamine) in the same condition                                                                          | 140  |
| 4.122     | Comparison of CV of 2mM catechol + 250mM diethylamine in GC electrode (3.0mm), Au electrode (1.6mm) and Pt electrode (1.6mm) at pH 7 and scan rate $0.1\text{V/s}$ (1 <sup>st</sup> cycle)                                                   | 140  |
| 4.123     | Comparison of CV of 2mM catechol + 250mM diethylamine in GC electrode (3.0mm), Au electrode (1.6mm) and Pt electrode (1.6mm) at pH 7 and scan rate $0.1\text{V/s}$ (2 <sup>nd</sup> cycle)                                                   | 141  |
| 4.124     | Cyclic voltammogram of 15 cycle of 250mM diethylamine + 2mM catechol at GC electrode in buffer solution (pH 7) at scan rate $0.1\text{V/s}$                                                                                                  | 141  |
| 4.125     | Plots of peak current ( $I_p$ ) versus number of cycles of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at GC electrode and scan rate $0.1\text{V/s}$                                                                         | 142  |
| 4.126     | Cyclic voltammogram of 15 cycle of 250mM diethylamine + 2mM catechol at Au electrode in Buffer solution (pH 7) and at scan rate $0.1\text{V/s}$                                                                                              | 142  |
| 4.127     | Cyclic voltammogram of 15 cycle of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) at scan rate $0.1\text{V/s}$ of Pt electrode                                                                                                  | 143  |
| 4.128     | Cyclic voltammograms of 0.5mM Catechol in presence of 1mM diethylamine of GC electrode during controlled potential coulometry at potential 0.5V in pH 7 at scan rate $0.1\text{V/s}$                                                         | 143  |
| 4.129     | Differential pulse voltammogram (DPV) of pH (3, 5, 7 and 9) comparison of 250mM diethylamine + 2mM catechol at GC electrode and at scan rate $0.1\text{V/s}$ (1 <sup>st</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms) | 144  |
| 4.130     | DPV of pH (3, 5, 7 and 9) comparison of 250mM diethylamine + 2mM catechol at GC electrode and at scan rate $0.1\text{V/s}$ (2 <sup>nd</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                                   | 144  |
| 4.131     | Differential pulse voltammogram (DPV) of pH comparison of 250mM diethylamine + 2mM catechol of Au electrode at scan rate $0.1\text{V/s}$ (1 <sup>st</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                     | 145  |



| <b>Figure No</b> | <b>Description</b>                                                                                                                                                                                                             | <b>Page</b> |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 4.132            | DPV of pH comparison of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                                                  | 145         |
| 4.133            | DPV of pH comparison of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1V/s (1 <sup>st</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                                                  | 146         |
| 4.134            | DPV of pH comparison of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                                                  | 146         |
| 4.135            | Differential pulse voltammogram (DPV) of deposition time change (0, 10, 30, 90 and 120s) of 2mM catechol + 250mM diethylamine of pH7 at $E_{\text{pulse}}$ 0.02V, $t_{\text{pulse}}$ 20ms and scan rate 0.1Vs <sup>-1</sup>    | 147         |
| 4.136            | DPV of concentration comparison of different mM diethylamine and fixed 2mM catechol of GC electrode and scan rate 0.1V/s (1 <sup>st</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                       | 147         |
| 4.137            | DPV of concentration comparison of different mM diethylamine and fixed 2mM catechol of GC electrode and scan rate 0.1V/s (2 <sup>nd</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20ms)                       | 148         |
| 4.138            | DPV of concentration comparison of different mM diethylamine + fixed 2mM catechol of Au electrode at scan rate 0.1V/s in buffer solution (pH 7) (1 <sup>st</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20s) | 148         |
| 4.139            | DPV of concentration comparison of different mM diethylamine + fixed 2mM catechol of Au electrode at scan rate 0.1V/s in buffer solution (pH 7) (2 <sup>nd</sup> cycle) ( $E_{\text{pulse}}$ 0.02V and $t_{\text{pulse}}$ 20s) | 149         |
| 4.140            | CV of concentration comparison (150,200, 250, 300 and 350mM) of diethylamine + 2mM catechol at Pt electrode in buffer solution (pH 7) and at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                          | 149         |
| 4.141            | CV of concentration comparison (150,200, 250, 300 and 350mM) of diethylamine + 2mM catechol at Pt electrode in buffer solution (pH 7) and at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                          | 150         |
| 4.142            | Comparison of FTIR of only catechol, only diethylamine and catechol-diethylamine adduct                                                                                                                                        | 150         |
| 4.143            | Chronoamperogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 0.32V potential                                                                                                             | 151         |



| Figure No | Description                                                                                                                                                                                                                                                                                                                                                                | Page |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.144     | Cottrell plots of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 0.32V potential                                                                                                                                                                                                                                                           | 151  |
| 4.145     | Chronoamperogram of 250mM diethylamine + 2mM catechol at Au electrode in buffer solution (pH 7) (potential 0.31V)                                                                                                                                                                                                                                                          | 152  |
| 4.146     | Cottrell plots of 250mM diethylamine + 2mM catechol at Au electrode in buffer solution (pH 7) (potential 0.31V)                                                                                                                                                                                                                                                            | 152  |
| 4.147     | Comparison of cyclic voltammogram of only 2mM sulfanilic acid (red), only 2mM catechol (blue), 2mM catechol + 2mM sulfanilic acid (black) of GC electrode in buffer solution (pH 3) at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                                                                                                                            | 153  |
| 4.148     | Comparison of cyclic voltammogram of only 2mM sulfanilic acid, only 2mM catechol, 2mM catechol + 2mM sulfanilic acid of GC electrode buffer solution (pH 3) at scan rate 0.1V/s (2 <sup>nd</sup> cycle). A <sub>0</sub> = Appeared anodic peak, A <sub>1</sub> = 1 <sup>st</sup> anodic peak, A <sub>2</sub> = 2 <sup>nd</sup> anodic peak, C <sub>1</sub> = cathodic peak | 153  |
| 4.149     | Comparison of cyclic voltammogram of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                                                                                                                                              | 154  |
| 4.150     | Comparison of cyclic voltammogram of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s (2 <sup>nd</sup> cycle), C <sub>0</sub> = appeared cathodic peak, C <sub>2</sub> = 2 <sup>nd</sup> cathodic peak                                                                     | 154  |
| 4.151     | Comparison of cyclic voltammogram of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Pt electrode buffer solution (pH 3) at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                                                                                                                                                 | 155  |
| 4.152     | Comparison of cyclic voltammogram of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Pt electrode buffer solution (pH 3) at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                 | 155  |
| 4.153     | Cyclic voltammogram of 15 cycles of 2mM catechol + 2mM sulfanilic acid in buffer solution (pH 3) of GC electrode at scan rate 0.1V/s                                                                                                                                                                                                                                       | 156  |
| 4.154     | Plots of peak current (I <sub>p</sub> ) versus number of cycles of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of GC electrode at scan rate 0.1V/s                                                                                                                                                                                                        | 156  |
| 4.155     | Cyclic voltammogram of 15 cycles of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Au electrode at scan rate 0.1V/s                                                                                                                                                                                                                                       | 157  |

| Figure No | Description                                                                                                                                                                                                                                                                 | Page |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.156     | Cyclic voltammogram of 15 cycles of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Pt electrode at scan rate 0.1V/s                                                                                                                                        | 157  |
| 4.157     | Cyclic voltammogram of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                          | 158  |
| 4.158     | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) at GC electrode (2 <sup>nd</sup> cycle)                                                                                       | 158  |
| 4.159     | Variation of peak current ratio of corresponding peak ( $I_{pa1}/I_{pc1}$ ) and anodic peak ( $I_{pa1}/I_{pa0}$ ) vs scan rate ( $v$ ) of 2mM catechol + 2 mM sulfanilic acid in the second scan of potential at GC electrode in buffer solution (pH 3) at scan rate 0.1V/s | 159  |
| 4.160     | Plots of current function ( $I_p/v^{1/2}$ ) versus scan rate ( $v$ ) of 2mM catechol + 2mM sulfanilic acid in buffer solution (pH 3) at GC electrode in appeared peak of oxidation                                                                                          | 159  |
| 4.161     | Plots of peak potential ( $E_p$ ) versus scan rate ( $v$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) at GC electrode (2 <sup>nd</sup> cycle)                                                                                                          | 160  |
| 4.162     | Cyclic voltammogram of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Au electrode at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                          | 160  |
| 4.163     | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) at Au electrode (2 <sup>nd</sup> cycle)                                                                                       | 161  |
| 4.164     | Cyclic voltammogram of 2mM sulfanilic acid + 2mM Catechol in buffer solution (pH 3) of Pt electrode at different scan rate (2 <sup>nd</sup> cycle)                                                                                                                          | 161  |
| 4.165     | Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM sulfanilic acid + 2mM Catechol in buffer solution (pH 3) at Pt electrode (2 <sup>nd</sup> cycle)                                                                                       | 162  |
| 4.166     | Cyclic voltammogram of pH comparison (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (1 <sup>st</sup> cycle)                                                                                                                   | 162  |
| 4.167     | Cyclic voltammogram of pH comparison (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                   | 163  |
| 4.168     | Plots of peak current ( $I_p$ ) versus different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                    | 163  |



| Figure No | Description                                                                                                                                                                                                                                                                                                                                       | Page |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.169     | Plots of peak potential vs different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                                      | 164  |
| 4.170     | Cyclic voltammogram of pH comparison (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                                         | 164  |
| 4.171     | Plots of peak current ( $I_p$ ) versus pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                                    | 165  |
| 4.172     | Plots of peak potential ( $E_p$ ) versus pH of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                                                     | 165  |
| 4.173     | Cyclic voltammogram of pH comparison (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                                         | 166  |
| 4.174     | Plots of peak current ( $I_p$ ) versus pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol at Pt electrode and at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                                | 166  |
| 4.175     | Plots of peak potential ( $E_p$ ) versus pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol at Pt electrode and at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                                              | 167  |
| 4.176     | Cyclic voltammogram of concentration comparison (2, 10, 20, 30 and 40) mM sulfanilic acid + fixed 2mM catechol in buffer solution (pH 3) of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle). $A_0$ = appeared anodic peak, $A_1$ = 1 <sup>st</sup> anodic peak, $A_2$ = 2 <sup>nd</sup> anodic peak, $A_3$ = 3 <sup>rd</sup> anodic peak | 167  |
| 4.177     | Plots of peak current ( $I_p$ ) versus concentration of sulfanilic acid (2, 10, 20, 30 and 40) mM + fixed 2mM catechol in buffer solution (pH 3) of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                      | 168  |
| 4.178     | Cyclic voltammogram of concentration comparison (2, 10, 20, 30 and 40) mM sulfanilic acid + fixed 2mM catechol in buffer solution (pH 3) of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                              | 168  |
| 4.179     | Cyclic voltammogram of concentration comparison (2, 10, 20, 30 and 40) mM sulfanilic acid + fixed 2mM catechol in buffer solution (pH 3) Pt electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                                                                                                                 | 169  |
| 4.180     | CV of composition change of catechol (2, 4 and 6mM) + the fixed composition (2mM) of sulfanilic acid of GC (3mm) electrode at pH3 and at scan rate 0.1Vs <sup>-1</sup> (2 <sup>nd</sup> cycle)                                                                                                                                                    | 169  |



| Figure No | Description                                                                                                                                                                                                                      | Page |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.181     | Plots of anodic peak current ( $I_p$ ) vs concentration, C of catechol (fixed 2mM sulfanilic acid) in the same condition                                                                                                         | 170  |
| 4.182     | Plots of peak potential ( $E_p$ ) versus concentration (C) of catechol (2, 4 and 6 mM) + fixed 2mM sulfanilic acid in buffer solution (pH 3) at GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                         | 170  |
| 4.183     | Cyclic voltammogram of 1mM Catechol in presence of 1mM sulfanilic acid of GC electrode during controlled potential coulometry at 0.5V in pH 3 at scan rate 0.1V/s                                                                | 171  |
| 4.184     | Cyclic voltammogram of electrode comparison (GC, Au and Pt) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH3) at scan rate 0.1V/s (2 <sup>nd</sup> cycle)                                                           | 171  |
| 4.185     | Differential pulse voltammogram (DPV) of electrode comparison (GC, Au, Pt) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) at scan rate 0.1V/s (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms   | 172  |
| 4.186     | DPV of pH comparison 2mM sulfanilic acid + 2mM Catechol of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms                                                                      | 172  |
| 4.187     | DPV of pH comparison 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms                                                                      | 173  |
| 4.188     | DPV of pH comparison of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms                                                                   | 173  |
| 4.189     | DPV of deposition time change of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of GC electrode at scan rate 0.1V/s, $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms                                                        | 174  |
| 4.190     | DPV of concentration comparison of different concentration of sulfanilic acid + fixed 2mM catechol in buffer solution (pH 3) of GC electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms | 174  |
| 4.191     | DPV of concentration comparison of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms                                                        | 175  |
| 4.192     | DPV of concentration comparison in different concentration of sulfanilic acid + fixed 2mM catechol of Pt electrode at scan rate 0.1V/s in buffer solution (pH 3) (2 <sup>nd</sup> cycle), $E_{pulse}$ 0.02V and $t_{pulse}$ 20ms | 175  |
| 4.193     | Comparison of FTIR of only catechol, only sulfanilic acid and catechol-sulfanilic acid adduct                                                                                                                                    | 176  |

| Figure No | Description                                                                                                                                                                                                                            | Page |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.194     | Chronoamperometry curve of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) for forward direction of GC electrode at potential 0.34V                                                                                       | 176  |
| 4.195     | Chronoamperometry curve of 2mM sulfanilic acid + 2mM catechol of Au electrode in buffer solution (pH 3)                                                                                                                                | 177  |
| 4.196     | Cottrell plots of the background subtracted currents for 2mM catechol + 2mM sulfanilic acid in buffer solution (pH 3) at GC electrode                                                                                                  | 177  |
| 4.197     | Cottrell plots of the background subtracted currents for 2mM catechol + 2mM sulfanilic acid in buffer solution (pH 3) at Au electrode                                                                                                  | 178  |
| 4.198     | Comparison of CV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 10mM SA + 10mM DEA in buffer solution pH 7 of GC electrode at scan rate 0.1V/s. Inset: appeared anodic peak                     | 178  |
| 4.199     | Comparison of DPV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 10mM SA + 10mM DEA in buffer solution pH 7 of GC electrode at scan rate 0.1V/s                                                 | 179  |
| 4.200     | Comparison of CV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 10mM SA + 50mM DEA in buffer solution pH 7 of GC electrode at scan rate 0.1V/s. Inset: appeared anodic peak                     | 179  |
| 4.201     | Comparison of DPV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 10mM SA + 50mM DEA in buffer solution pH 7 of GC electrode at scan rate 0.1V/s                                                 | 180  |
| 4.202     | Comparison of CV of 2mM catechol in presence of 2mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 2mM (SA) + 50mM DEA in buffer solution pH 7 of GC electrode at scan rate 0.1V/s. Inset: appeared anodic peak                     | 180  |
| 4.203     | Comparison of DPV of 2mM catechol in presence of 2mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 2mM SA + 50mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1V/s                                                 | 181  |
| 4.204     | Comparison of CV of 2mM catechol in presence of 40mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 40mM SA + 10mM (DEA) in buffer solution pH 7 of GC electrode at scan rate 0.1V/s. Inset: appeared anodic peak and cathodic peak | 181  |
| 4.205     | Comparison of DPV of 2mM catechol in presence of 40mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 40mM SA + 10mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1V/s                                               | 182  |



## CHAPTER I

### Introduction

#### 1.1 General

Electrochemistry has become a powerful tool for the study of chemical reaction. The majority of organic electrode reactions are characterized by the generation of a reactive intermediate at the electrode by electron transfer and subsequent chemical reactions. The electrochemical generation and study of the intermediates may be advantageous because of the mild reaction conditions employed and the additional selectivity introduced in controlled-potential experiments [1-2]. The neutral organic compounds through electron transfer reactions are converted to cationic or anionic radicals. Oxidation and reduction of functional groups are also important transformations in organic synthesis, and the electrochemical methods for such transformations are greener way. Electrochemical study of different organic compound has been studied in the presence of various nucleophiles using various electrochemical methods.

Electrochemical methods are divided into static methods and dynamic methods. In static methods no current passes between the electrodes and the concentrations of species in the electrochemical cell remain unchanged, or static. Potentiometry, in which the potential of an electrochemical cell is measured under static conditions, is one of the most important quantitative electrochemical methods. The largest division of electrochemical methods is the group of dynamic methods, in which current flows and concentrations change as the result of a redox reaction. Dynamic methods are further subdivided by whether we choose to control the current or the potential. In controlled-current coulometry, we completely oxidize or reduce the analyte by passing a fixed current through the analytical solution. Controlled-potential methods are subdivided further into controlled-potential coulometry and amperometry, in which a constant potential is applied during the analysis, and voltammetry, in which the potential is systematically varied.

Electrochemical methods also classified as- (1) measuring the potential under static conditions of no current flow; (2) measuring the potential while controlling the current; and (3) measuring the current while controlling the potential.

The analytical advantages of the various voltammetric techniques include excellent sensitivity with a very large useful linear concentration range for both inorganic and organic species, a large number of useful solvents and electrolytes, a wide range of temperatures, rapid analysis times (seconds), simultaneous determination of several analytes, the ability to determine kinetic and mechanistic parameters, a well-developed theory and thus the ability to reasonably estimate the values of unknown parameters, and the ease with which different potential waveforms can be generated and small currents measured.

Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances. Inorganic, physical and biological chemists widely use voltammetric techniques for a variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption and/or diffusion processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes, transport, speciation, and thermodynamic properties of solvated species. Voltammetric methods are also applied to the determination of compounds of pharmaceutical interest and effective tools for the analysis of complex mixtures.

There has been a growing interest in the study of the reactions between quinones produced from the oxidation of 1,2-dihydroxybenzene (catechol), 1,3-dihydroxy benzene (resorcinol), 1,4-dihydroxy benzene (hydroquinone) and nucleophiles for mechanistic [3-7] reasons. Catechol, resorcinol and hydroquinone are the compounds of dihydroxy isomers in which two hydroxyl groups are substituted onto benzene ring. The nucleophilic attacks that lead to the formation of dihydroxybenzene derivatives with more or less positive oxidation potentials are followed by more E (electron transfer) steps and C (chemical reaction) steps depends on the structure of intermediates by EC reaction [8]. The following drug or drug making compounds for example sulfanilic acid, nicotinamide, diethylamine, metronidazole, diisopropylamine, pyridoxine etc. may be used as nucleophiles. Among



them diethylamine are also used as a precursor to two herbicides, dilate and triallate, as well as formation of certain organosulfur drugs [9]. Due to weak alkaline nature it may act a neutral nucleophile and presence of one lone pair electron on nitrogen enables it to take participation in 1,4-Michael addition reaction with o-benzoquinone. Sulfanilic acid and certain related substituted derivatives are of considerable medicinal importance. As the compound readily forms diazo compounds, it is used to make sulfa drugs and dyes [10].

The electrocatalytic effect of catechol in presence of diethylamine and sulfanilic acid for three different electrodes (Au, GC and Pt) and various concentration of diethylamine (150-350mM) and sulfanilic acid (2-40mM) at different scan rate were studied. However because of the importance of aminoquinones as biologically important compounds [11] in this direction that demands detail electrochemical studies of catechol in the presence of diethylamine and sulfanilic acid as representative of secondary aliphatic and aromatic amines. Although the peoples have used the above compounds enormously but the reaction mechanism of most of the compounds are still unknown.

The aim of the present study is thus a fundamental pursuit to have better insight of the possible redox interactions of 1,2-dihydroxybenzene with sulfanilic acid and diethylamine compounds. These compounds undergo oxidation and/or reduction on the electrode surface within the potential range. The electro activity of such compounds depends upon the pH of the medium, nature of the electrode and active moiety (electrophore) present in their structures. Their redox behavior can be influenced by the change in pH, substituents, concentration and scan rate. Cyclic voltammetry (CV), Differential pulse voltammetry (DPV) and Chronoamperometry (CA) techniques have used to study the mechanism the redox processes.

### 1.2.1 Catechol (Cate)

Catechol is also known as 1,2-dihydroxybenzene or pyrocatechol. It's molecular formula is  $C_6H_4(OH)_2$  shown in Figure 1.1. It is the ortho isomer of the three isomeric benzenediols. This colorless compound occurs naturally in trace amounts. The cate skeleton occurs in a variety of natural products such as urushiols, which are the skin-irritating poisons are

found in plants [12]. It occurs as feathery white crystals which are very rapidly soluble in water.

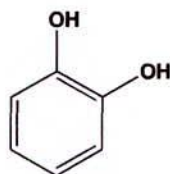


Figure 1.1: Structure of catechol

### 1.2.2 Natural occurrence of Cate

Cate is a natural polyphenolic compound that widely exists in higher plants such as tea, vegetables, fruits, tobacco and in crude beet sugar coal and some traditional Chinese medicines. It is also found in the leaves and branches of oak and willow trees. Cate moieties are also found widely within the natural world.

### 1.2.3 Use of Cate

Cate is an organic aromatic compound, appearing under the form of colorless solid flakes which darken upon exposure to air and light. Cate is mainly used as an intermediate for the synthesis of pharmaceuticals, agrochemicals and in formulation. Cate is a precursor to various flavorings such as vanillin or eugenol (synthetic “vanilla” aroma and flavor), used in food industry, perfumery, home and personal care products. The Cate route of vanillin synthesis is far more environmentally friendly than the o-nitrochlorobenzene route. The production is performed using conventional closed vessels.

### 1.2.4 Diethylamine

Diethylamine is an organic compound with the molecular formula  $(C_2H_5)_2NH$  shown in Figure 1.2. This secondary amine is a colorless, flammable gas with an ammonia-like odor. It is used as a corrosion inhibitor and in the production of rubber, resins, dyes and pharmaceuticals. Diethylamine is commonly encountered commercially as a solution in water at concentrations up to around 40%. It is also found as a natural product [9].



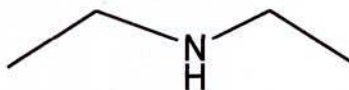


Figure 1.2: Structure of diethylamine

### 1.2.5 Use of Diethylamine

Diethylamine is a precursor to several industrially significant compounds. It reacts with carbon disulfide to give diethyl dithiocarbamate, a precursor to a family of chemicals widely used in the vulcanization of rubber. The solvents diethylformamide and diethylacetamide are derived from diethylamine. It is raw material for the production of many agrichemicals and pharmaceuticals, such as dimefox and diphenhydramine, respectively. The chemical weapon tabun is derived from diethylamine. The surfactant lauryl diethylamine oxide is found in soaps and cleaning compounds. Unsymmetrical diethylhydrazine, a rocket fuel, is prepared from diethylamine.

### 1.2.6 Sulfanilic acid

The Sulfanilic acid (p-aminobenzene sulfonic acid) shown in Figure 1.4, is an important and interesting compound, which finds a number of applications in the syntheses of organic dyes. Sulfanilic acid and certain related substituted derivatives are of considerable medicinal importance as the sulfa drugs. Although they have been supplanted to a wide extent by antibiotics such as penicillin, tetramycin, chloromycetin, and aureomycin, the sulfa drugs still have their medical uses, and make up a considerable portion of the output of the pharmaceutical sector [10].



Figure 1.4: Structure of sulfanilic acid

### 1.2.7 Use of Sulfanilic acid

It is used to make dyes and sulpha drugs. It is also used in the manufacture pesticides which can cure wheat rust disease. In addition, it can be used in many organic syntheses. For example: it reacts with 6-chloro-pyrimidine-2,4-diamine to get 2,4-diamino-6-p-sulphoanilinopyrimidine. This reaction needs reagent HCl and solvent ethanol by heating. The reaction time is 4.0 hours.

### 1.3 Electrochemical properties of Catechol derivatives

The electrochemical study of catechols in the presence of some other nucleophiles such as methanol, 4-hydroxycoumarin, ethanol, 2-thiobarbituric acid,  $\beta$ -diketones, 4-hydroxy-6-methyl-2-pyrone, 2-thiouracil, dimedone, 4,7-dihydroxycoumarin, 4,5,7-trihydroxycoumarin, 4-hydroxy-6-bromocoumarin, 3-hydroxycoumarin, 4-hydroxy-6-methyl-a-pyrone, 4-hydroxy-6-methyl-2-pyridone, 4-hydroxycarbostyrile, sulfonic acid and 4-amino-3-thio-1,2,4-triazole were studied [13-27].

Few works have been done on electrochemical oxidation of catechols with amines [11]. They were studied the electrocatalytic effect of catechol with amines in only GC electrode and limited concentration and pH. However, Aminoquinones are biologically important compounds in this direction, therefore, it demand detail electrochemical studies of catechol in the presence of amines. In this research work, we have studied the electrocatalytic effect of catechol in presence of diethylamine, sulfanilic acid and their mixtures for three different electrodes (Au, GC and Pt) and various concentration (diethylamine (100-350mM), sulfanilic acid (2-40mM)) and different pH (2-11)) at different scan rate. The primary aim of the present study is thus a fundamental realization to have better insight of the possible redox interactions of 1,2-dihydroxybenzene with sulfanilic acid and diethylamine compounds. To the best of our knowledge, comparison of electrochemical study of catechol with diethylamine, sulfanilic acid and their mixtures at different conditions has not been reported before this work.



### 1.4 Objectives of this Thesis

Attempt will be made in the present research work is systematic study of electro-synthesis and mechanism of redox process of biologically important catechol compound and its amine derivatives which may be help to understand the role of the derivatives in the biological processes. Electrochemical study of nucleophilic substitution reactions of catechol in presence of diethylamine, sulfanilic acid and catechol in presence of mixture of sulfanilic acid + diethylamine were carried out in different pH media.

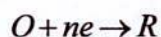
The objectives of this study are:

- ❖ to synthesize biologically important catechol-diethylamine, catechol-sulfanilic acid derivatives by electrochemically.
- ❖ to diagnose the mechanism of the redox processes of these compounds at different pH and different scan rate.
- ❖ to know the redox interaction of the species by Cyclic voltammetry (CV), Controlled potential coulometry (CPC), Differential pulse voltammetry (DPV) and Chronoamperometry (CA) techniques.
- ❖ to study the effect of pH, scan rate, concentration on the voltammogram.
- ❖ to recognize the most favorable condition (concentration, pH) for the reaction.
- ❖ to characterize the new features of the synthesized species by electrochemical and spectral analysis.

## CHAPTER II

**Theoretical Background**

Electroanalytical chemistry encompasses a group of quantitative analytical methods that are based upon the electrical properties of an analyte solution when it is made part of an electrochemical cell. There are two general types of electrochemical methods. Electroanalytical methods are a class of techniques in analytical chemistry which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte. These methods can be broken down into several categories depending on which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential). Voltammetry applies a constant and/or varying potential at an electrode's surface and measures the resulting current with a three electrode system. This method can reveal the reduction potential of an analyte and its electrochemical reactivity. This method in practical terms is nondestructive since only a very small amount of the analyte is consumed at the two-dimensional surface of the working and auxiliary electrodes. In practice the analyte solutions is usually disposed of since it is difficult to separate the analyte from the bulk electrolyte and the experiment requires a small amount of analyte. Electrodes are employed for electrochemical determination of organic molecules as well as metal ions. The electrode can act as a source (for reduction) or a sink (for oxidation) of electrons transferred to or from the species in solution:



Where, O and R are the oxidized and reduced species. In order for the electron transfer to occur, there must be a correspondence between the energies of the electron orbitals where transfer takes place in the donor and acceptor. In the electrode this level is the highest filled orbital, which in a metal is Fermi energy level. In the soluble species it is the orbital of the valence electron to be given or received. For reduction, there is a minimum energy that the transferable electrons from the electrode must have before the transfer can occur,



which corresponds to a sufficiently negative potential. For an oxidation, there is a maximum energy that the lowest unoccupied level in the electrode can have in order to receive electrons from the species in solution, corresponding to a sufficiently positive potential.

In order to study electrode reactions, reproducible experimental conditions must be created which enable minimization of all unwanted factors that can contribute to the measurements and diminish their accuracy. That means to suppress migration effects, confine the interfacial region as close as possible to the electrode, and minimize solution resistance. These objectives are achieved by the addition of large amount (around  $1 \text{ mol dm}^{-3}$ ) of inert electrolyte, the electroactive species being at a concentration of 5 mM or less [28].

Since an electrode predominantly attracts positively and negatively charged species, which may or may not undergo reaction at the surface, it should be remembered that the species may adsorb at the electrode surface. This makes it clear that in the description of any electrode process we have to consider the transport of species to the electrode surface as well as the electrode reaction itself. This transport can occur by diffusion, convection or migration.

## 2.1 Mass transfer process in voltammetry

Mass transfer is the movement of material from one location to another in solution. In electrochemical systems, three modes of mass transport are generally considered which a substance may be carried to the electrode surface from bulk solution including diffusion, convection and migration. Any of these or more than one might be operating in a given experiment which is depended on the experimental conditions.

In general, there are three types of mass transfer processes:

- Migration
- Diffusion
- Convection

### 2.1.1 Migration

Migration is the movement of ions through a solution as a result of electrostatic attraction between the ions and the electrodes. It is the primary cause of mass transfer in the bulk of the solution in a cell. This motion of charged particle through solution, induced by the

charges on the electrodes is called migration [29]. This charge movement constitutes a current. This current is called migration current. The larger the number of different kinds of ions in a given solution, the smaller is the fraction of the total charge that is carried by a particular species. Electrolysis is carried out with a large excess of inert electrolyte in the solution so the current of electrons through the external circuit can be balanced by the passage of ions through the solution between the electrodes, and a minimal amount of the electroactive species will be transported by migration. Migration is the movement of charged species due to a potential gradient. In voltammetric experiments, migration is undesirable but can be eliminated by the addition of a large excess of supporting electrolytes in the electrolysis solution. The effect of migration is applied zero by a factor of fifty to hundred ions excess of an inert supporting electrolyte.

### 2.1.2 Diffusion

Diffusion refers to the process by which molecules intermingle as a result of their kinetic energy of random motion. Whereas a concentration difference between two regions of a solution, ions or molecules move from the more concentrated region to the dilute and leads to a disappearance of the concentration difference.

The one kind of mode of mass transfer is diffusion to an electrode surface in an electrochemical cell. The rate of diffusion is directly proportional to the concentration difference. When the potential is applied, the cations are reduced at the electrode surface and the concentration is decreased at the surface film. Hence a concentration gradient is produced. Finally, the result is that the rates of diffusion current become larger.

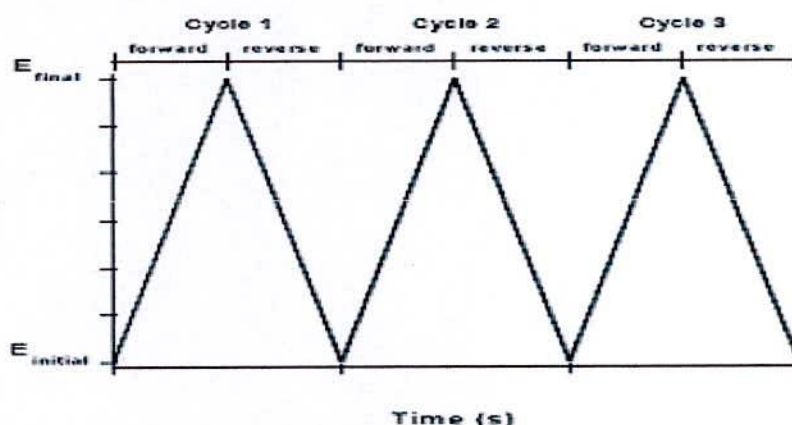
### 2.1.3 Convection

By mechanical way reactants can also be transferred to or from an electrode. Thus forced convection is the movement of a substance through solution by stirring or agitation. This will tend to decrease the thickness of the diffuse layer at an electrode surface and thus decrease concentration polarization. Natural convection resulting from temperature or density differences also contributes to the transport of species to and from the electrode [30]. At the same time a type of current is produced. This current is called convection current. Removing the stirring and heating can eliminate this current. Convection is a far more efficient means of mass transport than diffusion.



## 2.2 Cyclic voltammetry (CV)

Cyclic voltammetry is a very versatile electrochemical technique which allows to probe the mechanics of redox and transport properties of a system in solution. This is accomplished with a three electrode arrangement whereby the potential relative to some reference electrode is scanned at a working electrode while the resulting current flowing through a counter (or auxiliary) electrode is monitored in a quiescent solution. The technique is ideally suited for a quick search of redox couples present in a system; once located, a couple may be characterized by more careful analysis of the cyclic voltammogram. More precisely, the controlling electronic is designed such that the potential between the reference and the working electrodes can be adjusted but the big impedance between these two components effectively forces any resulting current to flow through the auxiliary electrode. Usually the potential is scanned back and forth linearly with time between two extreme values – the switching potentials using triangular potential waveform (see Figure 2.1). When the potential of the working electrode is more positive than that of a redox couple present in the solution, the corresponding species may be oxidized (i.e. electrons going from the solution to the electrode) and produce an anodic current. Similarly, on the return scan, as the working electrode potential becomes more negative than the reduction potential of a redox couple, reduction (i.e. electrons flowing away from the electrode) may occur to cause a cathodic current. By IUPAC convention, anodic currents are positive and cathodic currents negative.

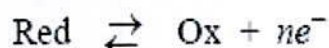


**Figure 2.1: A cyclic voltammetry potential waveform with switching potentials**

The magnitude of the observed faradaic current can provide information on the overall rate of the many processes occurring at the working electrode surface. As is the case for any

multi-step process, the overall rate is determined by the slowest step. For an redox reaction induced at a working electrode, the rate determining step may be any one of the following individual step depending on the system: rate of mass transport of the electro-active species, rate of adsorption or de-sorption at the electrode surface, rate of the electron transfer between the electro-active species and the electrode, or rates of the individual chemical reactions which are part of the overall reaction scheme.

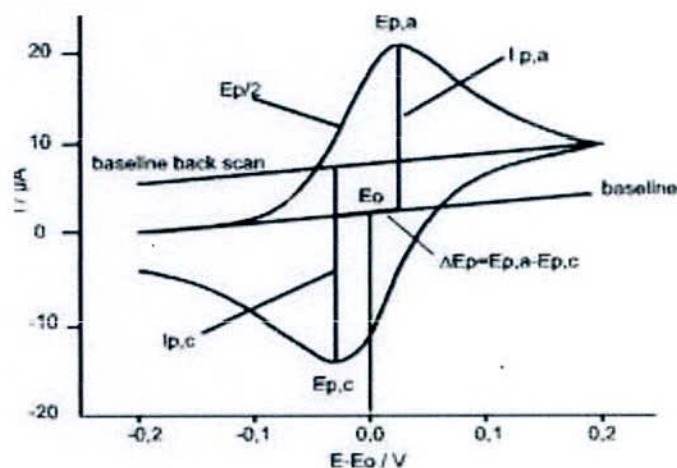
For the oxidation reaction involving  $n$  electrons



the *Nernst Equation* gives the relationship between the potential and the concentrations of the oxidized and reduced form of the redox couple at equilibrium (at 298 K):

$$E = E^0 + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]_e}{[\text{Red}]}$$

where  $E$  is the applied potential and  $E^0$  the formal potential; [OX] and [Red] represent surface concentrations at the electrode/solution interface, *not* bulk solution concentrations. Note that the Nernst equation may or may not be obeyed depending on the system or on the experimental conditions.



**Figure 2.2: The expected response of a reversible redox couple during a single potential cycle**

A typical voltammogram is shown in Figure 2.2. The scan shown starts at a slightly negative potential, (A) up to some positive switching value, (D) at which the scan is reversed back to the starting potential. The current is first observed to peak at  $E_{pa}$  (with value  $i_{pa}$ ) indicating that an oxidation is taking place and then drops due to depletion of the reducing species from the diffusion layer. During the return scan the processes are reversed



(reduction is now occurring) and a peak current is observed at  $E_{pc}$  (corresponding value,  $i_{pc}$ ).

Providing that the charge-transfer reaction is reversible, that there is no surface interaction between the electrode and the reagents, and that the redox products are stable (at least in the time frame of the experiment), the ratio of the reverse and the forward current  $i_{pr}/i_{pf} = 1.0$  (in Figure 2.2  $i_{pa} = i_{pf}$  and  $i_{pc} = i_{pr}$ ). In addition, for such a system it can be shown that:

- ❖ the corresponding peak potentials  $E_{pa}$  and  $E_{pc}$  are independent of scan rate and concentration
- ❖ the formal potential for a reversible couple  $E^0$  is centered between  $E_{pa}$  and  $E_{pc}$ :  $E^0 = (E_{pa} + E_{pc})/2$
- ❖ the separation between peaks is given by  $\Delta E_p = E_{pa} - E_{pc} = 59/n$  mV (for a  $n$  electron transfer reaction) at all scan rates (however, the measured value for a reversible process is generally higher due to uncompensated solution resistance and non-linear diffusion. Larger values of  $\Delta E_p$ , which increase with increasing scan rate, are characteristic of slow electron transfer kinetics).

It is possible to relate the half-peak potential ( $E_{p/2}$ , where the current is half of the peak current) to the polarographic half-wave potential,  $E_{1/2}$ :  $E_{p/2} = E_{1/2} \pm 29\text{mV}/n$  (The sign is positive for a reduction process.)

Simply stated, in the forward scan, the reaction is  $O + e^- \rightarrow R$ ,  $R$  is electrochemically generated as indicated by the cathodic current. In the reverse scan,  $R \rightarrow O + e^-$ ,  $R$  is oxidized back to  $O$  as indicated by the anodic current. The CV is capable of rapidly generating a new species during the forward scan and then probing its fate on the reverse scan. This is a very important aspect of the technique [31].

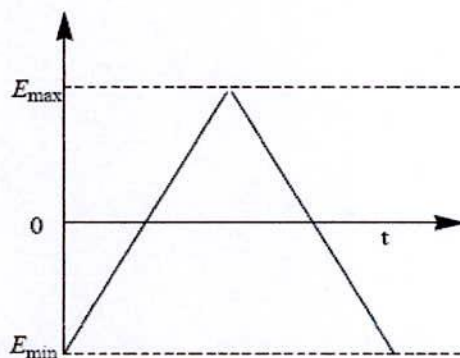


Figure 2.3: Variation of potential with time in cyclic voltammetry

A characteristic feature is the occurrence of peaks, identified by the peak potential  $E_p$ , which corresponds to electron transfer reactions. The repetitive triangular potential excitation signal for CV causes the potential of the working electrode to sweep backward and forward between two designate values (the switching potentials).

In cyclic voltammetry of reversible system, the product of the initial oxidation or reduction is then reduced or oxidized, respectively, on reversing the scan direction.

Adsorbed species lead to changes in the shape of the cyclic voltammogram, since they do not have to diffuse from the electrode surface. In particular, if only adsorbed species are oxidized or reduced, in the case of fast kinetics the cyclic voltammogram is symmetrical, with coincident oxidation and reduction peak potentials [32].

Cyclic voltammetry is one of the most versatile techniques for the study of electroactive species, as it has a provision for mathematical analysis of an electron transfer process at the electrode [33-36]. It is an electroanalytical tool for monitoring and recognition of many electrochemical processes taking place at the surface of electrode and can be used to study redox processes in biochemistry and macromolecular chemistry [37].

### 2.2.1 Single electron transfer process

Based upon the values of electrochemical parameters, i.e., peak potential  $E_p$ , half peak potential ( $E_{p/2}$ ), half wave potential ( $E_{1/2}$ ), peak current ( $I_p$ ), anodic peak potential  $E_{pa}$ , cathodic peak potential  $E_{pc}$  etc, it can be ascertained whether a reaction is reversible, irreversible or quasi-reversible. The electrochemical parameters can be graphically obtained from the voltammogram as shown in the Figure 2.3.

Three types of single electron transfer process can be studied.

- a. Reversible process. b. Irreversible process and c. Quasi-reversible.

#### 2.2.1(a) Reversible processes

The peak current for a reversible couple (at 25°C), is given by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2}$$



where  $n$  is the number of electrons,  $A$  the electrode area (in  $\text{cm}^2$ ),  $C$  the concentration (in  $\text{mol}/\text{cm}^3$ ),  $D$  the diffusion coefficient (in  $\text{cm}^2/\text{s}$ ), and  $v$  the scan rate (in  $\text{V}/\text{s}$ ). Accordingly, the current is directly proportional to concentration and increases with the square root of the scan rate. The ratio of the reverse-to-forward peak currents,  $i_{\text{pr}}/i_{\text{pf}}$ , is unity for a simple reversible couple. This peak ratio can be strongly affected by chemical reactions coupled to the redox process. The current peaks are commonly measured by extrapolating the preceding baseline current. The position of the peaks on the potential axis ( $E_p$ ) is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between  $E_{\text{pa}}$  and  $E_{\text{pc}}$ :

$$E^\circ = (E_{\text{pa}} + E_{\text{pc}})/2$$

The separation between the peak potentials (for a reversible couple) is given by:

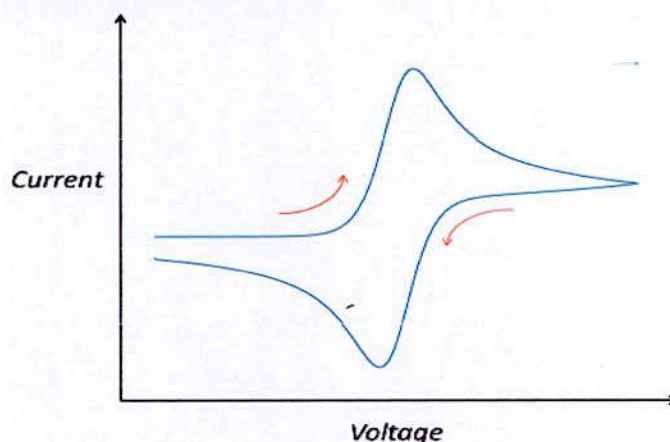
$$\Delta E_p = E_{\text{pa}} - E_{\text{pc}} = 59\text{mV}/n$$

Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nernstian behavior. Accordingly, a fast one-electron process exhibits a  $\Delta E_p$  of about 59 mV. Both the cathodic and anodic peak potentials are independent of the scan rate. It is possible to relate the half-peak potential ( $E_{\text{p}/2}$ , where the current is half of the peak current) to the polarographic half-wave potential,  $E_{1/2}$

$$E_{\text{p}/2} = E_{1/2} \pm 29\text{mV}/n$$

(The sign is positive for a reduction process.) For multi electron-transfer (reversible) processes, the cyclic voltammogram consists of several distinct peaks, if the  $E^\circ$  values for the individual steps are successively higher and are well separated. An example of such mechanism is the six-step reduction of the fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$  to yield the hexaanion products  $\text{C}_{60}^{6-}$  and  $\text{C}_{70}^{6-}$  where six successive reduction peaks can be observed.

The situation is very different when the redox reaction is slow or coupled with a chemical reaction. Indeed, it is these "nonideal" processes that are usually of greatest chemical interest and for which the diagnostic power of cyclic voltammetry is most useful. Such information is usually obtained by comparing the experimental voltammograms with those derived from theoretical (simulated) ones.



**Figure 2.4: Reversible cyclic voltammogram of redox process**

### 2.2.1(b) Irreversible processes

For irreversible processes (those with sluggish electron exchange), the individual peaks are reduced in size and widely separated. Totally irreversible systems are characterized by a shift of the peak potential with the scan rate:

$$E_p = E^\circ - (RT/\alpha n_a F) [0.78 - \ln(k^\circ/(D)^{1/2}) + \ln(\alpha n_a F v / RT)^{1/2}]$$

where  $\alpha$  is the transfer coefficient and  $n_a$  is the number of electrons involved in the charge-transfer step. Thus,  $E_p$  occurs at potentials higher than  $E^\circ$ , with the overpotential related to  $k^\circ$  and  $a$ . Independent of the value  $k^\circ$ , such peak displacement can be compensated by an appropriate change of the scan rate. The peak potential and the half-peak potential (at 25°C) will differ by  $48/\alpha n$  mV. Hence, the voltammogram becomes more drawn-out as  $\alpha n$  decreases.



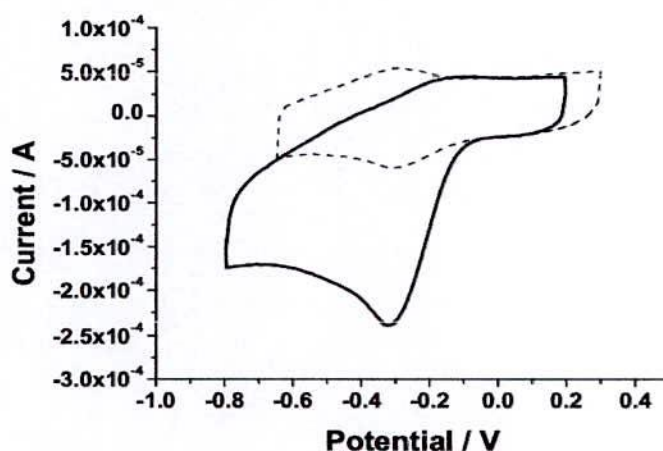


Figure 2.5: Cyclic voltammogram of irreversible redox process

### 2.2.1(c) Quasi-reversible process

Quasi-reversible process is termed as a process, which shows intermediate behavior between reversible and irreversible processes. In such a process the current is controlled by both the charge transfer and mass transfer.

Cyclic voltammogram for quasi-reversible process is shown in Figure 2.6 [38].

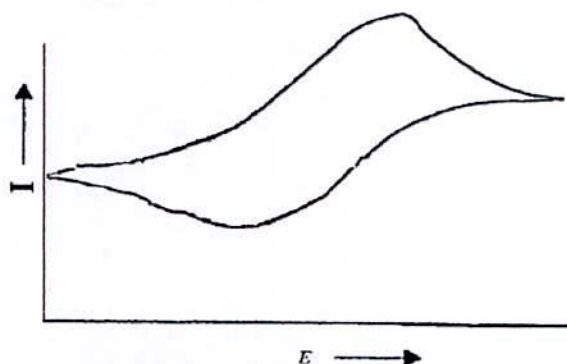


Figure 2.6: Cyclic voltammogram of quasi-reversible redox process

For quasi-reversible process the value of standard heterogeneous electron transfer rate constant,  $k_{sh}^o$  lies in the range of  $10^{-1}$  to  $10^{-5}$  cm sec<sup>-1</sup> [39]. An expression relating the current to potential dependent charge transfer rate was first provided by Matsuda and Ayabe [40].

$$I(t) = C_{o(0,t)} k_{sh}^o \exp\left[-\frac{\alpha n F}{RT} \{E(t) - E^o\}\right] - C_{R(0,t)} k_{sh}^o \exp\left[-\frac{\beta n F}{RT} \{E(t) - E^o\}\right] \dots 2.1$$

where  $k_{sh}^o$  is the heterogeneous electron transfer rate constant at standard potential  $E^o$  of redox system.  $\alpha$  is the transfer coefficient and  $\beta = 1 - \alpha$ . In this case, the shape of the peak and the various peak parameters are functions of  $\alpha$  and the dimensionless parameter,  $\Lambda$ , defined as [41]

$$\Lambda = \frac{k_{sh}^o}{D^{1/2} (nF/RT)^{1/2} \nu^{1/2}} \dots\dots\dots 2.2$$

when  $D_o = D_r = D$

$D_o$  and  $D_r$  are the diffusion coefficients of oxidized and reduced species respectively.

For quasi-reversible process current value is expressed as a function of  $\psi(E)$  [41].

$$I = nFAC_o^* \frac{k_{sh}^o}{\Lambda} \psi(E) \dots\dots\dots 2.3$$

where  $\psi(E)$  is expressed as

$$\psi(E) = \frac{I}{nFAC_o^* D_o^{1/2} (nF/RT)^{1/2} \nu^{1/2}} \dots\dots\dots 2.4$$

It is observed that when  $\Lambda \geq 10$ , the behavior approaches that of a reversible system [42].

For three types of electrode processes, Matsuda and Ayabe [40] suggested following zone boundaries.

- Reversible (Nernstian)  
 $k_{sh}^o \geq 0.3 \nu^{1/2} \text{ cm s}^{-1}$
- Quasi-reversible  
 $0.3 \nu^{1/2} \geq k_{sh}^o \geq 2 \times 10^{-5} \nu^{1/2} \text{ cm s}^{-1}$
- Totally irreversible  
 $k_{sh}^o \leq 2 \times 10^{-5} \nu^{1/2} \text{ cm s}^{-1}$

## 2.2.2 Multi electron transfer processes

Multi-electron transfer process usually takes place in different steps. A two-step mechanism each characterized by its own electrochemical parameters is called an "EE mechanism".

A two step reversible "EE mechanism" is represented as;







Each heterogeneous electron transfer step is associated with its own electrochemical parameters i.e.,  $k_{sh}^o$  and  $\alpha_i$ , where  $i = 1, 2$  for the 1<sup>st</sup> and 2<sup>nd</sup> electron transfer respectively.

The value of  $k_{sh}^o$  for first reversible electron transfer limiting case can be calculated as [43]:

$$k_{sh} = k_{sh}^o \exp\left[-\alpha_1 F \Delta E^o / 2RT\right] \dots\dots\dots 2.7$$

where

$$\Delta E^o = E_2^o - E_1^o$$

For  $\Delta E^o$  greater than 180 mV, shape of wave does not dependent on the relative values of  $E^o$ , otherwise shapes of peak and peak currents depend upon  $\Delta E^o$  [44]. Based on the value of  $\Delta E^o$ , we come across different types of cases as shown in the Figure 2.6.

### Types of two electron transfer reactions

#### Case 1: $\Delta E^o \geq 150$ mV peaks separation

When  $\Delta E^o \geq 150$  mV the EE mechanism is termed as “disproportionate mechanism [45]. Cyclic voltammogram consists of two typical one-electron reduction waves. The heterogeneous electron transfer reaction may simultaneously be accompanied by homogenous electron transfer reaction, which in multi-electron system leads to disproportionation which can be described as:



$$k_{disp} = \frac{[O][R_2]}{[R_1]^2} \dots\dots\dots 2.9$$

$$\ln k_{disp} = \left[ \frac{nF}{RT} \right] (E_2^o - E_1^o) \dots\dots\dots 2.10$$

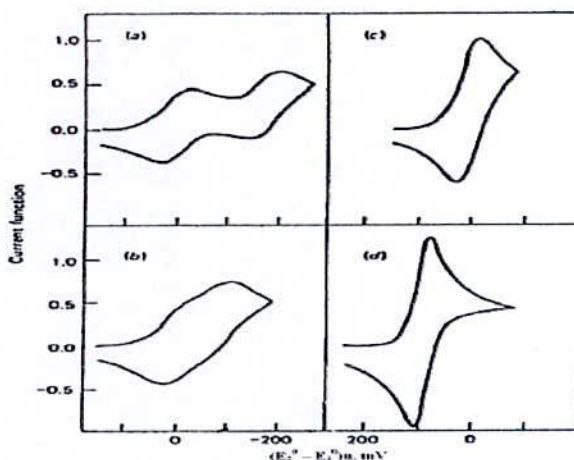
#### Case 2: $\Delta E^o < 100$ mV ----- Peaks overlapped

In this case, the individual waves merge into one broad distorted wave whose peak height and shape are no longer characteristics of a reversible wave. The wave is broadened

similar to an irreversible wave, but can be distinguished from the irreversible voltammogram, in that the distorted wave does not shift on the potential axis as a function of the scan rate.

**Case 3:  $\Delta E^0 = 0$  mV ----- Single peak**

In this case, in cyclic voltammogram, only a single wave would appear with peak current intermediate between those of a single step one electron and two electron transfer reactions and  $E_p - E_p/2 = 56$  mV.



**Figure 2.7** Cyclic voltammograms for a reversible two-step system (a)  $\Delta E^0 = -180$  mV, (b)  $\Delta E^0 = -90$  mV, (c)  $\Delta E^0 = 0$  mV, (d)  $\Delta E^0 = 180$  mV. (Taken from ref. [46])

Contrary to the convention the direction of the current in these voltammograms has been shown cathodic above the base line and anodic below the base line.

**Case 4:  $E_1^0 < E_2^0$  ----- 2nd Reduction is easy than 1<sup>st</sup> one**

If the energy required for the second electron transfer is less than that for the first, one wave is observed, having peak height equal to  $2^{3/2}$  times that of a single electron transfer process. In this case,  $E_p - E_p/2 = 29$  mV. The effective  $E^0$  for the composite two electron wave is given by  $\frac{(E_1^0 + E_2^0)}{2}$  as reported in literature [46].



## 2.3 Pulse techniques

The basis of all pulse techniques is the difference in the rate of decay of the charging and the faradaic currents following a potential step (or pulse). The charging current decays considerably faster than the faradaic current. A step in the applied potential or current represents an instantaneous alteration of the electrochemical system. Analysis of the evolution of the system after perturbation permits deductions about electrode reactions and their rates to be made. The potential step is the base of pulse voltammetry. After applying a pulse of potential, the capacitive current dies away faster than the faradic one and the current is measured at the end of the pulse. This type of sampling has the advantage of increased sensitivity and better characteristics for analytical applications. At solid electrodes there is an additional advantage of discrimination against blocking of the electrode reaction by adsorption [32].

### 2.3.1 Differential pulse voltammetry (DPV)

The potential wave form for differential pulse voltammetry (DPV) is shown in Figure 2.8. The potential wave form consists of small pulses (of constant amplitude) superimposed upon a staircase wave form. Unlike Normal pulse voltammetry (NPV), the current is sampled twice in each Pulse Period (once before the pulse, and at the end of the pulse), and the difference between these two current values is recorded and displayed.

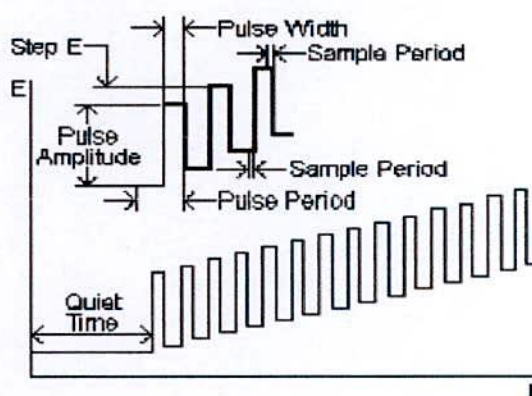


Figure 2.8: Scheme of application of potential

The important parameters for pulse techniques are as follows:

- Pulse amplitude is the height of the potential pulse. This may or may not be constant depending upon the technique.
- Pulse width is the duration of the potential pulse.
- Sample period is the time at the end of the pulse during which the current is measured.
- For some pulse techniques, the pulse period or drop time must also be specified. This parameter defines the time required for one potential cycle, and is particularly significant for polarography (i.e., pulse experiments using a mercury drop electrode), where this time corresponds to the lifetime of each drop (i.e., a new drop is dispensed at the start of the drop time, and is knocked off once the current has been measured at the end of the drop time - note that the end of the drop time coincides with the end of the pulse width).

Quantitative treatments for reversible systems demonstrated that, with only  $R$  (positive sign) or only  $O$  (negative sign) initially present, the following equation can be written as

$$E_{\max} = E_{1/2} \pm \frac{\Delta E}{2} \dots\dots\dots 2.11$$

where  $\Delta E$  is the pulse amplitude.

## 2.4 Chronoamperometry (CA)

As with all pulsed techniques, chronoamperometry (CA) is one of the simplest potential wave forms. The potential is changed instantaneously from the Initial Potential to the First Step Potential, and it is held at this value for the First Step Time. This is a single potential step experiment. In CA, the current is monitored as a function of time. The Faradaic current--which is due to electron transfer events and is most often the current component of interest--decays as described in the Cottrell equation. Since the current is integrated over relatively longer time intervals, CA gives a better signal to noise ratio in comparison to other amperometric technique. A chronoamperometric curve at a disk microelectrode varies from the Cottrell behavior to the steady state current. When potential is stepped to a diffusion-controlled potential domain at the disk electrode with radius,  $a$ , in the solution



including electroactive species with the concentration,  $c^*$ , and the diffusion coefficient,  $D$ , the responding current,  $I$ , at the electrolysis time,  $t$ , has been expressed as [47, 48]

$$I = 4nFc^*Da \left( 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2} \right) \dots\dots 2.12$$

$$I = 4nFc^*Da \left[ \left( \pi/4\tau \right)^{1/2} + \pi/4 + 0.094\tau^{1/2} \right] \dots\dots\dots 2.13$$

where  $\tau = 4Dt/a^2$ . Equations 2.12 and 2.13 are valid for  $\tau > 1.44$  and  $\tau < 0.82$ , respectively.

Some expressions for the chronoamperometric curves obtained by finite difference or the related methods [49-54] are closed to Equation (2.12) and (2.13). When  $\tau$  is small enough to neglect the third term in Equation (2.13), the potential-depending current for the reversible case is expressed by

$$I = \left( \pi^{1/2} nFD^{1/2} a^2 t^{-1/2} + \pi nFDa \right) c^* (1 + e^{-\zeta})^{-1} \dots\dots\dots 2.14$$

where  $\zeta = (F/RT)(E - E^{0'})$

The Cottrell plot ( $I$  vs.  $t^{1/2}$ ) gives the slope and the intercept, respectively

$$s = \pi^{1/2} nFD^{1/2} a^2 c^* (1 + e^{-\zeta})^{-1}$$

$$p = \pi nFDa c^* (1 + e^{-\zeta})^{-1}$$

The ratio of the square of the slope to the intercept is

$$s^2 / p = nFa^3 c^* (1 + e^{-\zeta})^{-1} \text{ or } n(1 + e^{-\zeta})^{-1} = s^2 / pFa^3 c^* \dots\dots 2.15$$

This equation does not include  $D$ , and hence is the basic equation of evaluating  $n$  without knowing  $D$  from the chronoamperometric curves.

## CHAPTER III

## Experimental

The redox behavior of catechol with sulfanilic acid, diethylamine and their mixture in buffer solution at different pH has been measured using Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) at Glassy carbon (GC), Gold (Au) and Platinum (Pt) electrode. Details of the instrumentation are given in the following sections. The source of different chemicals, the instruments and brief description of the methods are given below.

## 3.1 Chemicals

All chemicals and solvents used in the electrochemical synthesis and analytical work were of analytical grade. The used chemicals were-

| Sl. No. | Chemicals                         | Molecular formula | Molar mass | Reported purity | Producer                                 |
|---------|-----------------------------------|-------------------|------------|-----------------|------------------------------------------|
| 1.      | Catechol                          | $C_6H_4(OH)_2$    | 110.11     | 99%             | Fisher Scientific UK Ltd.                |
| 2.      | Diethylamine                      | $C_3H_{11}N$      | 73.14      | 99%             | E-Merck, Germany                         |
| 3.      | Sulfanilic Acid                   | $C_6H_7NO_3S$     | 173.19     | 99%             | Merk Specialities Pvt. Ltd., India       |
| 4.      | Glacial Acetic Acid               | $CH_3COOH$        | 60.05      | 99.5%           | Loba Chemie Pvt. Ltd., India             |
| 5.      | Sodium Acetate                    | $CH_3COONa.3H_2O$ | 136.08     | 99%             | Merk Specialities Pvt. Ltd., India       |
| 6.      | Potassium Chloride                | KCl               | 74.6       | 99.5%           | E-Merck, Germany                         |
| 7.      | Sodium Di-hydrogen Orthophosphate | $NaH_2PO_4.2H_2O$ | 156.01     | 98-100%         | Loba Chemie Pvt. Ltd., India             |
| 8.      | Di-sodium Hydrogen Orthophosphate | $Na_2HPO_4.2H_2O$ | 177.99     | 97-100%         | Thermo Fisher Scientific India Pvt. Ltd. |



| Sl. No. | Chemicals          | Molecular formula  | Molar mass | Reported purity | Producer         |
|---------|--------------------|--------------------|------------|-----------------|------------------|
| 9.      | Sodium Hydroxide   | NaOH               | 40.0       | 97%             | E-Merck, Germany |
| 10.     | Sodium Bicarbonate | NaHCO <sub>3</sub> | 84.0       | 99%             | E-Merck, Germany |

### 3.2 Equipments

During this research work the following instruments were used-

- The electrochemical studies (CV, DPV) were performed with a computer controlled potentiostats/ galvanostats ( $\mu$ stat 400, Drop Sens, Spain)
- A Pyrex glass micro cell with teflon cap
- Glassy carbon (GC)/ Gold (Au)/ Platinum (Pt) as working electrode (BASi, USA)
- Three carbon rods (Local market Dhaka, Bangladesh)
- Ag/ AgCl as reference electrode (BASi, USA)
- Liquid micro size (0.05 $\mu$ m) polishing alumina (BAS Inc. Japan)
- Pt wire as counter electrode (Local market, Dhaka, Bangladesh)
- A HR 200 electronic balance with an accuracy of  $\pm 0.0001$ g was used for weighting and
- A pH meter (pH Meter, Hanna Instruments, Italy) was employed for maintaining the pH of the solutions.

### 3.3 Cyclic voltammetry (CV)

In several well established electrochemical techniques for the study of electrochemical reactions, we have chosen the CV technique to study and analyze the redox reactions occurring at the polarizable electrode surface. This technique helps us to understand the mechanism of electron transfer reaction of the compounds as well as the nature of adsorption of reactants or products on the electrode surface. CV is often the first experiment performed in an electrochemical study. CV consists of imposing an excitation potential nature on an electrode immersed in an unstirred solution and measuring the current and its potential ranges varies from a few millivolts to hundreds of millivolts per second in a cycle. This variation of anodic and cathodic current with imposed potential is termed as voltammogram [30].

The technique involves under the diffusion controlled mass transfer condition at a stationary electrode utilizing symmetrical triangular scan rate ranging from  $1 \text{ mVs}^{-1}$  to hundreds millivolts per second.

In CV the current function can be measured as a function of scan rate. The potential of the working electrode is controlled vs a reference electrode such as Ag/AgCl electrode. The electrode potential is ramped linearly to a more negative potential and then ramped is reversed back to the starting voltage. The forward scan produces a current peak for any analyte that can be reduced through the range of potential scan. The current will increase as the current reaches to the reduction potential of the analyte [55].

The current at the working electrode is monitored as a triangular excitation potential is applied to the electrode. The resulting voltammogram can be analyzed for fundamental information regarding the redox reaction. The potential at the working electrode is controlled vs a reference electrode, Ag/AgCl (standard NaCl) electrode. The excitation signal varies linearly with time. First scan positively and then the potential is scanned in reverse, causing a negative scan back to the original potential to complete the cycle. Signal on multiple cycles can be used on the scan surface. A cyclic voltammogram is plot of response current at working electrode to the applied excitation potential.

### 3.4 Important features of CV

An electrochemical system containing species 'O' capable of being reversibly reduced to 'R' at the electrode is given by,



Nernst equation for the system is

$$E = E^0 + \frac{0.059}{n} \log \frac{C_0^s}{C_R^s} \dots\dots\dots 3.2$$

Where,

$E$  = Potential applied to the electrode

$E^0$  = Standard reduction potential of the couple versus reference electrode

$n$  = Number of electrons in Equation (3.1)

$C_0^s$  = Surface concentration of species 'O'



$C_R^s$  = Surface concentration of species 'R'

A redox couple that changes electrons rapidly with the working electrode is termed as electrochemically reverse couple. The relation gives the peak current  $i_{pc}$

$$i_{pc} = 0.4463 nFA (D\alpha)^{1/2} C \dots\dots\dots 3.3$$

$$\alpha = \left( \frac{nFv}{RT} \right) = \left( \frac{nv}{0.026} \right)$$

Where,

$i_{pc}$  = peak current in amperes

$F$  = Faraday's constant (approximately 96500)

$A$  = Area of the working electrode in  $\text{cm}^2$

$v$  = Scan rate in volt/ sec

$C$  = Concentration of the bulk species in mol/L

$D$  = Diffusion coefficient in  $\text{cm}^2/\text{sec}$

In terms of adjustable parameters, the peak current is given by the Randless- Sevcik equation,

$$i_{pc} = 2.69 \times 10^5 \times n^{3/2} A D^{1/2} C v^{1/2} \dots\dots\dots 3.4$$

The peak potential  $E_p$  for reversible process is related to the half wave potential  $E_{1/2}$ , by the expression,

$$E_{pc} = E_{1/2} - 1.11 \left( \frac{RT}{nF} \right), \quad \text{at } 25^\circ\text{C} \dots\dots\dots 3.5$$

$$E_{pc} = E_{1/2} - \left( \frac{0.0285RT}{n} \right) \dots\dots\dots 3.6$$

The relation relates the half wave potential to the standard electrode potential

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{f_{red}}{f_{ox}} \left( \frac{D_{ox}}{D_{red}} \right)^{1/2}$$

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \left( \frac{D_{ox}}{D_{red}} \right)^{1/2} \dots\dots\dots 3.7$$

Assuming that the activity coefficient  $f_{ox}$  and  $f_{red}$  are equal for the oxidized and reduced species involved in the electrochemical reaction.

From Equation (3.6), we have,

$$E_{pa} - E_{pc} = 2.22 \left( \frac{RT}{nF} \right) \quad \text{at } 25^\circ\text{C} \dots\dots\dots 3.8$$

$$\text{or } E_{pa} - E_{pc} = \left( \frac{0.059}{n} \right) \quad \text{at } 25^\circ\text{C} \dots\dots\dots 3.9$$

This is a good criterion for the reversibility of electrode process. The value of  $i_{pa}$  should be close for a simple reversible couple,

$$i_{pa}/i_{pc} = 1 \dots\dots\dots 3.10$$

And such a system  $E_{1/2}$  can be given by,

$$E_{1/2} = \frac{E_{pa} + E_{pc}}{2} \dots\dots\dots 3.11$$

For irreversible processes (those with sluggish electron exchange), the individual peaks are reduced in size and widely separated, Totally irreversible systems are characterized by a shift of the peak potential with the scan rate [56];

$$E_p = E^0 - (RT/\alpha n_a F) [0.78 - \ln(k^0/(D)^{1/2}) + \ln(\alpha n_a F \alpha / RT)^{1/2}] \dots\dots\dots 3.12$$

Where  $\alpha$  is the transfer coefficient and  $n_a$  is the number of electrons involved in the charge transfer step. Thus  $E_p$  occurs at potentials higher than  $E^0$ , with the over potential related to  $k^0$  (standard rate constant) and  $\alpha$ . Independent of the value  $k^0$ , such peak displacement can be compensated by an appropriate change of the scan rate. The peak potential and the half-peak potential (at  $25^\circ\text{C}$ ) will differ by  $48/\alpha n$  mV. Hence, the voltammogram becomes more drawn-out as  $\alpha n$  decreases.

The peak current, given by

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} A C D^{1/2} \nu^{1/2} \dots\dots\dots 3.13$$

is still proportional to the bulk concentration, but will be lower in height (depending upon the value of  $\alpha$ ). Assuming  $\alpha = 0.5$ , the ratio of the reversible –to– irreversible current peaks is 1.27 (i.e. the peak current for the irreversible process is about 80% of the peak for a reversible one). For quasi-reversible systems (with  $10^{-1} > k^0 > 10^{-5}$  cm/s) the current is controlled by both the charge transfer and mass transport [57]. The shape of the cyclic voltammogram is a function of the ratio  $k^0 (\pi \nu n F D / RT)^{1/2}$ . As the ratio increases, the process approaches the reversible case. For small values of it, the system exhibits an irreversible behavior. Overall, the voltammograms of a quasi-reversible system are more drawn out and exhibit a larger separation in peak potential compared to a reversible system.

Unlike the reversible process in which the current is purely mass transport controlled, currents due to quasi-reversible process are controlled by a mixture of mass transport and charge transfer kinetics [57, 58]. The process occurs when the relative rate of electron



transfer with respect to that of mass transport is insufficient to maintain Nernst equilibrium at the electrode surface.

### 3.5 Differential pulse voltammetry (DPV)

Differential pulse voltammetry (DPV) is a technique that is designed to minimize background charging currents. The waveform in DPV is a sequence of pulses, where a baseline potential is held for a specified period of time prior to the application of a potential pulse. Current is sampled just prior to the application of the potential pulse. The potential is then stepped by a small amount (typically  $< 100$  mV) and current is sampled again at the end of the pulse. The potential of the working electrode is then stepped back by a lesser value than during the forward pulse such that baseline potential of each pulse is incremented throughout the sequence.

By contrast, in normal pulse voltammetry the current resulting from a series of ever larger potential pulse is compared with the current at a constant 'baseline' voltage. Another type of pulse voltammetry is square wave voltammetry, which can be considered a special type of differential pulse voltammetry in which equal time is spent at the potential of the ramped baseline and potential of the superimposed pulse. The potential wave form consists of small pulses (of constant amplitude) superimposed upon a staircase wave form [59]. Unlike NPV, the current is sampled twice in each pulse Period (once before the pulse, and at the end of the pulse), and the difference between these two current values is recorded and displayed.

### 3.6 Important features of DPV

Differential pulse voltammetry has these prominence:

- i) Current is sampled just prior to the application of the potential pulse.
- ii) Reversible reactions show symmetrical peaks and irreversible reaction show asymmetrical peaks.
- iii) The peak potential is equal to  $E_{1/2}^r - \Delta E$  in reversible reactions, and the peak current is proportional to the concentration.

### 3.7 Chronoamperometry (CA)

Chronoamperometry is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrode is monitored as a function of time. This technique has advantage of without knowing a value of a diffusion coefficient [60]. When potential is stepped from a non-reacting domain to  $E$ , a Cottrell plot ( $I$  vs.  $t^{1/2}$ ) shows the slope by the linear diffusion.

$$s = \pi^{1/2} n F D^{1/2} a^2 c^*$$

together with the intercept for the edge effect

$$p = \pi n F D a c^*$$

where  $a$  is the radius of the electrode,  $c^*$  is the concentration of the electroactive species,  $D$  is the diffusion coefficient. The ratio of the square of the slope,  $s$ , to the intercept,  $p$ , is

$$n = s^2 / p F a^3 c^* \dots\dots\dots 3.14$$

Since this equation does not include  $D$ , values of  $n$  can be determined from  $s$  and  $p$  without knowing  $D$  values.

### 3.8 Computer controlled potentiostats (for CV, DPV and CA experiment)

The main instrument for voltammetry is the Potentiostats/ Galvanostats ( $\mu$ Stat 400, DropSens, Spain), which will be applied to the desired potential to the electrochemical cell (i.e. between a working electrode and a reference electrode), and a current-to-voltage converter, which measures the resulting current, and the data acquisition system produces the resulting voltammogram.

### 3.9 Electrochemical cell

This research work was performed by a three electrode electrochemical cell. The voltammetric cell also contains a Teflon cap. The electrochemical reaction of interest takes place at the working electrode and the electrical current at this electrode due to electron transfer is termed as faradic current. The counter electrode is driven by the potentiostatic circuit to balance the faradic process at the working electrode with an electron transfer of opposite direction.



### **3.10 Electrodes**

Three types of electrodes are used in this research:

- i) Working electrodes are Glassy carbon (GC) electrode with 3.0 mm diameter disc, Gold (Au) & Platinum (Pt) electrode with 1.6 mm diameter disc and three carbon rods (diameter 6.0 mm)
- ii) Ag/ AgCl (standard NaCl) electrode used as reference electrode from BASi, USA
- iii) Counter electrode is a Pt wire

The working electrode is an electrode on which the reaction of interest is occurring. The reference electrode is a half-cell having a known electrode potential and it keeps the potential between itself and the working electrode. The counter electrode is employed to allow for accurate measurements to be made between the working and reference electrodes.

### **3.11 Preparation of electrodes**

In this study, Glassy carbon (GC), Gold (Au) and Platinum (Pt) electrodes purchase from the BASi, USA are used as working electrode. Electrode preparation includes polishing and conditioning of the electrode. The electrode was polished with 0.05 $\mu$ m alumina powder on a wet polishing cloth. For doing so a part of the cloth was made wet with deionized water and alumina powder was sprinkled over it. Then the electrode was polished by softly pressing the electrode against the polishing surface at least 10 minutes. The electrode surface would look like a shiny mirror after thoroughly washed with deionized water.

### **3.12 Removing dissolved Oxygen from solution**

Dissolved oxygen can interfere with observed current response so it is needed to remove it. Experimental solution was indolented by purging for at least 5-10 minutes with 99.99% pure and dry nitrogen gas (BOC, Bangladesh). By this way, traces of dissolved oxygen were removed from the solution.

### 3.13 Electrode polishing

Materials may be adsorbed to the surface of a working electrode after each experiment. Then the current response will degrade and the electrode surface needs to clean. In this case, the cleaning required is light polishing with 0.05 $\mu$ m alumina powder. A few drops of polish are placed on a polishing pad and the electrode is held vertically and the polish rubbed on in a figure-eight pattern for a period of 30 seconds to a few minutes depending upon the condition of the electrode surface. After polishing the electrode surface is rinsed thoroughly with deionized water.

### 3.14 Experimental procedure

The electrochemical cell filled with solution 50mL of the experimental solution and the Teflon cap was placed on the cell. The working electrode together with reference electrode and counter electrode was inserted through the holes. The electrodes were sufficiently immersed. The solution system is deoxygenated by purging the nitrogen gas for about 10 minutes. The solution has been kept quiet for 10 seconds. After determining the potential window the voltammogram is taken at various scan rates, pH and concentrations from the Drop View Software.

### 3.15 Preparation of buffer solutions

**Acetate Buffer Solution:** To prepare acetate buffer (pH 3.0-5.0) solution definite amount of sodium acetate was dissolved in 0.1M acetic acid in a volumetric flask and the pH was measured. The pH of the buffer solution was adjusted by further addition of acetic acid and / or sodium acetate.

**Phosphate Buffer Solution:** Phosphate buffer solution (pH 6.0-8.0) was prepared by mixing a solution of 0.1M sodium dihydrogen ortho-phosphate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) with a solution of 0.1M disodium hydrogen ortho-phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ). The pH of the prepared solution was measured with pH meter.



Hydroxide Buffer Solution: To prepare hydroxide buffer (pH 9.0-11.0) solution definite amount of sodium hydroxide was dissolved in 0.1M sodium bicarbonate in a volumetric flask. The pH of the prepared solution was measured with pH meter.



Figure 3.1: Experimental setup (Software controlled Potentiostats ( $\mu$ stat 400))

## CHAPTER IV

### Results and Discussion

The redox behavior of catechol in presence of diethylamine, sulfanilic acid and catechol in presence of sulfanilic acid + diethylamine mixtures in buffer solution of different pH has been studied at different scan rates by Cyclic voltammetry (CV), Controlled potential coulometry (CPC), Differential pulse voltammetry (DPV) and Chronoamperometry (CA) techniques using Glassy carbon (GC), Gold (Au) and Platinum (Pt) electrodes. The techniques provide important information regarding nucleophilic substitution reaction of catechol with diethylamine, sulfanilic acid and their mixtures.

#### 4.1.1 Electrochemical behavior of Catechol

Figure 4.1 shows the cyclic voltammograms of the first 5 cycles of 2 mM catechol of GC (3 mm) electrode in buffer solution of pH 7. The voltammogram at the  $0.1 \text{Vs}^{-1}$  scan rate has one anodic peak at 0.39 V and corresponding cathodic peak at 0.03 V versus Ag/AgCl. In the subsequent potential cycles no new anodic peak appeared. This can be attributed that catechol showed one anodic peak related to its transformation to *o*-quinone and corresponding cathodic peak related to its transformation to catechol from *o*-quinone (Scheme 1) within a quasi-reversible two-electron transfer process. The anodic and corresponding cathodic peak current ratios at different scan rates are nearly unity at low scan rate which is tabulated in Table 4.1, it indicates that the redox reactions are quasi-reversible. It can be also considered as criteria for the stability of *o*-quinone produced at the surface of electrode [61] under the experimental conditions. In other words, any hydroxylation [62-65] or dimerization [66, 67] reactions are too slow that can be observed in the time-scale of cyclic voltammetry [61]. The corresponding peak potentials at different scan rates are tabulated in Table 4.1. The peak separation potential increases with the increase of scan rate that indicates there is a limitation according to ohmic potential drop or charge transfer kinetics [68].



#### 4.1.2 Electrochemical behavior of Catechol + Diethylamine

Figure 4.2 shows the cyclic voltammograms of the first 5 cycles of only 250 mM diethylamine at GC (3 mm) electrode in buffer solution of pH 7. Pure diethylamine is electrochemically inactive having no redox peaks in the potential range investigated.

Figure 4.3 shows the CV of catechol (2 mM) in the presence of diethylamine (250 mM) at Glassy carbon (GC) electrode in the first scan of potential at pH 7. In the first scan of potential, it shows one anodic peak and two cathodic peaks (black line). A new reduction peak ( $C_0$ ) appears at - 0.02 V after the addition of 250 mM diethylamine to the solution at first scan of potential (Figure 4.3). The reduction peak shifted due to catechol species diminishes by addition of diethylamine. The peak current decreases significantly compared with the only catechol, which may be due to the addition of catechol with diethylamine.

Figure 4.4 shows the CV of catechol (2 mM) in the presence of diethylamine (250 mM) in the second scan of potential (black line). In the second scan of potential, it shows two anodic peaks at - 0.05 V and 0.38 V and two cathodic peaks at - 0.02 V and - 0.23 V respectively. Upon addition of diethylamine to catechol solution, the anodic peak  $A_1$  decreases gradually and a new anodic peak  $A_0$  appears. In the second scan of potential (Figure 4.4), a new oxidation peak appears at - 0.05 V. The newly appearance of  $A_0$  and  $C_0$  peaks and decreases of  $A_1$  and  $C_1$  peaks and also shifting of the positions of peaks  $A_1$  and  $C_1$  in the presence of diethylamine indicates that it is due to follow up reaction of catechol with diethylamine (Scheme 1). This observation can be explained by considering nucleophilic attack of diethylamine to *o*-benzoquinone. The nucleophilic attack of diethylamine to *o*-benzoquinone reduces the *o*-benzoquinone concentration in reaction layer, consequently the  $A_1$  and  $C_1$  peaks reduces, whereas in the same time produces catechol-diethylamine adduct and consequently the peaks  $A_0$  and  $C_0$  appears. In the first scan of potential, the anodic peak of catechol in presence of diethylamine is very similar to only catechol (Figure 4.3). But in the second scan of potential the peak current of  $A_1$  (black line) decreases significantly compared with that of only catechol (green line). The peak current ratios ( $I_{pa1}/I_{pc1}$ ) in the first and second scan of catechol-diethylamine at different scan rate are tabulated in the Table 4.2 and 4.3, respectively. The peak current ratio for the peaks  $A_1$  and  $C_1$  ( $I_{pa1}/I_{pc1}$ ) decreased noticeably, which is indicative of a chemical reaction of diethylamine (**2**) with the *o*-quinone (**1a**) produced at the surface of electrode. These



observations may ascribe the formation of 4-(diethylamino)-benzene-1,2-diol through nucleophilic substitution reaction (Scheme 1). If the constituent is such that the potential for the oxidation of product is lower, then further oxidation of the product is lower, the further oxidation and further addition may occur [69]. In the case of catechol in presence of diethylamine, the oxidation of diethylamine substituted *o*-benzoquinone is easier than the oxidation of parent catechol. This substitution product can also be attacked by diethylamine, however, it was not observed during the voltammetric experiments because of the low activity of *o*-quinone **4** toward **2**.

The corresponding peak potential differences ( $\Delta E$ ) in the first and second scan of potential are tabulated in Table 4.2 and 4.3. The peak potential differences are usually independent of scan rate. The peak separation potential increases with the increasing of scan rate that indicates there is a limitation according to ohmic potential drop or charge transfer kinetics [68].

Figures 4.5-4.6 show the CV of first and second scan of potential of 2 mM catechol + 250 mM diethylamine at Platinum (Pt) (1.6mm) electrode in pH 7 and at scan rate 0.1V/s. Figure 4.5 shows the cyclic voltammogram of only 2mM catechol (green line), pure diethylamine (pink line) and catechol (2 mM) with diethylamine (250 mM) (black line) in the first scan of potential at the same condition. A new reduction peak ( $C_0$ ) appears at - 0.22 V after the addition of 250 mM diethylamine to the solution at first scan of potential (Figure 4.5). The peak current decreases significantly with respect to the only catechol. In Figure 4.6, the second scan of potential catechol with diethylamine shows two anodic peaks at - 0.05 V and 0.34 V and the corresponding two cathodic peaks at - 0.22 V and - 0.04 V, respectively. Upon addition of diethylamine to catechol solution, the cathodic peak  $C_1$  decreases and a new cathodic peak  $C_0$  appears. Also, in the second scan of potential a new anodic peak  $A_0$  appears and anodic peak  $A_1$  decreases similar to GC electrode. This observation can be stated by considering nucleophilic attack of diethylamine to *o*-benzoquinone. The nucleophilic attack of diethylamine to *o*-benzoquinone reduces the *o*-benzoquinone concentration in reaction layer. Accordingly the  $A_1$  and  $C_1$  peaks reduce, whereas in the same time produces catechol-diethylamine adduct and consequently the peak  $A_0$  and  $C_0$  appears (Scheme 1).



A similar behavior is observed when we used a Gold (Au) electrode for the investigation of same solution in the same condition. Figure 4.7 shows the CV of catechol (2 mM) in the presence of diethylamine (250 mM) at Au electrode in the first scan of potential. Figure 4.8 shows the CV of catechol (2 mM) in the presence of diethylamine (250 mM) at Au electrode in the second scan of potential. Upon addition of diethylamine to catechol solution at the Gold (Au) electrode it shows three anodic and three cathodic peaks for the second scan of potential. The newly appearance of  $A_0$  and  $C_0$  peak, and decrease of  $A_1$  and  $C_1$  peak, and also shifting of the positions of peaks  $A_1$  and  $C_1$  also indicates that it is due to follow up reaction of catechol with diethylamine (Scheme 1) at Au electrode. In case of GC and Pt electrodes, it shows two anodic and two cathodic peaks. The third peak of Au electrodes is due to the oxidation of Au in buffer solution. This unlike behavior will discuss in the effect of electrode materials section.

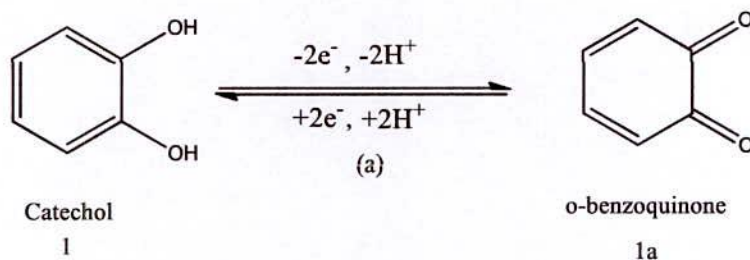
#### 4.1.3 Effect of scan rate of Catechol + Diethylamine

Figures 4.9-4.10 show the CV of first and second cycles of 2 mM catechol in presence of 250 mM diethylamine of GC (3 mm) electrode in buffer solution (pH 7) at different scan rates. The peak current of both the anodic and the corresponding cathodic peaks increases with the increase of scan rate. The cathodic peaks are shifted towards left and the anodic peaks are to the right direction with increase in scan rate. As can be seen in Figure 4.9 and 4.10, the cathodic peak for reduction of *o*-benzoquinone is very small in the scan rate of 0.05 V/s. By increasing the scan rate, the cathodic peak for reduction of *o*-benzoquinone begins to appear and increase. The anodic and cathodic peak current, peak current ratio and peak potential difference are tabulated in Tables 4.2-4.3.

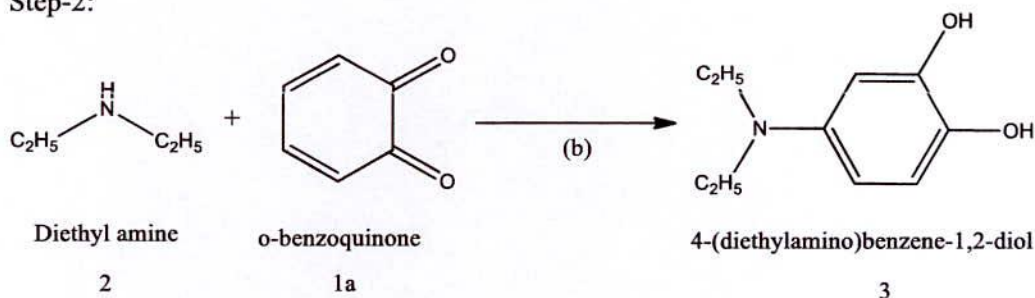
Figure 4.11 and 4.12 shows the plots of the anodic and cathodic net peak currents of 2 mM catechol with 250 mM diethylamine for first and second cycles respectively against the square-root of scan rates where the net current means the second peak subtracted from the first one by the scan-stopped method [69]. The nearly proportionality of the anodic and corresponding cathodic peaks suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process [66]. The corresponding peak current ratio ( $I_{pa1}/I_{pc1}$ ) vs scan rate for a mixture of catechol and diethylamine decreases with increasing scan rate firstly and then after 0.2 V/s, it is almost unchanged (Figure 4.13, left scale). The

anodic peak current ratio ( $I_{pa0}/I_{pa1}$ ) vs scan rate for a mixture of catechol and diethylamine firstly increases and then after 0.2 V/s scan rate it decreases (Figure 4.13, right scale). On the other hand, the value of current function ( $I_p/v^{1/2}$ ) was found to be decreased with increasing scan rate (Figure 4.14). The exponential nature of the current function versus the scan rate plot is indicative of an electron transfer-chemical reaction-electron transfer (ECE) mechanism for electrode process [13]. This confirms the reactivity of *o*-benzoquinone (1a) towards diethylamine (2) firstly increases at slow scan rate and then at higher scan rate it decreases. Figure 4.15 and 4.16 shows the plots of the anodic and cathodic peak potentials of 2 mM catechol with 250 mM diethylamine against scan rate. The slopes of the plot are non-zero, indicating that there is a limitation according to IR drop [68].

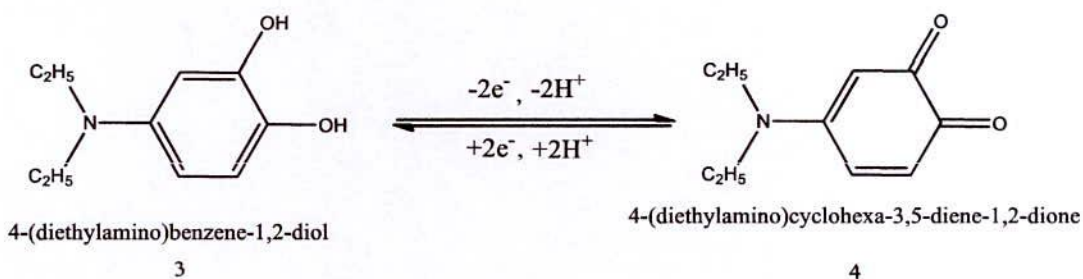
Step-1:



Step-2:



Step-3:



**Scheme 1**



The reactivity of catechol towards diethylamine is pH and concentration dependent. So the voltammetric behavior of the above systems verified at different pH, concentration and scan rate. Figures 4.17-4.23 show the CV at different scan rate for first and second cycle of 2 mM catechol in presence of 250 mM diethylamine at different pH (3-11). Figures 4.24-4.30 show the plots of the anodic and cathodic net peak currents against the square-root of the scan rates at the same condition. The peak currents and peak potentials are tabulated in Tables 4.4-4.11. Figures 4.31-4.38 show the CV of 2mM catechol in presence of 150 mM-350 mM of diethylamine at different scan rate. Figures 4.39-4.46 show the plots of the anodic and cathodic net peak currents against the square-root of the scan rates in same condition. The peak currents and peak potentials are tabulated in Tables 4.12-4.19. The nearly proportionality of the anodic and the cathodic peaks for the studied all pH and concentration suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process. Although most of the lines have non zero intercept.

Figure 4.47 and 4.48 shows the CV of first and second scan of potential respectively at Au electrode of 2 mM catechol with 250 mM diethylamine at pH 7 and different scan rate. The peak current of both the anodic and cathodic peaks increases with the increase of scan rate. The anodic peaks are shifted towards right direction and the cathodic peaks are to the left with increase in the scan rate. Figure 4.49 and 4.50 shows plots of the anodic and cathodic peak currents for the first and second scan of potential as a function of square-root of the scan rates. The proportionality of the anodic and the cathodic peaks ascribed that the peak current of the reactant at each redox reaction is controlled by diffusion process. The anodic and cathodic peak currents, peak potentials, corresponding peak potential differences and peak current ratio are tabulated in Tables 4.20-4.21.

Similarly the voltammetric behavior of the above systems verified at Au electrode in different concentration, pH and scan rate. Figures 4.51-4.56 show the CV of catechol with 250 mM diethylamine for first and second cycle of potential at different scan rate in pH (3-11). Figures 4.56-4.62 show the plots of the anodic and cathodic net peak currents against the square-root of the scan rates at different pH in the same condition. The nearly proportionality of the anodic and the cathodic peaks for all studied systems at different pH and concentration suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process.



Figure 4.63 and 4.64 shows the CV of first and second scan of potential at Pt (1.6mm) electrode of 2 mM catechol with 250 mM diethylamine in pH 7 and different scan rate. The peak currents of both the anodic and cathodic peaks increases with the increasing of scan rate. The anodic peaks are shifted slightly towards right direction and the cathodic peaks are to the left with increase in scan rates. Figure 4.65 and 4.66 shows plots of the anodic and cathodic peak currents for the first and second scan of potential as a function of square-root of the scan rates in the same condition. The proportionality of the anodic and the cathodic peaks ascribed that the peak current of the reactant at each redox reaction is controlled by diffusion process. Figure 4.67 and 4.68 shows the plots of the anodic and cathodic peak potentials against scan rate. The anodic and cathodic peak potentials, peak currents, corresponding peak potential differences and peak current ratios are tabulated in Table 4.22-4.23. Similarly the voltammetric behavior of the studied systems verified at Pt electrode in different concentration, pH and scan rate. Figures 4.69-4.74 show the CV of 2 mM catechol with 250 mM diethylamine for 1<sup>st</sup> and 2<sup>nd</sup> cycle of potential at different pH (3-11). Figures 4.75-4.80 show the plots of the anodic and cathodic net peak currents for first and second cycle against the square-root of the scan rates in the same condition. Figures 4.81- 4.88 show the CV of different scan rate at different concentration of diethylamine (150 mM-350 mM) and fixed concentration of catechol (2 mM) in pH 7. Figures 4.89-4.96 show the plots peak currents for first and second cycle against the square-root of the scan rates in the same condition. The nearly proportionality of the anodic and the cathodic peaks for all the studied systems at different pH and concentration suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process.

#### 4.1.4 Effect of pH of Catechol + Diethylamine

The influence of pH on the cyclic voltammogram of catechol in presence of diethylamine at GC (3 mm) electrode in the first and second scan of potential was studied at pH from 3 to 11 (Figure 4.97 and 4.98). The voltammetric behavior of 2 mM catechol in the presence of 250 mM diethylamine at pH 3-5 shows that no new anodic peak appeared after repetitive cycling, indicating that the reaction between o-benzoquinone and diethylamine has not occurred. This can be attributed to the fact that at pH 3-5, the nucleophilic property of amine groups is diminished through protonation (Figure 4.98). In the pH 7-11, the o-benzoquinone undergoes diethylamine attack by the amine through a 1,4-Michael addition



reaction reflected that voltammetric new anodic peak  $A_0$  appeared after repetitive cycling (Figure 4.96). Whereas, in the higher pH range (e.g., pH 9-11), the cyclic voltammograms of catechol show irreversible behavior. It was thus suggested that the oxidation of catechol followed by an irreversible chemical reaction with hydroxyl ion, especially in alkaline solutions [70]. However amines in this condition can also act as nucleophiles. The peak position of the redox couple is found to be dependent upon pH.

Figure 4.100 shows the plot of oxidation peak ( $A_0$  and  $A_1$ ) current,  $I_p$  against pH of solution. It is seen that the maximum peak current is obtained at pH 7 suggested that nucleophilic addition reaction is most favorable in neutral media. Figure 4.101 and 4.102 shows the plot of peak potential,  $E_p$  values against pH. As shown, the peak potential for  $A_1$  peak shifted to the negative potentials by increasing pH. This is expected because of participation of proton in the reaction of catechol with diethylamine. From the Figure 4.101, the slope of the plot was determined graphically as the anodic peak (73 mV/pH for 1<sup>st</sup> oxidation peak  $A_1$ ) at 0.1 V/s, which is close to the theoretical value (60 mV/pH) for one-electron, one-proton transfer process. From the Figure 4.102, the slopes of the plot was determined graphically as the anodic peaks (55 mV/pH for the appeared peak  $A_0$  and 69 mV/pH for 1<sup>st</sup> oxidation peak  $A_1$ ) at 0.1 V/s, which is close to the theoretical value for one-electron, one-proton transfer process. This indicates that both the oxidation of the catechol and catechol-diethylamine adduct proceeded via the  $1e^-/1H^+$  processes. This also suggests that during the reaction not only electron but also proton are released from the catechol-diethylamine adduct.

The peak current ratio ( $I_{pc1}/I_{pa1}$ ) increases with decreasing pH. This can be related to protonation of amine and inactivation of it towards Michael addition reaction with o-benzoquinone (2a). This suggests that the rate of coupling reaction is pH dependent and enhanced by increasing pH. The peak current of the redox couple also is found to be dependent upon pH that is tabulated in Table 4.24-4.25. At pH 7, the difference between the peak current ratio ( $I_{pc1}/I_{pa1}$ ) in the presence and absence of diethylamine is maximum. Consequently, in this study buffer solution of pH 7 has been selected as suitable medium for electrochemical study of catechol in the presence of diethylamine. This ascribed that the electrochemical oxidation of catechol in presence of diethylamine is facilitated in neutral media and hence the rate of electron transfer is faster.



The effect of pH on the cyclic voltammogram of 2 mM catechol in presence of 250 mM diethylamine at Au (1.6 mm) electrode in the first and second scan of potential was studied at pH from 3 to 11 (Figure 4.103 and 4.104). The influence of pH for Au electrode in the same systems, the voltammetric properties are some different from GC electrode. The voltammetric behavior of catechol at pH 3 in the presence of diethylamine shows that a very small anodic peak  $A_0$  appeared in the second scan of potential (Figure 4.104). This can be indicated to the fact that in lower pH, the nucleophilic property of amine groups is diminished through protonation. In the pH 7-9, the *o*-benzoquinone undergoes diethylamine attack by the amine through Michael addition reaction reflected that voltammetric new anodic peak  $A_0$  appeared after repetitive cycling. In the higher pH (e.g., pH 11), catechol shows that no new anodic peak appeared in the second scan of potential (Figure 4.104). However, the peak position of the redox species is found to be dependent upon pH. Figure 4.105 and 4.106 shows the plots of oxidation peak current,  $I_p$  against pH of solution. It is seen that the maximum peak current is obtained at pH 7 attributed that nucleophilic addition reaction is most favorable in neutral media. Figure 4.107 shows the plot of the peak potential,  $E_p$  against pH at second cycle in the same condition. The slopes of the plot were (43 mV/pH for appeared peak  $A_0$  and 37 mV/pH for anodic peak  $A_1$ ) which is close to theoretical value for two electron, two proton transfer process.

CV of catechol in presence of 250 mM diethylamine at Platinum (Pt) (1.6 mm) electrode in the first and second scan of potential was also studied in pH 3 and 9 (Figure 4.108 and 4.109). The voltammetric behavior of 2 mM catechol at pH 3- 5 in the presence of 250 mM diethylamine showed one anodic peak and corresponding cathodic peak after repetitive cycling expressing that the reaction between *o*-quinone and diethylamine has not occurred. This can be assigned to the fact that at pH 3-5, the nucleophilic property of amine groups is diminished through protonation (Figure 4.109). In the pH 7-9, the *o*-quinone undergoes diethylamine attack by the amine through a Michael addition reaction suggests that voltammetric new anodic peak  $A_0$  appeared after repetitive cycling. However amines in this condition can also act as nucleophiles. The peak position of the redox couple is found to be dependent upon pH. Figure 4.110 shows the plot of oxidation peak current,  $I_p$  against pH solution. It is seen that the maximum peak current is obtained at pH 7. Figure 4.111 shows the plot of peak potential,  $E_p$  vs pH. The slope of the plot was 71 mV/pH which close to the value of one electron, one proton transfer process.



#### 4.1.5 Concentration effect of Diethylamine

Figure 4.112 and 4.113 shows the variation of voltammogram pattern by the addition of different concentration of diethylamine (150, 200, 250, 300 and 350 mM) into fixed concentration of catechol (2mM) for the 1<sup>st</sup> and 2<sup>nd</sup> scan of potential of GC (3 mm) electrode at pH 7 and scan rate 0.1V/s. From Figure 4.112 (1<sup>st</sup> cycle), it is seen that no new anodic peak appears but a new cathodic peak ( $C_0$ ) appears at - 0.22 V. In the second scan of potential the appeared anodic peaks shifted and a new anodic peak  $A_0$  appeared at ~ - 0.01 V upon addition of diethylamine which suggests the formation of catechol-diethylamine adduct (Figure 4.113). The net current intensity of the newly appeared anodic and cathodic peak increases with the increase of diethylamine composition upto ~ 250 mM where the net current means the peak current is measured from the baseline consideration. After further addition of diethylamine (> 250 mM), the anodic and cathodic peak current is slightly decreased (Figure 4.113). The nucleophilic substitution reaction of catechol in presence of diethylamine was maximum favorable up to 250 mM of diethylamine at pH 7 (Figures 4.114-4.115). The corresponding peak current ratio ( $I_{pc1}/I_{pa1}$ ) varies with the concentration of diethylamine. This is related to the increase of the homogenous reaction rate of following chemical reaction between o-benzoquinone 1a and diethylamine 2 with increasing concentration of diethylamine upto 250 mM. At higher concentration of diethylamine (> 250 mM), the excess electroinactive diethylamine may be deposited on the electrode surface and consequently the peak current decreased.

In addition of different concentration of diethylamine (150, 200, 250, 300 and 350 mM) into fixed concentration of catechol (2 mM) at Gold (Au) and Platinum (Pt) electrodes has been also examined in the same conditions (Figures 4.116-4.119). From Figure 4.116 and 4.118, the first scan of potential show a new cathodic peak ( $C_0$ ) appeared at -0.18 V and - 0.22 V at Au and Pt electrode respectively. Upon addition of diethylamine in the second scan of potential, (Figure 4.117 and 4.119) the anodic peaks shifted and a new anodic peak appeared at ~ - 0.1 V and - 0.03 V at Au and Pt electrodes respectively which suggests the formation of catechol-diethylamine adduct. The net current intensity of the newly appeared anodic and cathodic peak increases with the increase of composition upto 250-300 mM of diethylamine. After further addition of diethylamine (> 300 mM), the anodic and cathodic peak current is slightly decreased. At higher concentration of diethylamine (>250mM), the



excess electroinactive diethylamine may be accumulated on the electrode surface and the peak current decreased. Therefore, the concentration effects of diethylamine into the fixed concentration of catechol (2 mM) for Au and Pt electrodes are few different from GC electrode.

#### 4.1.6 Concentration effect of Catechol

In Figure 4.120, in contrast, with the addition of different concentration of catechol (2, 5, 10 and 15 mM) into fixed concentration of diethylamine (250 mM) of GC (3mm) electrode, the first anodic peak ( $A_1$ ) current increases and shifted positively with the increase of catechol composition in the second scan of potential. The newly appearing anodic peak ( $A_0$ ) is remaining upto ~ 5 mM of catechol and then further addition of catechol (> 5 mM) peak  $A_0$  completely disappears (Figure 4.120). Appeared anodic peak disappears at higher concentration of catechol (> 5 mM) ascribed the non-availability of diethylamine for the formation of substitution reaction. Figure 4.121 shows the plots of peak currents against concentration of catechol species. The relation between catechol concentration (2, 5, 10 and 15 mM) and cyclic voltammetric anodic peak current ( $I_p$ ) is linear for first anodic peak ( $A_1$ ). With the increase in concentration there is a gradual linear increase in  $A_1$  peak current, which may be due to the presence of a large amount of electroactive species at higher concentration. The linear dependence of peak current of catechol concentration is depicted from the calibration curve shown in Figure 4.121.

#### 4.1.7 Effect of electrode materials

Electrochemical properties of catechol in absence and presence of diethylamine was examined by different electrodes for example Glassy carbon (GC), Gold (Au) and Platinum (Pt) at different pH. The Cyclic voltammograms of 2 mM catechol + 250 mM diethylamine at GC, Au and Pt electrodes in the first and second scan of potential are shown in Figures 4.122-4.123.

The nature of voltammograms, the peak position and current intensity for the studied systems are different for different electrodes although the diameter of GC electrode (3 mm) is higher than Au and Pt (1.6 mm) electrodes. The CV of Au electrode is significantly different from those of the GC and Pt electrodes. At the Au electrode it shows three anodic and three cathodic peaks for the second scan of potential (Figure 4.123). In case of GC



electrode it shows two anodic and two cathodic peaks for the second scan of potential whereas at Pt electrode it shows two anodic and corresponding cathodic peaks (Figure 4.118). Voltammetric measurements performed at a Au electrode in only buffer solution of without catechol and diethylamine at pH 7, showed a peak at 1.1 V to the formation of Au(III) hydroxide. Consequently, the third peak (1.08 V) of Au electrode in presence of catechol and diethylamine at pH 7 is due to the oxidation of Au in buffer solution. Similar behavior of oxidation of Au electrode in different pH has been reported [71]. In the case of GC and Pt electrodes for the second cycle of potential a new oxidation and reduction peak appear at lower oxidation potential which can be attributed to the oxidation of adduct formed between the o-benzoquinone and diethylamine. Electrochemical properties of catechol with diethylamine for example change of pH, concentration, scan rate etc. were studied in detail using Pt and Au electrodes. But among the electrodes, the voltammetric response of GC electrode was better than Pt and Au electrodes in the studied systems.

#### 4.1.8 Subsequent cycles of CV of Catechol + Diethylamine

Figure 4.124 shows the cyclic voltammograms of the first 15 cycles of 2 mM catechol with 250 mM diethylamine of GC (3 mm) electrode in buffer solution of pH 7 for the potential range between - 0.6 V to 1.1 V. The voltammogram at the scan rate  $0.1 \text{ Vs}^{-1}$  has one anodic peak at 0.3V and two cathodic peaks at 0.01 V and - 0.23 V when considered the first scan of potential (red line). In the subsequent potential cycles a new anodic peak appeared at  $\sim - 0.01\text{V}$  and intensity of the first anodic peak current increased progressively on cycling but the second anodic peak current decreases and shifted positively on cycling. This can be attributed to produce of the catechol-diethylamine adduct through nucleophilic substitution reaction in the surface of electrode (Scheme 1). The successive decrease in the height of the catechol oxidation and reduction peaks with cycling can be ascribed to the fact that the concentrations of catechol-diethylamine adduct formation increased by cycling leading to the decrease of concentration of catechol or quinone at the electrode surface. The positive shift of the second anodic peak in the presence of diethylamine is probably due to the formation of a thin film of product at the surface of the electrode, inhibiting to a certain extent the performance of electrode process. Along with the increase in the number of potential cycles the first anodic peak current increased upto 10 cycles and



then the peak current almost unchanged with subsequent cycle (Figure 4.125). This may be due to the block of electrode surface by the newly formed species after more cycling.

The effect of the cyclic voltammograms of the first 15 cycles of 2 mM Catechol with 250 mM diethylamine of Gold (Au) electrode and Platinum (Pt) electrode in buffer solution of pH 7 were also studied in the same condition. In Figure 4.126 at Au electrode there were three anodic peaks at 0.24 V, 1.0 V and 1.32 V and three cathodic peaks at - 0.15 V, 0.13 V and 0.49 V respectively in the first scan of potential (red line). In the subsequent scan of potential Au electrode shows a new anodic peak at - 0.09 V with another three anodic peaks (black line). But at Pt electrode there was one anodic peak at 0.36 V and two cathodic peaks at - 0.2 V and - 0.05 V in the first scan of potential (red line) (Figure 4.127). In the subsequent potential cycles a new anodic peak appeared at - 0.05 V and the first anodic peak current increased progressively on cycling but the second anodic peak current decreases and shifted positively on cycling. This can be suggested to produce the catechol-diethylamine adduct through nucleophilic substitution reaction in the surface of electrode (Scheme 1).

#### 4.1.9 Controlled-potential coulometry of Catechol + Diethylamine

Controlled-potential coulometry was performed containing 1 mM of catechol and 1 mM of diethylamine at 0.5 V in buffer solution of pH 7 by using the three carbon rods. The electrolysis progress was monitored by cyclic voltammetry (Figure 4.128). During the course of coulometry the peaks  $A_0$  and  $C_0$  appeared and the height of the  $A_0$  peak increase proportionally to the advancement of coulometry, parallel to the decrease in height of anodic peak  $A_1$ . All anodic and cathodic peaks disappeared after consumption of 4 electrons per catechol. These observations allow us to propose the pathway in Scheme 1 for the electro-oxidation of catechol (1) in the presence of diethylamine (2). According to our results, it seems that the 1,4 addition reaction of 2 to *o*-quinone (1a) (reaction step (2)) is faster than other secondary reactions, leading to the intermediate 3. The oxidation of this compound (3) is easier than the oxidation of parent starting molecule (1) by virtue of the presence of electron-donating group. Like *o*-quinone 1a, *o*-quinone 4 can also be attacked from the C-5 position by diethylamine (2). However, no over reaction was observed during



the voltammetric experiments because of the low activity of the *o*-quinone 4 toward 1,4-(Michael) addition reaction with diethylamine (2).

We have isolated the products (3) originated from catechol with diethylamine electrosynthesis process. As the electrosynthesis process gradually small amount of reagent used for the formation of reaction causing the yield of the product was limited. The product 3 was further confirmed by FTIR in the next section.

#### 4.1.10 pH effect of DPV of Catechol + Diethylamine

Differential pulse voltammetry (DPV) technique was applied to make more clear for catechol-diethylamine addition reaction. DPV of 2mM catechol in the presence of 250 mM diethylamine in first and second scan of potential at different pH (3-11) was shown in Figures 4.129-4.130, respectively using GC (3 mm) electrode ( $E_{\text{pulse}}$  0.02 V,  $t_{\text{pulse}}$  20 ms and scan rate 0.1 V/s). In the buffer solution of pH 7-9, the voltammogram of catechol gave two well-developed wave in the presence of diethylamine (Figure 4.130). In pH 7, the first and second anodic peaks were showed at  $\sim -0.07$  V and 0.30 V, respectively. But in pH 3-5 for second scan of potential the first anodic peak current intensity is very small and in pH 11, the second anodic peak is fully diminished. As can be seen two completely separated anodic peaks with high current intensity are observed in pH 7, which can be attributed to the oxidations of *o*-benzoquinone-diethylamine new compound and *o*-benzoquinone, respectively.

Gold (Au) electrode is also used for the investigation of DPV of 2mM catechol with 250 mM diethylamine in different buffer solution at  $0.1 \text{ Vs}^{-1}$ . Figures 4.131-4.132 show the first and second scan of potential of catechol + diethylamine solution at different pH, respectively. However, in pH 7 new peak  $A_0$  appeared which may be attributed to the formation of catechol-diethylamine adduct. But, in lower and higher pH media no new anodic peak appeared. In the buffer solution of pH 7, the voltammogram shows two well-developed peak ascribed the formation of adduct similar to GC electrode.

The effect of pH on the DPV technique was also employed to make clearer for catechol-diethylamine addition reaction at Pt electrode in same condition. DPV of 2mM catechol in



the presence of 250 mM diethylamine in first and second scan of potential at different pH (3-11) were shown in Figures 4.133-4.134, respectively ( $E_{\text{pulse}}$  0.02 V,  $t_{\text{pulse}}$  20 ms and scan rate 0.1 V/s). It is noticed that the peak positions of the DPV of catechol with diethylamine was shifted negatively this introduces that the nucleophilic reaction is easier to pH 7. In the buffer solution of pH 7-9, the voltammogram of catechol gave two well-developed wave in the presence of diethylamine (Figure 4.135). In pH 7, the first and second anodic peaks were showed at - 0.11 V and 0.29 V, respectively. But, in pH 3-5 no new peak appears in the second scan of potential and in pH 11, the species are totally electroinactive. High current intensity is observed at pH 7, which can be attributed to the formation of catechol-diethylamine adduct. The DPV of Au and Pt electrodes are consistent with the GC electrode in the studied systems at the same condition.

#### 4.1.11 Effect of deposition time change of DPV of Catechol + Diethylamine

Figure 4.135 shows the DPV of deposition time change (0, 10, 30, 90 and 120 s) of 2 mM catechol with 250 mM diethylamine in pH 7 at GC electrode. It is seen that the increasing of deposition time from 0 s to 10 s leads to develop a new peak at 0.09 V. When the deposition time increases 30 s, more nucleophilic attack occurs and consequently more catechol-diethylamine adducts leads to decreasing in the concentration of *o*-benzoquinone and increasing in the concentration of catechol-diethylamine adduct at the surface of electrode. For further increase of deposition time from 30 s to 120 s, the first anodic peak current increases and second anodic peak current decreases. This confirmed that with the increase of time decreases the concentration of *o*-benzoquinone and increases the concentration of catechol-diethylamine adduct at the surface of electrode.

#### 4.1.12 Effect of concentration of DPV of Catechol + Diethylamine

The effect of diethylamine concentration on the differential pulse voltammograms of catechol was studied. Figures 4.136-4.137 show DPV for 2 mM of catechol solution containing buffer (pH 7) in the presence of various concentration of diethylamine from 150 to 350 mM at the surface of GC electrode at first and second scan of potential. As indicated in Figure 4.132, there are two separated anodic peaks appeared after addition of diethylamine into catechol. In this case, the increasing of the concentration of diethylamine



from 150 to 300 mM leads to increasing of first anodic peak current. For further increase of concentration from 300 to 350 mM, the first and second anodic peak current decreases gradually. In lower concentration of diethylamine ( $< 250$  mM), the nucleophilic substitution reaction take place in comparable degree, whereas increasing the concentration of diethylamine ( $< 300$  mM) make favorable nucleophilic attack of diethylamine toward *o*-benzoquinone generated at the surface of electrode. For further addition of diethylamine ( $> 300$  mM) into catechol solution, the excess electroinactive diethylamine deposited on the electrode surface and hence the peak current decreases.

In this study comparatively high concentration of diethylamine (150-350 mM) was used sequentially to determine the optimum condition for the nucleophilic substitution reaction of catechol with diethylamine. As the reaction was occurred at high concentration of nucleophiles, consequently the voltammetric peaks (DPV) for adduct appeared noticeably. In contrast, comparatively low concentration of diethylamine was used arbitrarily by Kiani et al [72], hence the appearing peak was not so prominent.

Gold (Au) electrode was also used for the investigation on the DPV of fixed 2 mM catechol with different concentration (150-350 mM) of diethylamine in buffer solution pH 7 at  $0.1 \text{ Vs}^{-1}$ . Figures 4.138-4.139 show the first and second scan of potential of the studied systems at different concentration, respectively. In second scan of potential an appeared peak,  $A_0$  was obtained which may be attributed the formation of catechol-diethylamine adduct.

The effect of diethylamine concentration on the DPV of catechol was also studied Platinum (Pt) (1.6 mm) electrode in the same condition. Figures 4.140-4.141 show DPV for 2 mM of catechol solution containing buffer (pH 7) in the presence of various concentration of diethylamine from 150 mM to 350 mM at the surface of Pt electrode for the first and second scan of potential. As reported in Figure 4.141, in the second scan there are two separated anodic peaks appeared after addition of diethylamine into catechol. In lower concentration of diethylamine ( $< 250$  mM), the nucleophilic substitution reaction take place in comparable degree, whereas increasing the concentration of diethylamine ( $< 250$  mM) make pointful nucleophilic attack of diethylamine towards *o*-benzoquinone generated at the surface of electrode. For more addition of diethylamine ( $> 250$  mM) into

catechol solution, the excess electroinactive diethylamine accumulated on the electrode surface and hence the peak current decreases.

#### 4.1.13 Spectral analysis of Catechol + Diethylamine

The FTIR spectral assignments of the vibrational modes of the catechol-diethylamine adduct, pure diethylamine and pure catechol were compared (Figure 4.142). The diethylamine showed the N-H stretching sharp band at  $3410\text{ cm}^{-1}$ . The absorption peak was broad and shifted negatively at  $3390\text{ cm}^{-1}$  for the introduction of -OH group in the catechol-diethylamine adduct (Figure 4.142). In adduct the peaks at finger print region are different from pure catechol and diethylamine.

#### 4.1.14 Chronoamperometry of Catechol + Diethylamine

The chronoamperogram of 2 mM catechol in presence of 250 mM diethylamine in buffer solution in pH 7 at GC and Au electrodes are shown in Figures 4.143-4.144. The cottrell plots of the background- subtracted current for catechol-diethylamine fell on straight line as is shown in Figures 4.145-4.146. From the equation 4.1 the values of  $n$  (number of transfer electrons) was obtained from the slope and intercept of the cottrell plot. Determination of electron transfer number,  $n$  at different stepping potential is very essential for the estimation of redox interaction. When potential is stepped from a non-reacting domain to  $E$ , a cottrell plot ( $I$  vs  $t^{1/2}$ ) shows the slope by the linear diffusion

$$s = \pi^{1/2} n F D^{1/2} a^2 c^*$$

together with the intercept for the edge effect

$$p = \pi n F D a c^*$$

where  $a$  is the radius of the electrode,  $c^*$  is the concentration of the electroactive species,  $D$  is the diffusion coefficient. The ratio of the square of the slope,  $s$ , to the intercept,  $p$ , is

$$n = s^2 / p F a^3 c^* \dots \dots \dots 4.1$$

Catechol in buffer solution (pH 7- 11), it is seen that total electron transfer numbers is found to be very high. This is may be due to the big electrode.



#### 4.2.1 Electrochemical redox behavior of Catechol + Sulfanilic acid

Figures 4.147-4.148 show the comparison of pure catechol, pure sulfanilic acid and catechol with sulfanilic acid in the first and second scan of potential respectively in pH 3 at scan rate 0.1 V/s. In the second cycle (Figure 4.148), the cyclic voltammogram of catechol (blue line) displays one anodic peak at (0.63 V) and corresponding cathodic peak at (0.11 V) connected to its transformation to *o*-quinone and vice versa. Pure sulfanilic acid is electrochemically active having anodic peak 1.02 V and corresponding cathodic peak at 0.25 V in the potential range studied (Figure 4.148, red line). Figure 4.148 (black line) shows the CV of catechol (2 mM) in the presence of sulfanilic acid (2 mM) in the second scan of potential in the same condition. In the second cycle of potential catechol with sulfanilic acid shows three anodic peaks at 0.31 V, 0.72 V and 1.11 V and the corresponding two cathodic peaks at - 0.02 V and 0.48 V, respectively. The nature of voltammograms of catechol in presence of sulfanilic acid is quasi-reversible. Upon addition of sulfanilic acid to catechol solution, the cathodic peak  $C_1$  shifted negatively. Also, in the second cycle of potential a new anodic peak  $A_0$  appears and anodic peaks  $A_1$  and  $A_2$  shifted positively. In the first scan of potential, the anodic peak of catechol in presence of sulfanilic acid is very similar to pure catechol and pure sulfanilic acid (Figure 4.147). But in the second scan of potential appearance of new peak  $A_0$  and shifting of  $A_1$ ,  $A_2$  and  $C_1$  peaks positions, which is indicative of a chemical reaction of sulfanilic acid (2) with the *o*-quinone (1a) produced at the surface of electrode (Scheme 2). In the case of catechol in presence of sulfanilic acid, the oxidation of sulfanilic acid substituted *o*-benzoquinone is easier than the oxidation of parent catechol [63]. This behavior is in agreement with that reported by other research groups for similar electrochemically generated compounds such as catechol and different nucleophiles [73-76, 15, 22- 23, 25, 29]. In the absence of other nucleophiles, water or hydroxide ion often adds to the *o*-benzoquinone.

The corresponding peak potential differences ( $\Delta E$ ) in the second scan of potential of 2 mM catechol + 2 mM sulfanilic acid at GC electrode are tabulated in Table 4.26. The peak potential differences are usually independent of scan rate. The peak separation potential increases with the increasing of scan rate that indicates there is a limitation according to ohmic potential drop or charge transfer kinetics [68].



The comparison of CV of pure catechol (blue line), pure sulfanilic acid (red line) and catechol with sulfanilic acid (black line) of Au electrode in the first and second scan of potential at the same condition are shown in Figures 4.149-4.150. The CV of catechol in presence of sulfanilic acid shows two anodic peaks at 0.75 V, 1.11 V and three cathodic peaks at 0.05 V, 0.28 V and 0.67 V, respectively in the first scan of potential (Figure 4.149). In the second scan of potential (Figure 4.150) a new oxidation peak appears at 0.25 V. The peak position of the CV of catechol with sulfanilic acid in the second cycle was shifted positively and the anodic peak current increases but the cathodic peak current decreases. The peak current, peak potential, corresponding peak potential differences ( $\Delta E$ ) in the second scan of potential of 2 mM catechol + 2 mM sulfanilic acid at Au electrode are tabulated in Tables 4.27-4.28.

Figures 4.151-4.152 show the CV of 2 mM catechol with 2 mM sulfanilic acid in the first and second scan of potential at Pt (1.6 mm) electrode in pH 3. In Figure 4.152, the second scan of potential catechol with sulfanilic acid shows three anodic peaks at 0.22 V, 0.65 V and 1.05 V and the corresponding two cathodic peaks at - 0.01 V and 0.86 V, respectively. Upon addition of sulfanilic acid to catechol solution, the cathodic peak  $C_1$  decreases. Also, in the second scan of potential a new anodic peak  $A_0$  appears and anodic peak  $A_1$  and  $A_2$  decreases. This observation can be stated by considering nucleophilic attack of sulfanilic acid to *o*-benzoquinone. The peak potential, corresponding peak potential differences, peak current in the second scan of potential of 2 mM catechol + 2 mM sulfanilic acid at Pt electrode are tabulated in Tables 4.29.

#### 4.2.2 Subsequent cycles of CV of Catechol + Sulfanilic acid

Figure 4.153 shows the cyclic voltammogram of the first 15 cycles of 2 mM catechol with 2 mM sulfanilic acid in buffer solution of pH 3 for the potential range between - 0.4 V to 1.75 V at a GC electrode. The voltammogram at the  $0.1 \text{ Vs}^{-1}$  scan rate has three anodic peaks at 0.65 V, 1.05 V, 1.24 V and a cathodic peak at 0.03 V when considered the first scan of potential (red line). In the subsequent potential cycles a new anodic peak appeared at  $\sim 0.24 \text{ V}$  and intensity of the appeared anodic peak ( $A_0$ ) current increased progressively on cycling but the first ( $A_1$ ), second ( $A_2$ ) and third ( $A_3$ ) anodic peak current decreases and shifted negatively on cycling. This can be attributed to produce the catechol-sulfanilic



acid adduct through nucleophilic substitution reaction in the surface of electrode (Scheme 2). The successive decrease in the height of the catechol oxidation and reduction peaks with cycling can be ascribed to the fact that the concentrations of catechol-sulfanilic acid adduct formation increased by cycling leading to the decrease of concentration of catechol or quinone at the electrode surface. The positive shift of the second anodic peak in the presence of sulfanilic acid is probably due to the formation of a thin film of product at the surface of the electrode, inhibiting to a certain extent the performance of electrode process. Along with the increase in the number of potential cycles the first anodic peak current increased up to 10 cycles and then the peak current almost unchanged with subsequent cycle (Figure 4.154). This may be due to the block of electrode surface by the newly formed electroactive species after more cycling.

Figures 4.155-4.156 show the CV of the first 15 cycles of 2 mM catechol with 2 mM sulfanilic acid at Au and Pt (1.6 mm) electrode in the same condition. At Au electrode, the voltammogram in the  $0.1 \text{ Vs}^{-1}$  scan rate has two anodic peaks at 0.82 V, 1.12 V and three cathodic peaks at 0.04 V, 0.27 V and 0.7 V respectively when considered the first scan (red line) (Figure 4.155). In the subsequent potential cycles a new anodic peak appeared at  $\sim 0.26 \text{ V}$ . But there were two anodic peaks at 0.7 V, 1.05 V and a cathodic peak at 0.04 V in the first scan of potential (red line) of Pt electrode (Figure 4.156). A new anodic peak appeared at  $\sim 0.26 \text{ V}$  in the subsequent potential of cycles and intensity of the first anodic peak current increased progressively on cycling but the second anodic peak current decreases and shifted negatively on cycling. This can be attributed easy to produce the catechol-sulfanilic acid adduct through nucleophilic substitution reaction in the surface of electrode (Scheme 2).

#### 4.2.3 Scan rate effect of Catechol + Sulfanilic acid

Figure 4.157 shows the CV of second cycle of 2mM catechol in presence of 2 mM sulfanilic acid of GC (3 mm) electrode in buffer solution (pH 3) at different scan rates from 0.05 V/s to 0.50 V/s. The peak current of both the anodic and cathodic peaks increases with the increase of scan rate. The anodic peaks are shifted to the right direction and the cathodic peak is shifted towards left with increasing scan rate. Figure 4.158 shows the plots of the anodic and cathodic peak currents of 2 mM catechol with 2 mM sulfanilic

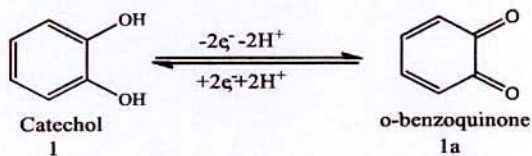


acid for the second cycle against the square-root of the scan rates. The nearly proportionality of the anodic and the cathodic peaks suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process. The corresponding peak current ratio ( $I_{pa1}/I_{pc1}$ ) vs scan rate for a mixture of catechol with sulfanilic acid decreases with increasing scan rate firstly and then after 0.15 V/s, it is almost unchanged (Figure 4.159, left scale). The anodic peak current ratio ( $I_{pa1}/I_{pa0}$ ) vs scan rate for a mixture of catechol and sulfanilic acid firstly increases and then after 0.15 V/s scan rate it decreases (Figure 4.159, right scale). On the other hand, the value of current function for the anodic peak  $A_0$ , ( $I_p/v^{1/2}$ ) was found to be decreased with increasing scan rate (Figure 4.160). The nature of the current function versus the scan rate plot indicates the electron transfer-chemical reaction- electron transfer- chemical reaction- electron transfer (ECECE) mechanism for electrode process [13]. This confirms the reactivity of *o*-benzoquinone (**1a**) towards sulfanilic acid (**2**) firstly increases at slow scan rate and then at higher scan rate it decreases. Figure 4.161 shows the plots of the anodic and cathodic peak potentials of 2 mM catechol with 2 mM sulfanilic acid against scan rate in the second scan of potential. In this figure it indicates that the anodic peak shifted positively and cathodic peak shifted negatively on increasing the scan rate.

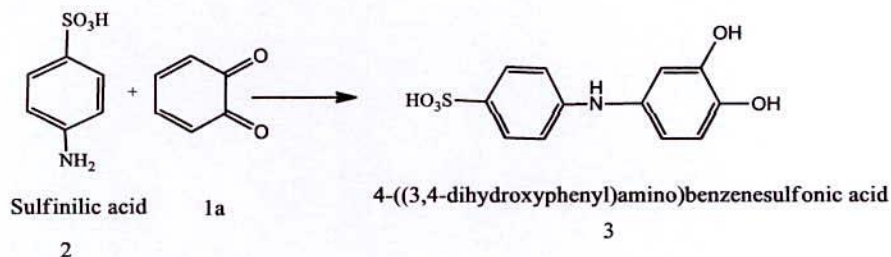
Figure 4.162 shows the CV of second scan at Au electrode of 2 mM catechol with 2 mM sulfanilic acid in the same condition. The peak current of both the anodic and cathodic peaks increases with the increase of scan rate. Figure 4.163 shows the plots of the anodic and cathodic peak currents for the first and second scan of potential against square-root of the scan rates. Figure 4.164 shows the CV of second scan of potential of 2 mM catechol with 2 mM sulfanilic acid of Pt electrode at scan rate from 0.05 V/s to 0.50 V/s. The peak current of both the anodic and cathodic peaks increases with the increase of scan rate. Figure 4.165 shows the plots of the anodic and cathodic peak currents for the second scan of potential against square-root of the scan rates of 2 mM catechol + 2 mM sulfanilic acid. A typical observation was found for the species of the redox system was linearly increased with the square root of scan rate for Au and Pt electrodes, suggesting diffusion controlled process.



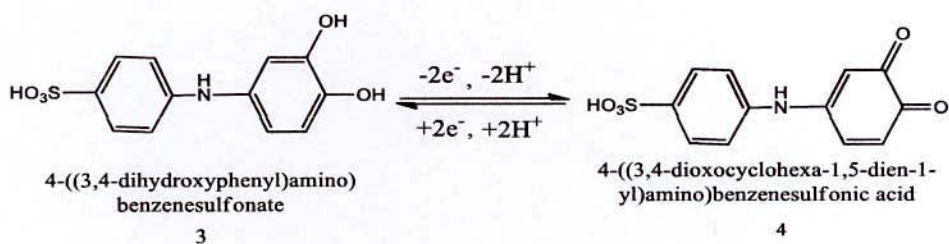
## Step-1:



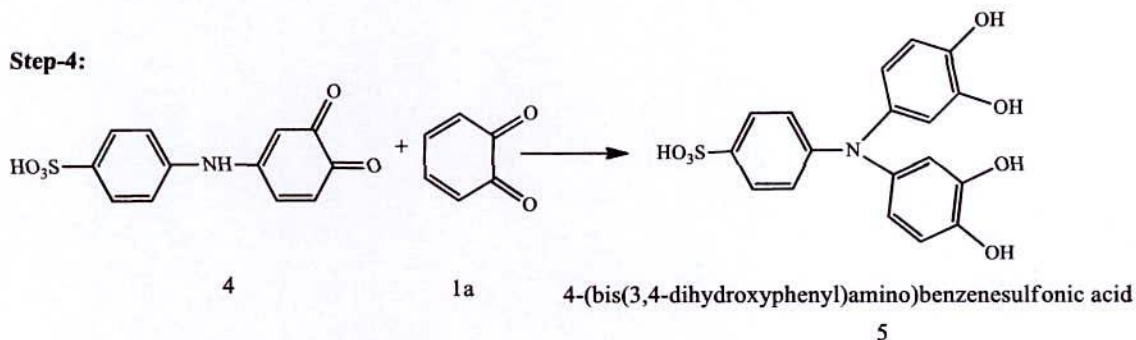
## Step-2:



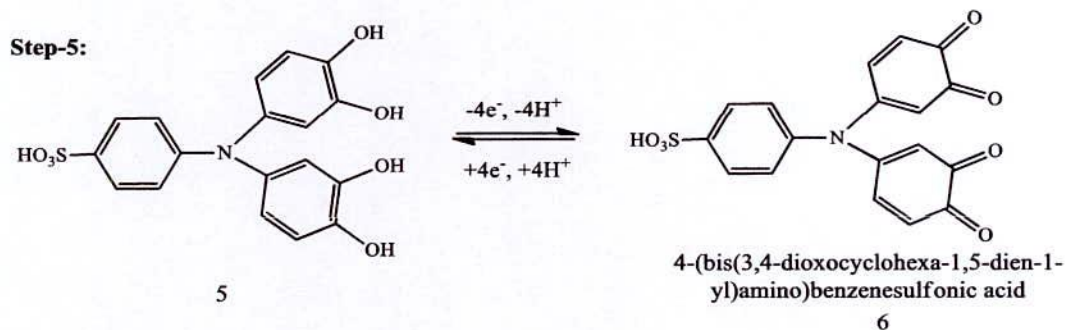
## Step-3:



## Step-4:



## Step-5:



Scheme 2

#### 4.2.4 Effect of pH of Catechol + Sulfanilic acid

Cyclic voltammetry detailing the oxidation of 2 mM catechol in different pH at scan rate 0.1 V/s was measured. In the buffer solution of pH 3, catechol gave a well-developed reversible wave. The electrochemical reaction of catechol occurring at pH below 7 is a two-proton, two-electron transfer process (Scheme 2). This behavior is in agreement with that reported by other research groups for catechol and its derivatives [76, 70].

Figures 4.166-4.167 show cyclic voltammogram of catechol in presence of 2 mM sulfanilic acid in the first and second cycle respectively of GC (3 mm) electrode was studied at pH from 2 to 9. The voltammetric behavior of catechol at pH 9 in the presence of 2 mM sulfanilic acid shows that no new anodic peak appeared after repetitive cycling indicating that the reaction between *o*-benzoquinone and sulfanilic acid has not occurred (Figure 4.167). In the pH 2-5, voltammetric new anodic peak appeared after repetitive cycling. Whereas in the pH 7, the cyclic voltammogram show a small appearing peak. It was thus suggested that the *o*-benzoquinone undergoes attack by the sulfanilic acid at pH 2-7 reflected that voltammetric new anodic peak appeared after repetitive cycling.

Figure 4.168 shows the plot of oxidation peak ( $A_0$  and  $A_1$ ) current,  $I_p$  against pH of solution in the second cycle at GC electrode. From the Figure it is seen that the maximum peak current is obtained at pH 3 (Table 4.30). In this study buffer solution of pH 3 has been selected as suitable medium for electrochemical study of catechols in the presence of sulfanilic acid. This ascribed that the electrochemical oxidation of catechol in presence of sulfanilic acid is facilitated in acidic media.

Figure 4.169 shows the plot of oxidation peak potential,  $E_p$  values against pH of 2 mM catechol + 2 mM sulfanilic acid in the same condition. The slopes of the plot was determined graphically as the anodic peaks (36 mV/pH for second anodic peak  $A_1$  or 44 mV/pH for appeared peak  $A_0$ ) at 0.1 V/s, which is close to the theoretical value for two-electron, two-proton transfer process. This indicates that both the oxidation of the catechol and catechol-sulfanilic acid adduct proceeded via the  $2e^-/2H^+$  processes. This also suggests that during the reaction not only electron but also proton are released from the catechol-sulfanilic acid adduct. Other research groups also reported similar behavior for catechol



and its derivatives [76]. The peak current of the redox couple also is found to be dependent upon pH.

The influence of pH for Au electrode in the same systems, the voltammetric properties are some different from GC electrode. In Figure 4.170, the second scan of potential we found the appeared peak current is maximum in pH 3. Figure 4.171 shows the plot of oxidation peak current,  $I_p$  against pH of solution of 2 mM catechol + 2 mM sulfanilic acid in the same condition. From the Figure 4.171 it is seen that the maximum peak current of the appeared peak ( $A_0$ ) is obtained at pH 3 (Table 4.31). In this study buffer solution of pH 3 has been selected as suitable medium for electrochemical study of catechol in the presence of sulfanilic acid. This ascribed that the electrochemical oxidation of catechol in presence of sulfanilic acid is facilitated in acidic media and hence the rate of electron transfer is faster. Figure 4.172 shows the plot of oxidation peak potential,  $E_p$  values against pH at Au electrode in the same condition. In Figure 4.172 the slopes of the plot was determined graphically as the anodic peaks (35.4 mV/pH for first anodic peak  $A_1$  or 41.5 mV/pH for appeared peak  $A_0$ ) at 0.1 V/s, which is close to the theoretical value of two-electron, two-proton transfer process (Scheme 2).

Figure 4.173 shows the second scan of potential in different pH (2-9) of 2 mM catechol + 2 mM sulfanilic acid at Pt electrode. In the second scan a new peak appeared at 0.18 V which is indicated catechol-sulfanilic acid adduct formation. Figure 4.174 shows the plot of peak current,  $I_p$  vs pH at Pt electrode in the second scan of potential, this attributed that the peak current in buffer solution of pH 3 is founded maximum (Table 4.32). In pH 3 the transfer of electron is faster than other buffer solution. The plot of peak potential,  $E_p$  versus pH is shown in Figure 4.175 according to the second scan of potential. The slops of the equation of this Figure are founded 31.7 mV/pH for appeared peak  $A_0$  and 29.8 mV/pH for anodic peak  $A_1$  which are near about the theoretical value 30 mV per pH. This indicates that both the oxidation of the catechol and catechol-sulfanilic acid adduct proceeded via the  $2e^-/2H^+$  processes (Scheme 2).

#### 4.2.5 Concentration effect of Sulfanilic acid

Figure 4.176 shows the variation of voltammogram by the addition of different concentration of sulfanilic acid (2, 10, 20, 30 and 40 mM) into fixed concentration of catechol (2 mM) of GC (3 mm) electrode in pH 3 and at scan rate 0.1 V/s. The cathodic peak  $C_1$  disappeared at the same concentration of catechol (2 mM) and sulfanilic acid (2 mM) in the experimental conditions. By increasing the concentration of sulfanilic acid, the cathodic peak  $C_1$  increases. In the second scan the anodic peaks shifted positively and a new peak appeared at  $\sim -0.01$  V. The net current intensity of the newly appeared anodic and cathodic peak increases with the increase of sulfanilic acid composition. At higher concentration of sulfanilic acid ( $> 2$  mM), another new peak appeared at 0.39 V (Figure 4.176). At this condition the anodic peak current is proportionally varied with the scan rate. This suggests that the peak current of the species at higher concentration is controlled by adsorption process. At higher concentration of sulfanilic acid ( $> 2$  mM), the excess electroactive sulfanilic acid may be deposited on the electrode surface and formation of some side reaction or polymerization reaction at electrode surface for the abundant of sulfanilic acid. The reaction of catechol in presence of sulfanilic acid was favorable in 2 mM of sulfanilic acid, 2mM catechol and at pH 3. Figure 4.177 shows the plot of oxidation peak current versus different concentration of sulfanilic acid at the second cycle. The anodic peak  $A_3$  increased with the increasing of sulfanilic acid.

In addition of different concentration of sulfanilic acid (2, 10, 20, 30 and 40 mM) into fixed concentration of catechol (2 mM) at Au and Pt electrode have been also examined in the same conditions. Figure 4.178 shows the CV of Au electrode at different concentration of sulfanilic acid in pH 3. Figure 4.179 shows the voltammogram of 2<sup>nd</sup> cycle at different concentration of sulfanilic acid with fixed concentration of catechol in pH 3 at Pt electrode. In the second scan of potential (Figure 4.179) the anodic peaks shifted positively and a new anodic peak appeared at  $\sim -0.03$  V. The net current intensity of the newly appeared anodic and cathodic peak increases with the increase of sulfanilic acid composition.



#### 4.2.6 Concentration effect of Catechol composition

In Figure 4.180, in contrast, with the addition of different concentration of catechol (2, 4, and 6 mM) into fixed concentration of sulfanilic (2 mM) of GC (3 mm) electrode, the second anodic peak ( $A_1$ ) current increases and shifted positively with the increase of catechol composition in the second scan of potential. The newly appearing anodic peak ( $A_0$ ) is remaining but second anodic peak ( $A_2$ ) totally disappeared. Figure 4.181 shows the plots of peak currents against concentration of catechol species in the same condition. The cyclic voltammetric anodic peak current ( $I_p$ ) is increased at first anodic peak ( $A_1$ ), but the appeared anodic peak current ( $A_0$ ) is unchanged and second anodic peak ( $A_2$ ) decreases upto 4 mM of catechol and after further addition it is unseen. With the increase in concentration there is a gradual linear increase in  $A_1$  peak current, which may be due to the presence of a large amount of electroactive species at higher concentration. The anodic peak potentials,  $E_p$  vs concentration curve is plotted in Figure 4.182 in which the slope for first anodic peak,  $A_1$  is found 42 mV/pH.

#### 4.2.7 Controlled-potential coulometry of Catechol + Sulfanilic acid

Controlled-potential coulometry was performed in aqueous solution containing 1 mM of catechol and 1 mM of sulfanilic acid at 0.5 V in pH 7. The electrolysis progress was monitored by cyclic voltammetry (Figure 4.183). As Figure 4.183 shows, during the course of coulometry the peaks  $A_0$  appeared and the height of the  $A_0$  peak was increased to the advancement of coulometry, parallel to the decrease in height of anodic peaks  $A_1$ ,  $A_2$  and  $A_3$ . These observations allow us to propose the pathway in Scheme 2 for the electro-oxidation of catechol (**1**) in the presence of sulfanilic acid (**2**). According to our results, it seems that the 1,4 addition reaction of **2** to o-quinone (**1a**) (reaction (2)) is faster than other secondary reactions, leading to the intermediate **3**. The oxidation of this compound (**3**) is easier than the oxidation of parent starting molecule (**1**) by virtue of the presence of electron-donating group.

#### 4.2.8 Effect of electrode materials

Electrochemical properties of catechol in absence and presence of sulfanilic acid was examined by different electrodes like Glassy carbon (GC), Gold (Au) and Platinum (Pt) electrode at different pH. The cyclic voltammograms of 2 mM catechol with 2 mM sulfanilic acid at GC, Au and Pt electrode are shown in Figure 4.184 in the second cycle.

The nature of voltammograms, the peak position and current intensity for the studied systems are different for different electrodes although the diameter of GC electrode (3 mm) is higher than Au and Pt (1.6 mm). The CV at Au electrode is significantly different from those of the GC and Pt electrodes. At the Au electrode it shows three anodic and three cathodic peaks for the second scan (Figure 4.184). In case of GC electrode it shows three anodic peaks and one cathodic peak for the second scan of potential whereas at Pt electrode it shows three anodic and two cathodic peaks. Voltammetric measurements performed at a Au electrode in only buffer solution of without catechol and sulfanilic acid at pH 3, showed a peak at 1.1 V to the formation of Au (III) hydroxide. Consequently, the third peak (1.08V) of Au electrode in presence of catechol and sulfanilic acid at pH 3 is due to the oxidation of Au in buffer solution. Similar behavior of oxidation of Au electrode in different pH has been reported [71]. In the case of GC and Pt electrodes for the second cycle of potential a new oxidation and reduction peak appear at lower oxidation potential which can be attributed to the oxidation of adduct formed between the *o*-benzoquinone and sulfanilic acid. Among the electrodes, the voltammetric response of GC electrode was better than Pt and Au electrodes in the studied systems.

Figure 4.185 shows the differential pulse voltammograms of 2 mM of catechol and 2 mM of sulfanilic acid at different electrodes in the same condition. At GC electrode the all anodic peaks are sharp than another electrodes. So, the reaction easily occurred at the surface of GC electrode.

#### 4.2.9 pH effect of DPV of Catechol + Sulfanilic acid

Differential pulse voltammetry (DPV) technique obtained for 2 mM catechol in the presence of 2 mM sulfanilic acid in second scan of potential at different pH (2-9) was



shown in Figure 4.186. In the buffer solution of pH 2-3, catechol gave well-developed wave in the presence of sulfanilic acid. A sharp anodic appeared peak was obtained at 0.185 V in (Figure 4.186) and other peaks (0.57 V, 0.96 V and 1.11 V) were showed for corresponding oxidation of catechol and sulfanilic acid, respectively. But, in pH > 3 of second scan of potential the first anodic peak current intensity is very small and in pH 9, the second anodic peak was fully diminished. Therefore, the reaction of sulfanilic acid with catechol was favorable at pH 3 which is consistent with the cyclic voltammogram.

Au electrode is also used for the investigation on the DPV of 2 mM catechol with 2 mM sulfanilic acid in buffer solution of different pH at  $0.1 \text{ Vs}^{-1}$ . Figure 4.187 shows the DPV of second scan at different pH of Au electrode. The peak positions of the DPV of catechol with sulfanilic acid were shifted. However, in pH 3 a well-developed appeared peak was obtained at 0.07 V on the negative potential compared with catechol which attributed the formation of catechol-sulfanilic acid adduct.

DPV obtained for 2 mM catechol in the presence of 2 mM sulfanilic acid in first and second scan of potential at different pH (2-9) of Pt electrode were shown in Figure 4.188 for the first and second scan of potential respectively using  $E_{\text{pulse}} 0.02 \text{ V}$ ,  $t_{\text{pulse}} 20 \text{ ms}$  and scan rate  $0.1 \text{ V/s}$ . It is noticed that the peak positions of the DPV of catechol with sulfanilic acid was shifted. The peak current at pH 3 was very high, this introduces that the nucleophilic reaction is easier in pH 3. In the second scan of potential a new anodic peak appeared at 0.295 V (Figure 4.188). In the buffer solution of pH 7, the voltammogram of catechol gave small developed wave in the presence of sulfanilic acid (Figure 4.188). But in pH 11, the species are totally electroinactive.

#### 4.2.10 Effect of deposition time change of DPV of Catechol + Sulfanilic acid

Figure 4.189 shows the DPV of deposition time change (0, 10, 30, 60, 90, 120 and 180 s) of 2 mM catechol + 2 mM sulfanilic acid at pH 3. From the Figure, it was seen that the increasing of deposition time from 0 s to 10 s leads to develop a new peak at 0.18 V. When the deposition time increases 120 s, more nucleophilic attack occurs and consequently more catechol-sulfanilic acid adducts leads to decreasing in the concentration of *o*-benzoquinone and 4-aminosulfonate and increasing in the concentration of catechol-

sulfanilic acid adduct at the surface of electrode. For further increase of deposition time from 120 s to 180 s, appeared, first and second anodic peak current decreases. This confirmed that with the increase of time decreases the concentration of *o*-benzoquinone and sulfanilic acid and also decreases the concentration of catechol-sulfanilic acid adduct at the surface of electrode.

#### 4.2.11 Effect of concentration of DPV of Sulfanilic acid

The effect of sulfanilic acid concentration on the differential pulse voltammogram of catechol was studied. Figure 4.190 shows the DPV for 2 mM of catechol solution containing buffer (pH 3) in the presence of various concentration of sulfanilic acid from 2 mM to 30 mM at the surface of GC electrode in the second scan of potential. For further addition of sulfanilic acid ( $> 2$  mM) into catechol solution, the excess electro active sulfanilic acid deposited on the electrode surface and hence some side reaction or polymerization reaction occurred. In lower concentration of sulfanilic acid ( $< 5$  mM), the nucleophilic substitution reaction takes place in comparable degree (scheme 2), whereas increasing the concentration of sulfanilic acid ( $> 5$  mM) make favorable nucleophilic attack of sulfanilic acid toward *o*-benzoquinone generated at the surface of electrode (Scheme 2). The DPV behavior is consistent with CV.

Figures 4.191- 4.192 show the DPV for 2 mM of catechol solution containing buffer (pH 3) in the presence of various concentration of sulfanilic acid from 2 to 40 mM at the surface of Au and Pt electrode. As reported in Figure 4.191 and 4.192, in the second scan there are four separated anodic peaks appeared after addition of sulfanilic acid into catechol solution at Au and Pt electrode respectively.

#### 4.2.12 Spectral analysis of Catechol + Sulfanilic acid

The FTIR spectral assignments of the vibrational modes of the catechol-sulfanilic acid adduct, sulfanilic acid and catechol were studied. The sulfanilic acid showed the N-H stretching sharp band at  $2930\text{ cm}^{-1}$  and O-H stretching band at  $3370\text{ cm}^{-1}$ . Catechol showed O-H stretching at  $3467\text{ cm}^{-1}$ . The absorption peaks due to the O-H broad stretching vibration was appeared at  $3478\text{ cm}^{-1}$ , S=O stretching at  $1425\text{ cm}^{-1}$  and aromatic C=C



stretching at  $1577\text{ cm}^{-1}$  for the catechol-sulfanilic acid adduct (Figure 4.193). The absorption peaks due to the N-H stretching vibration was disappeared at the wave number for the catechol-sulfanilic acid adduct.

#### 4.2.13 Chronoamperometry of Catechol + Sulfanilic acid

The chronoamperogram of 2 mM catechol in presence of 2 mM sulfanilic acid in buffer solution in pH 3 at GC and Au electrodes are shown in Figures 4.194-4.195. The cottrell plots of the background-subtracted current for catechol-diethylamine fell on straight line as is shown in Figures 4.196-4.197.

#### 4.2.14 CV of Sulfanilic acid + Diethylamine mixture with Catechol

Figures 4.198-4.199 show the comparison of CV and DPV at second scan of potential of catechol in presence of sulfanilic acid, diethylamine and the mixture of sulfanilic acid + diethylamine. From Figure 4.198, (solid line) shows the cyclic voltammogram of 2 mM catechol + 10 mM sulfanilic acid of GC electrode in buffer solution of pH 7 and scan rate 0.1 V/s. It shows that appeared anodic and first anodic peak at - 0.1 V and 0.39 V respectively and a cathodic peak at - 0.16 V. The CV of catechol (2 mM) in the presence of diethylamine (10 mM) (dashed line) in the second scan of potential at the same condition is shown in Figure 4.198. This Figure shows one anodic peak at 0.37 V and a cathodic peak at 0.08 V. Deep solid line shows the CV of catechol in presence of both sulfanilic acid and diethylamine at the same condition. In the mixture the appeared anodic peak obtained at -0.1 V which is located in between diethylamine and sulfanilic acid. The appeared anodic peak current of mixture is lower than that the catechol-diethylamine, but higher than that of catechol-sulfanilic acid. We have monitored the variation of CV and DPV with the change of composition of sulfanilic acid and diethylamine into the fixed composition of catechol shown in Figures 4.200-4.205. From these Figures it is suggest that as the mixture of diethylamine and sulfanilic acid was added into catechol solution, both the nucleophiles attack different catechol simultaneously. But the diethylamine is less reactive than the sulfanilic acid toward the catechol.

Table 4.1: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM catechol in aqueous buffer solution (pH 7) of GC electrode at different scan rate

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|--------------------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.37        | 0.04        | 0.33                           | 5.23            | -5.22           | 1.01              |
| 0.10        | 0.38        | 0.04        | 0.34                           | 5.89            | -5.75           | 1.03              |
| 0.15        | 0.38        | 0.04        | 0.34                           | 3.78            | -8.23           | 0.46              |
| 0.20        | 0.40        | 0.04        | 0.36                           | 3.99            | -7.46           | 0.53              |
| 0.25        | 0.42        | 0.03        | 0.39                           | 5.27            | -7.59           | 0.69              |
| 0.30        | 0.43        | 0.03        | 0.40                           | 3.53            | -7.64           | 0.46              |
| 0.35        | 0.50        | 0.01        | 0.49                           | 3.64            | -7.27           | 0.69              |
| 0.40        | 0.51        | -0.03       | 0.54                           | 3.52            | -8.21           | 0.43              |
| 0.45        | 0.52        | -0.04       | 0.56                           | 4.61            | -9.99           | 0.46              |

Table 4.2: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | 0.28        | 0.05        | -0.20       | 0.23                           | 0.16               | 37.43           | -15.75          | -10.67          | 2.37              |
| 0.10        | 0.31        | 0.03        | -0.21       | 0.28                           | 0.17               | 50.53           | -27.04          | -12.34          | 1.86              |
| 0.15        | 0.31        | 0.03        | -0.21       | 0.28                           | 0.17               | 61.19           | -39.04          | -11.75          | 1.56              |
| 0.20        | 0.31        | 0.02        | -0.20       | 0.29                           | 0.16               | 71.73           | -45.66          | -9.23           | 1.57              |
| 0.25        | 0.31        | 0.02        | -0.20       | 0.29                           | 0.16               | 69.39           | -52.53          | -9.28           | 1.32              |
| 0.30        | 0.32        | 0.02        | -0.21       | 0.30                           | 0.17               | 85.90           | -59.56          | -7.34           | 1.44              |
| 0.35        | 0.33        | 0.02        | -0.21       | 0.31                           | 0.17               | 91.22           | -66.66          | -6.37           | 1.36              |
| 0.40        | 0.34        | 0.01        | -0.21       | 0.33                           | 0.17               | 97.83           | -72.06          | -3.22           | 1.35              |
| 0.45        | 0.34        | 0.01        | -0.21       | 0.33                           | 0.17               | 107.19          | -87.19          | -3.62           | 1.22              |
| 0.50        | 0.34        | 0.01        | -0.22       | 0.33                           | 0.17               | 109.86          | -89.43          | -2.54           | 1.22              |



Table 4.3: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E_l = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2}$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa0}/I_{pa1}$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|----------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | -0.01       | 0.35        | 0.03        | -0.22       | 0.32                             | 0.19             | 9.66            | 24.12           | -14.79          | -13.40          | 0.40              | 1.63              |
| 0.10        | 0.00        | 0.37        | 0.01        | -0.23       | 0.36                             | 0.19             | 12.44           | 32.08           | -21.56          | -16.49          | 0.38              | 1.48              |
| 0.15        | -0.01       | 0.38        | 0.01        | -0.22       | 0.37                             | 0.19             | 16.18           | 34.65           | -25.98          | -20.25          | 0.46              | 1.33              |
| 0.20        | -0.01       | 0.39        | 0.00        | -0.23       | 0.39                             | 0.19             | 17.06           | 41.23           | -37.92          | -19.55          | 0.41              | 1.08              |
| 0.25        | 0.00        | 0.40        | 0.00        | -0.24       | 0.40                             | 0.19             | 18.30           | 44.54           | -43.15          | -18.26          | 0.41              | 1.03              |
| 0.30        | 0.00        | 0.40        | -0.01       | -0.24       | 0.41                             | 0.19             | 17.34           | 50.76           | -50.12          | -20.59          | 0.34              | 1.01              |
| 0.35        | 0.01        | 0.40        | -0.01       | -0.24       | 0.41                             | 0.19             | 18.92           | 56.95           | -55.86          | -18.20          | 0.33              | 1.01              |
| 0.40        | 0.00        | 0.40        | -0.01       | -0.24       | 0.41                             | 0.19             | 19.08           | 64.30           | -59.70          | -18.05          | 0.29              | 1.07              |
| 0.45        | 0.01        | 0.40        | -0.01       | -0.25       | 0.41                             | 0.19             | 17.42           | 66.64           | -66.01          | -18.44          | 0.26              | 1.00              |
| 0.50        | 0.00        | 0.40        | -0.01       | -0.25       | 0.41                             | 0.19             | 20.46           | 68.80           | -70.97          | -15.14          | 0.29              | 0.96              |

Table 4.4 : Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.24        | -0.29       | 0.53                           | 0.02               | 25.87           | -9.63           | 2.68              |
| 0.10        | 0.23        | -0.28       | 0.51                           | 0.02               | 35.75           | -14.74          | 2.42              |
| 0.15        | 0.24        | -0.29       | 0.53                           | 0.02               | 42.82           | -15.68          | 2.73              |
| 0.20        | 0.25        | -0.31       | 0.56                           | 0.03               | 48.32           | -19.50          | 2.47              |
| 0.25        | 0.25        | -0.29       | 0.54                           | 0.02               | 50.95           | -22.01          | 2.31              |
| 0.30        | 0.22        | -0.29       | 0.51                           | 0.03               | 55.89           | -26.14          | 2.13              |
| 0.35        | 0.20        | -0.28       | 0.48                           | 0.04               | 62.39           | -28.55          | 2.18              |
| 0.40        | 0.24        | -0.31       | 0.55                           | 0.03               | 66.15           | -26.58          | 2.48              |
| 0.45        | 0.21        | -0.29       | 0.50                           | 0.04               | 60.81           | -29.00          | 2.09              |
| 0.50        | 0.22        | -0.28       | 0.50                           | 0.03               | 68.51           | -28.60          | 2.39              |

Table 4.5: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.55        | 0.01        | 0.54                           | 0.28               | 19.49           | -10.81          | 1.80              |
| 0.10        | 0.60        | -0.01       | 0.61                           | 0.29               | 24.95           | -15.89          | 1.57              |
| 0.15        | 0.50        | 0.07        | 0.43                           | 0.28               | 38.03           | -25.11          | 1.51              |
| 0.20        | 0.52        | 0.05        | 0.47                           | 0.28               | 40.29           | -28.71          | 1.40              |
| 0.25        | 0.53        | 0.05        | 0.48                           | 0.29               | 41.60           | -31.42          | 1.32              |
| 0.30        | 0.65        | -0.05       | 0.70                           | 0.30               | 40.71           | -27.59          | 1.47              |
| 0.35        | 0.61        | -0.02       | 0.63                           | 0.29               | 45.13           | -34.67          | 1.30              |
| 0.40        | 0.64        | -0.04       | 0.68                           | 0.30               | 46.42           | -34.34          | 1.35              |
| 0.45        | 0.59        | 0.01        | 0.58                           | 0.30               | 56.63           | -43.00          | 1.31              |
| 0.50        | 0.57        | 0.02        | 0.55                           | 0.29               | 56.65           | -46.17          | 1.22              |

Table 4.6: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.51        | 0.04        | 0.47                           | 0.27               | 22.75           | -11.12          | 2.04              |
| 0.10        | 0.56        | 0.02        | 0.54                           | 0.29               | 30.25           | -17.21          | 1.75              |
| 0.15        | 0.48        | 0.09        | 0.39                           | 0.28               | 40.13           | -26.34          | 1.52              |
| 0.20        | 0.50        | 0.08        | 0.42                           | 0.29               | 43.45           | -29.53          | 1.47              |
| 0.25        | 0.51        | 0.08        | 0.43                           | 0.29               | 45.98           | -31.32          | 1.46              |
| 0.30        | 0.59        | 0.00        | 0.59                           | 0.29               | 51.97           | -29.10          | 1.78              |
| 0.35        | 0.58        | 0.01        | 0.57                           | 0.29               | 57.35           | -36.83          | 1.55              |
| 0.40        | 0.59        | 0.01        | 0.58                           | 0.30               | 58.83           | -36.48          | 1.61              |
| 0.45        | 0.54        | 0.04        | 0.50                           | 0.29               | 65.38           | -43.71          | 1.49              |
| 0.50        | 0.54        | 0.04        | 0.50                           | 0.29               | 67.37           | -45.38          | 1.48              |



Table 4.7: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 5) of GC electrode at different scan rate ( $2^{\text{nd}}$  cycle)

| $\nu/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|---------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05          | 0.53        | 0.04        | 0.49                           | 0.28               | 20.97           | -10.90          | 1.92              |
| 0.10          | 0.58        | 0.00        | 0.58                           | 0.29               | 27.13           | -16.36          | 1.65              |
| 0.15          | 0.49        | 0.07        | 0.42                           | 0.28               | 40.02           | -25.85          | 1.54              |
| 0.20          | 0.51        | 0.06        | 0.45                           | 0.28               | 42.99           | -28.19          | 1.52              |
| 0.25          | 0.52        | 0.07        | 0.45                           | 0.29               | 45.43           | -30.92          | 1.46              |
| 0.30          | 0.61        | -0.02       | 0.63                           | 0.29               | 45.47           | -29.76          | 1.52              |
| 0.35          | 0.60        | 0.00        | 0.60                           | 0.30               | 52.83           | -37.67          | 1.40              |
| 0.40          | 0.61        | -0.02       | 0.63                           | 0.29               | 52.97           | -37.25          | 1.42              |
| 0.45          | 0.56        | 0.03        | 0.53                           | 0.29               | 62.28           | -47.19          | 1.31              |
| 0.50          | 0.56        | 0.03        | 0.53                           | 0.29               | 63.42           | -47.12          | 1.34              |

Table 4.8: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) of GC electrode at different scan rate ( $1^{\text{st}}$  cycle)

| $\nu/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|---------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05          | 0.24        | -0.29       | 0.53                           | 0.02               | 25.87           | -9.63           | 2.68              |
| 0.10          | 0.23        | -0.28       | 0.51                           | 0.02               | 35.75           | -14.74          | 2.42              |
| 0.15          | 0.24        | -0.29       | 0.53                           | 0.02               | 42.82           | -15.68          | 2.73              |
| 0.20          | 0.25        | -0.31       | 0.56                           | 0.03               | 48.32           | -19.50          | 2.47              |
| 0.25          | 0.25        | -0.29       | 0.54                           | 0.02               | 50.95           | -22.01          | 2.31              |
| 0.30          | 0.22        | -0.29       | 0.51                           | 0.03               | 55.89           | -26.14          | 2.13              |
| 0.35          | 0.20        | -0.28       | 0.48                           | 0.04               | 62.39           | -28.55          | 2.18              |
| 0.40          | 0.24        | -0.31       | 0.55                           | 0.03               | 66.15           | -26.58          | 2.48              |
| 0.45          | 0.21        | -0.29       | 0.50                           | 0.04               | 60.81           | -29.00          | 2.09              |
| 0.50          | 0.22        | -0.28       | 0.50                           | 0.03               | 68.51           | -28.60          | 2.39              |

Table 4.9: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 9) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | -0.15       | 0.31        | -0.32       | 0.63                           | 0.01               | 8.82            | 14.98           | -11.05          | 1.35              |
| 0.10        | -0.15       | 0.30        | -0.32       | 0.62                           | 0.01               | 8.79            | 14.91           | -12.05          | 1.23              |
| 0.15        | -0.13       | 0.30        | -0.31       | 0.61                           | 0.01               | 16.71           | 17.54           | -20.68          | 0.84              |
| 0.20        | -0.13       | 0.32        | -0.33       | 0.65                           | 0.01               | 18.91           | 20.86           | -23.58          | 0.88              |
| 0.25        | -0.12       | 0.33        | -0.33       | 0.66                           | 0.00               | 19.33           | 22.65           | -28.83          | 0.78              |
| 0.30        | -0.14       | 0.30        | -0.31       | 0.61                           | 0.01               | 26.77           | 26.12           | -33.93          | 0.76              |
| 0.35        | -0.15       | 0.29        | -0.30       | 0.59                           | 0.01               | 29.33           | 28.69           | -36.94          | 0.77              |
| 0.40        | -0.13       | 0.30        | -0.31       | 0.61                           | 0.01               | 27.67           | 28.40           | -38.66          | 0.73              |
| 0.45        | -0.15       | 0.28        | -0.30       | 0.58                           | 0.01               | 30.08           | 31.02           | -37.26          | 0.83              |
| 0.50        | -0.15       | 0.28        | -0.30       | 0.58                           | 0.01               | 33.16           | 30.17           | -49.95          | 0.60              |

Table 4.10: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 11) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.01        | -0.37       | 0.38                           | 0.18               | 25.89           | -3.76           | 6.88              |
| 0.10        | 0.01        | -0.36       | 0.37                           | 0.17               | 36.31           | -6.84           | 5.30              |
| 0.15        | 0.04        | -0.37       | 0.41                           | 0.16               | 36.58           | -7.83           | 4.67              |
| 0.20        | 0.05        | -0.37       | 0.42                           | 0.16               | 34.07           | -9.66           | 3.52              |
| 0.25        | 0.04        | -0.37       | 0.41                           | 0.16               | 44.30           | -12.59          | 3.51              |
| 0.30        | 0.05        | -0.37       | 0.42                           | 0.16               | 44.32           | -13.12          | 3.37              |
| 0.35        | 0.04        | -0.36       | 0.40                           | 0.16               | 54.05           | -17.35          | 3.11              |
| 0.40        | 0.04        | -0.37       | 0.41                           | 0.16               | 53.93           | -18.58          | 2.90              |
| 0.45        | 0.06        | -0.37       | 0.43                           | 0.15               | 51.83           | -18.90          | 2.74              |
| 0.50        | 0.07        | -0.38       | 0.45                           | 0.15               | 54.04           | -18.54          | 2.91              |



Table 4.11: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 11) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pc1} \sim E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-----------------------------------|--------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | -0.29       | 0.02        | -0.36       | 0.38                              | 0.17               | 3.88            | 15.58           | -4.76           | 3.27              |
| 0.10        | -0.29       | 0.02        | -0.37       | 0.39                              | 0.17               | 6.72            | 20.60           | -8.49           | 2.42              |
| 0.15        | -0.28       | 0.06        | -0.37       | 0.43                              | 0.15               | 8.97            | 16.52           | -10.89          | 1.51              |
| 0.20        | -0.27       | 0.07        | -0.37       | 0.44                              | 0.15               | 10.53           | 16.48           | -12.72          | 1.29              |
| 0.25        | -0.28       | 0.05        | -0.37       | 0.42                              | 0.16               | 13.76           | 19.43           | -16.13          | 1.20              |
| 0.30        | -0.27       | 0.07        | -0.38       | 0.45                              | 0.15               | 14.05           | 16.67           | -16.39          | 1.01              |
| 0.35        | -0.28       | 0.05        | -0.37       | 0.42                              | 0.16               | 17.39           | 21.70           | -20.11          | 1.07              |
| 0.40        | -0.28       | 0.04        | -0.37       | 0.41                              | 0.16               | 19.70           | 22.10           | -23.62          | 0.93              |
| 0.45        | -0.27       | 0.07        | -0.38       | 0.45                              | 0.15               | 19.32           | 19.95           | -21.69          | 0.91              |
| 0.50        | -0.27       | 0.12        | -0.38       | 0.50                              | 0.13               | 20.61           | 20.62           | -23.48          | 0.87              |

Table 4.12: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 150mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pa1} \sim E_{pc1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-----------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.35        | 0.03        | 0.32                              | 0.19               | 21.05           | -2.04           | 10.31             |
| 0.10        | 0.32        | 0.03        | 0.29                              | 0.17               | 30.70           | -6.28           | 4.88              |
| 0.15        | 0.38        | 0.01        | 0.37                              | 0.19               | 33.13           | -10.93          | 3.03              |
| 0.20        | 0.39        | 0.00        | 0.39                              | 0.19               | 39.39           | -14.32          | 2.75              |
| 0.25        | 0.39        | 0.00        | 0.39                              | 0.19               | 43.50           | -22.58          | 1.92              |
| 0.30        | 0.35        | 0.02        | 0.33                              | 0.18               | 46.17           | -25.52          | 1.80              |
| 0.35        | 0.35        | 0.01        | 0.34                              | 0.18               | 54.70           | -27.94          | 1.95              |
| 0.40        | 0.35        | 0.02        | 0.33                              | 0.18               | 61.20           | -35.04          | 1.74              |
| 0.45        | 0.41        | -0.01       | 0.42                              | 0.20               | 62.32           | -37.64          | 1.65              |
| 0.50        | 0.40        | 0.00        | 0.40                              | 0.20               | 59.95           | -38.31          | 1.56              |

Table 4.13: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 150mM diethylamine and 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}(V)$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa0}/I_{pa1}$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|---------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | -0.01       | 0.42        | 0.00        | -0.25       | 0.42                           | 0.21                | 1.91            | 17.08           | -1.97           | -3.21           | 0.11              | 8.67              |
| 0.10        | -0.04       | 0.38        | 0.02        | -0.21       | 0.36                           | 0.20                | 4.34            | 22.96           | -8.54           | -4.36           | 0.18              | 2.68              |
| 0.15        | -0.02       | 0.43        | -0.01       | -0.25       | 0.44                           | 0.21                | 3.68            | 25.22           | -12.56          | -2.61           | 0.14              | 2.00              |
| 0.20        | -0.01       | 0.46        | -0.02       | -0.28       | 0.48                           | 0.22                | 3.07            | 30.85           | -14.48          | -2.46           | 0.09              | 2.13              |
| 0.25        | -0.03       | 0.45        | -0.02       | -0.27       | 0.47                           | 0.21                | 2.34            | 35.16           | -17.29          | -1.99           | 0.06              | 2.03              |
| 0.30        | -0.04       | 0.41        | 0.00        | -0.23       | 0.41                           | 0.20                | 3.96            | 39.04           | -22.47          | -1.98           | 0.10              | 1.73              |
| 0.35        | -0.06       | 0.41        | -0.01       | -0.24       | 0.42                           | 0.20                | 4.54            | 43.11           | -26.83          | -1.33           | 0.10              | 1.60              |
| 0.40        | -0.06       | 0.40        | 0.01        | -0.21       | 0.39                           | 0.20                | 5.09            | 47.69           | -27.64          | -1.21           | 0.10              | 1.72              |
| 0.45        | -0.05       | 0.46        | -0.03       | -0.27       | 0.49                           | 0.21                | 2.97            | 47.27           | -29.98          | -0.11           | 0.06              | 1.57              |
| 0.50        | -0.07       | 0.44        | -0.02       | -0.24       | 0.46                           | 0.21                | 2.45            | 49.48           | -30.40          | -0.02           | 0.04              | 1.62              |

Table 4.14: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 200mM diethylamine and 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-------------------|
| 0.05        | 0.34        | 0.00        | 0.34                           | 0.17               | 33.44           | -8.11           | 4.12              |
| 0.10        | 0.35        | 0.00        | 0.35                           | 0.17               | 45.46           | -16.10          | 2.82              |
| 0.15        | 0.38        | -0.02       | 0.40                           | 0.18               | 53.19           | -22.84          | 2.32              |
| 0.20        | 0.38        | -0.01       | 0.39                           | 0.18               | 62.55           | -31.19          | 2.00              |
| 0.25        | 0.38        | -0.02       | 0.40                           | 0.18               | 70.86           | -35.70          | 1.98              |
| 0.30        | 0.39        | -0.01       | 0.40                           | 0.19               | 76.81           | -38.35          | 2.00              |
| 0.35        | 0.37        | -0.02       | 0.39                           | 0.17               | 85.91           | -47.75          | 1.79              |
| 0.40        | 0.40        | -0.02       | 0.42                           | 0.19               | 89.53           | -51.17          | 1.74              |
| 0.45        | 0.40        | -0.02       | 0.42                           | 0.19               | 91.36           | -60.27          | 1.51              |
| 0.50        | 0.42        | -0.02       | 0.44                           | 0.20               | 93.98           | -58.27          | 1.61              |



Table 4.15: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 200mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pa0} - E_{pc0}$ | $\Delta E = E_{pa1} - E_{pc1}$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa0}/I_{pa1}$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|--------------------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | -0.01       | 0.40        | 0.00        | -0.25       | 0.24                           | 0.40                           | 2.61            | 24.24           | -7.31           | -2.66           | 0.10              | 3.31              |
| 0.10        | -0.01       | 0.43        | -0.02       | -0.25       | 0.24                           | 0.45                           | 3.12            | 32.43           | -15.53          | -1.18           | 0.09              | 2.08              |
| 0.15        | 0.00        | 0.44        | -0.03       | -0.28       | 0.28                           | 0.47                           | 3.01            | 37.76           | -19.47          | -1.43           | 0.07              | 1.93              |
| 0.20        | -0.03       | 0.43        | -0.03       | -0.26       | 0.23                           | 0.46                           | 2.29            | 45.42           | -23.36          | -0.23           | 0.05              | 1.94              |
| 0.25        | -0.02       | 0.44        | -0.03       | -0.27       | 0.25                           | 0.47                           | 3.01            | 52.21           | -32.94          | -0.18           | 0.05              | 1.58              |
| 0.30        | -0.05       | 0.43        | -0.03       | -0.26       | 0.21                           | 0.46                           | 2.42            | 58.56           | -41.36          | -               | 0.04              | 1.41              |
| 0.35        | -0.06       | 0.43        | -0.03       | -           | -                              | 0.46                           | 2.30            | 61.22           | -47.60          | -               | 0.03              | 1.28              |
| 0.40        | -           | 0.46        | -0.04       | -           | -                              | 0.50                           | -               | 66.46           | -46.14          | -               | -                 | 1.44              |
| 0.45        | -           | 0.45        | -0.04       | -           | -                              | 0.49                           | -               | 71.27           | -54.25          | -               | -                 | 1.31              |
| 0.50        | -           | 0.46        | -0.04       | -           | -                              | 0.50                           | -               | 71.81           | -58.18          | -               | -                 | 1.23              |

Table 4.16: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|--------------------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | 0.33        | 0.05        | -0.21       | 0.28                           | 36.61           | -11.79          | -10.44          | 3.10              |
| 0.10        | 0.34        | 0.02        | -0.23       | 0.32                           | 49.46           | -20.5           | -8.58           | 2.41              |
| 0.15        | 0.36        | 0.00        | -0.25       | 0.36                           | 57.47           | -29.7           | -5.63           | 1.93              |
| 0.20        | 0.35        | 0.01        | -0.22       | 0.34                           | 77.84           | -40.49          | -5.01           | 1.92              |
| 0.25        | 0.37        | 0.00        | -0.22       | 0.37                           | 75.19           | -47.5           | -3.91           | 1.58              |
| 0.30        | 0.35        | 0.01        | -0.23       | 0.34                           | 79.25           | -54.21          | -1.08           | 1.46              |
| 0.35        | 0.36        | 0.01        | -0.22       | 0.35                           | 92.38           | -35.58          | -1.00           | 2.59              |
| 0.40        | 0.35        | 0.01        | -0.23       | 0.34                           | 98.13           | -45.9           | -0.80           | 2.13              |
| 0.45        | 0.37        | 0.00        | -0.22       | 0.37                           | 97.49           | -44.65          | -0.07           | 2.18              |
| 0.50        | 0.35        | 0.01        | -           | 0.34                           | 86.99           | -44.59          | -               | 1.95              |



Table 4.17: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 300mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pc1} - E_{pa2}$ | $\Delta E_{1/2}/V$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa0}/I_{pa1}$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | 0.00        | 0.39        | 0.04        | -0.22       | 0.35                           | 0.21               | 8.48            | 18.29           | -0.76           | -14.13          | 0.46              | 24.06             |
| 0.10        | 0.01        | 0.40        | 0.01        | -0.24       | 0.39                           | 0.20               | 9.29            | 26.11           | -3.25           | -16.58          | 0.35              | 8.03              |
| 0.15        | 0.04        | 0.45        | 0.02        | -0.28       | 0.43                           | 0.23               | 10.52           | 28.34           | -4.51           | -15.51          | 0.37              | 6.28              |
| 0.20        | 0.00        | 0.41        | 0.00        | -0.23       | 0.41                           | 0.20               | 13.85           | 36.68           | -8.91           | -15.88          | 0.37              | 4.11              |
| 0.25        | 0.03        | 0.43        | 0.01        | -0.26       | 0.42                           | 0.22               | 16.30           | 39.55           | -10.16          | -21.15          | 0.41              | 3.89              |
| 0.30        | 0.02        | 0.42        | 0.01        | -0.24       | 0.41                           | 0.21               | 17.74           | 49.95           | -18.45          | -16.78          | 0.35              | 2.70              |
| 0.35        | 0.01        | 0.42        | 0.01        | -0.25       | 0.41                           | 0.21               | 14.79           | 52.51           | -22.20          | -15.44          | 0.28              | 2.36              |
| 0.40        | 0.01        | 0.41        | 0.01        | -0.24       | 0.40                           | 0.21               | 14.87           | 57.27           | -30.30          | -17.16          | 0.25              | 1.89              |
| 0.45        | 0.01        | 0.42        | 0.01        | -0.25       | 0.41                           | 0.21               | 15.78           | 60.49           | -30.22          | -14.31          | 0.26              | 2.00              |
| 0.50        | 0.01        | 0.42        | 0.00        | -0.24       | 0.42                           | 0.21               | 10.46           | 61.40           | -28.60          | -11.89          | 0.17              | 2.14              |

Table 4.18: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|--------------------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | 0.62        | -           | 0.05        | -                              | 23.70           | -               | -8.10           | -                 |
| 0.10        | 0.54        | 0.22        | -0.04       | 0.32                           | 32.17           | -1.06           | -9.55           | 30.34             |
| 0.15        | 0.53        | 0.18        | -0.07       | 0.35                           | 37.29           | -4.05           | -9.94           | 9.20              |
| 0.20        | 0.52        | 0.15        | -0.10       | 0.37                           | 40.47           | -5.71           | -9.83           | 7.08              |
| 0.25        | 0.55        | 0.14        | -0.14       | 0.41                           | 42.14           | -4.86           | -4.72           | 8.67              |
| 0.30        | 0.49        | 0.14        | -0.09       | 0.35                           | 50.02           | -12.08          | -7.43           | 4.14              |
| 0.35        | 0.52        | 0.12        | -0.14       | 0.40                           | 50.33           | -10.17          | -6.45           | 4.94              |
| 0.40        | 0.50        | 0.12        | -0.13       | 0.38                           | 55.89           | -14.37          | -5.88           | 3.88              |
| 0.45        | 0.48        | 0.11        | -0.12       | 0.37                           | 58.78           | -17.23          | -4.73           | 3.41              |
| 0.50        | 0.48        | 0.10        | -0.14       | 0.38                           | 57.09           | -18.96          | -4.70           | 3.01              |



Table 4.19: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 350mM diethylamine + 2mM catechol in buffer solution (pH 7) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/V$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa0}/I_{pa1}$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | 0.21        | 0.63        | 0.20        | -0.01       | 0.43                           | 0.41               | 5.25            | 15.35           | -               | -8.58           | 0.34              | -                 |
| 0.10        | 0.16        | 0.59        | 0.20        | -0.06       | 0.39                           | 0.39               | 8.18            | 18.12           | -01.18          | -12.09          | 0.45              | 15.35             |
| 0.15        | 0.17        | 0.59        | 0.17        | -0.09       | 0.42                           | 0.38               | 8.83            | 20.12           | -2.05           | -13.42          | 0.43              | 9.81              |
| 0.20        | 0.16        | 0.60        | 0.15        | -0.12       | 0.45                           | 0.37               | 10.69           | 22.23           | -3.78           | -13.47          | 0.48              | 5.88              |
| 0.25        | 0.18        | 0.64        | 0.13        | -0.16       | 0.51                           | 0.38               | 10.28           | 23.59           | -6.31           | -13.86          | 0.43              | 3.73              |
| 0.30        | 0.14        | 0.56        | 0.13        | -0.13       | 0.43                           | 0.34               | 11.66           | 27.20           | -9.03           | -14.36          | 0.42              | 3.01              |
| 0.35        | 0.15        | 0.61        | 0.11        | -0.17       | 0.50                           | 0.36               | 11.27           | 27.77           | -7.50           | -12.56          | 0.40              | 3.70              |
| 0.40        | 0.16        | 0.59        | 0.11        | -0.16       | 0.48                           | 0.35               | 11.69           | 29.71           | -12.54          | -12.53          | 0.39              | 2.36              |
| 0.45        | 0.11        | 0.55        | 0.10        | -0.14       | 0.45                           | 0.32               | 12.10           | 31.77           | -15.62          | -12.48          | 0.38              | 2.03              |
| 0.50        | 0.11        | 0.54        | 0.10        | -0.15       | 0.44                           | 0.32               | 12.10           | 37.13           | -16.64          | -13.45          | 0.32              | 2.23              |

Table 4.20: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Au electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pa2}/V$ | $E_{pc2}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E = E_{pa2} - E_{pc2}$ | $I_{pa1}/\mu A$ | $I_{pa2}/\mu A$ | $I_{pc2}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|--------------------------------|-----------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | 0.33        | 1.00        | 0.49        | 0.08        | 0.25                           | 0.51                           | 10.43           | 14.67           | -4.73           | -5.46           | 1.91              |
| 0.10        | 0.34        | 1.06        | 0.48        | 0.08        | 0.26                           | 0.58                           | 13.74           | 18.47           | -8.42           | -9.44           | 1.45              |
| 0.15        | 0.31        | 1.08        | 0.46        | 0.08        | 0.23                           | 0.62                           | 14.97           | 25.87           | -11.20          | -11.33          | 1.32              |
| 0.20        | 0.33        | 1.09        | 0.46        | 0.08        | 0.25                           | 0.63                           | 17.48           | 32.77           | -15.38          | -13.61          | 1.28              |
| 0.25        | 0.33        | 1.11        | 0.45        | 0.07        | 0.26                           | 0.66                           | 18.70           | 42.55           | -18.72          | -14.06          | 1.33              |
| 0.30        | 0.31        | 1.11        | 0.45        | 0.07        | 0.24                           | 0.66                           | 19.28           | 45.38           | -20.27          | -16.17          | 1.19              |
| 0.35        | 0.33        | 1.12        | 0.44        | 0.06        | 0.27                           | 0.68                           | 20.88           | 45.64           | -22.03          | -18.55          | 1.12              |
| 0.40        | 0.33        | 1.12        | 0.44        | 0.07        | 0.26                           | 0.68                           | 22.94           | 61.57           | -27.35          | -21.30          | 1.07              |
| 0.45        | 0.41        | 1.13        | 0.43        | 0.07        | 0.34                           | 0.70                           | 19.44           | 64.11           | -29.30          | -18.37          | 1.05              |
| 0.50        | 0.38        | 1.03        | 0.43        | 0.06        | 0.32                           | 0.60                           | 20.26           | 71.25           | -31.95          | -21.39          | 0.94              |



Table 4.21: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Au electrode and at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pa2}/V$ | $E_{pc2}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E = E_{pa2} - E_{pc2}$ | $I_{pa1}/\mu A$ | $I_{pa2}/\mu A$ | $I_{pc2}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ | $I_{pa2}/I_{pc2}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|--------------------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | 0.27        | 1.02        | 0.48        | 0.09        | 0.18                           | 0.54                           | 8.06            | 19.12           | -2.47           | -4.34           | 1.85              | 7.74              |
| 0.10        | 0.28        | 1.06        | 0.47        | 0.10        | 0.18                           | 0.59                           | 9.44            | 35.11           | -6.07           | -6.73           | 1.40              | 5.78              |
| 0.15        | 0.29        | 1.08        | 0.46        | 0.08        | 0.21                           | 0.62                           | 9.34            | 51.66           | -9.61           | -7.44           | 1.25              | 5.37              |
| 0.20        | 0.28        | 1.09        | 0.46        | 0.06        | 0.22                           | 0.63                           | 9.33            | 62.88           | -11.67          | -6.69           | 1.39              | 5.38              |
| 0.25        | 0.29        | 1.11        | 0.44        | 0.08        | 0.21                           | 0.67                           | 10.19           | 77.77           | -15.66          | -8.15           | 1.25              | 4.96              |
| 0.30        | 0.29        | 1.11        | 0.45        | 0.08        | 0.21                           | 0.66                           | 12.11           | 101.76          | -22.46          | -9.35           | 1.29              | 4.53              |
| 0.35        | 0.30        | 1.13        | 0.43        | 0.07        | 0.23                           | 0.70                           | 12.05           | 107.82          | -22.17          | -9.26           | 1.30              | 4.86              |
| 0.40        | 0.28        | 1.14        | 0.43        | 0.07        | 0.21                           | 0.71                           | 13.72           | 134.50          | -26.04          | -10.82          | 1.26              | 5.16              |
| 0.45        | 0.29        | 1.13        | 0.44        | 0.07        | 0.22                           | 0.69                           | 12.05           | 133.97          | -35.54          | -7.19           | 1.67              | 3.76              |
| 0.50        | 0.28        | 1.14        | 0.42        | 0.08        | 0.20                           | 0.72                           | 12.18           | 171.40          | -35.26          | -8.06           | 1.51              | 4.86              |

Table 4.22: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode at different scan rate (1<sup>st</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2}/V$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | 0.35        | 0.03        | -0.20       | 0.32                           | 0.19               | 10.51           | -4.48           | -0.81           | 2.34              |
| 0.10        | 0.36        | 0.04        | -0.22       | 0.32                           | 0.20               | 11.83           | -5.34           | -0.10           | 2.21              |
| 0.15        | 0.39        | 0.05        | -0.24       | 0.34                           | 0.22               | 15.03           | -8.62           | -0.38           | 1.74              |
| 0.20        | 0.37        | 0.00        | -0.25       | 0.37                           | 0.185              | 17.29           | -9.15           | -0.22           | 1.88              |
| 0.25        | 0.38        | 0.02        | -           | 0.36                           | 0.20               | 18.83           | -11.35          | -               | 1.65              |
| 0.30        | 0.40        | 0.03        | -           | 0.37                           | 0.215              | 19.22           | -12.60          | -               | 1.52              |
| 0.35        | 0.38        | 0.05        | -           | 0.33                           | 0.215              | 19.63           | -15.37          | -               | 1.27              |
| 0.40        | 0.35        | 0.04        | -           | 0.31                           | 0.195              | 20.44           | -16.22          | -               | 1.26              |
| 0.45        | 0.35        | 0.05        | -           | 0.30                           | 0.20               | 18.61           | -13.75          | -               | 1.35              |
| 0.50        | 0.42        | 0.06        | -           | 0.36                           | 0.24               | 22.45           | -14.78          | --              | 1.51              |



Table 4.23: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 250mM diethylamine + 2mM catechol in buffer solution (pH 7) of Pt electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $E_{pc0}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2}/V$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pc0}/\mu A$ | $I_{pa0}/I_{pa1}$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| 0.05        | -0.05       | 0.35        | -0.02       | -0.19       | 0.37                           | 0.15               | 2.94            | 7.25            | -4.88           | -2.36           | 0.40              | 1.48              |
| 0.10        | -0.05       | 0.35        | -0.02       | -0.20       | 0.37                           | 0.15               | 4.45            | 10.01           | -7.32           | -2.20           | 0.44              | 1.36              |
| 0.15        | -0.02       | 0.37        | -0.02       | -0.20       | 0.39                           | 0.17               | 5.26            | 11.28           | -10.68          | -1.44           | 0.46              | 1.05              |
| 0.20        | -0.03       | 0.37        | -0.02       | -0.20       | 0.39                           | 0.17               | 5.23            | 11.98           | -12.14          | -0.52           | 0.43              | 0.98              |
| 0.25        | -0.04       | 0.37        | -0.02       | -0.21       | 0.39                           | 0.16               | 5.09            | 15.51           | -15.33          | -0.40           | 0.32              | 1.01              |
| 0.30        | -0.04       | 0.37        | -0.03       | -0.21       | 0.40                           | 0.16               | 4.88            | 16.34           | -14.97          | -0.38           | 0.29              | 1.09              |
| 0.35        | -0.03       | 0.38        | -0.04       | -0.21       | 0.42                           | 0.17               | 4.66            | 17.42           | -18.00          | -0.68           | 0.26              | 0.96              |
| 0.40        | -0.03       | 0.39        | -0.04       | -0.21       | 0.43                           | 0.18               | 3.68            | 19.37           | -21.21          | -0.52           | 0.18              | 0.91              |
| 0.45        | -0.02       | 0.40        | -0.05       | -0.23       | 0.45                           | 0.19               | 4.35            | 19.69           | -20.53          | -               | 0.22              | 0.95              |
| 0.50        | -0.03       | 0.41        | -0.04       | -0.23       | 0.45                           | 0.19               | 4.59            | 21.21           | -22.71          | -               | 0.21              | 0.93              |

Table 4.24: Peak Current  $I_p$  ( $\mu A$ ), peak potential  $E_p$  (V) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s in different pH media (1<sup>st</sup> cycle)

| pH | Peak Current, $I_p$ ( $\mu A$ ) |             | Peak potential, $E_p$ (V) |             |
|----|---------------------------------|-------------|---------------------------|-------------|
|    | Oxidn, $A_1$                    | Redn, $C_1$ | Oxidn, $A_1$              | Redn, $C_1$ |
| 3  | 35.75                           | -14.74      | 0.23                      | -0.28       |
| 5  | 30.25                           | -17.21      | 0.56                      | 0.02        |
| 7  | 50.53                           | -27.04      | 0.31                      | 0.03        |
| 9  | 35.75                           | -14.74      | 0.23                      | -0.28       |
| 11 | 36.31                           | -6.84       | 0.01                      | -0.36       |

Table 4.25: Peak Current  $I_p$  ( $\mu\text{A}$ ), peak potential  $E_p$  (V) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s in different pH media (2<sup>nd</sup> cycle)

| pH | Peak Current $I_p$ ( $\mu\text{A}$ ) |              |             | Peak potential $E_p$ (V) |              |             |
|----|--------------------------------------|--------------|-------------|--------------------------|--------------|-------------|
|    | Oxidn, $A_0$                         | Oxidn, $A_1$ | Redn, $C_1$ | Oxidn, $A_0$             | Oxidn, $A_1$ | Redn, $C_1$ |
| 3  | 27.13                                | -            | -16.36      | 0.58                     | -            | 0.00        |
| 5  | 27.13                                | -            | -16.36      | 0.58                     | -            | 0.00        |
| 7  | 9.35                                 | 35.67        | -23.84      | -0.03                    | 0.35         | 0.01        |
| 9  | 9.18                                 | 21.03        | -17.27      | -0.16                    | 0.28         | -0.30       |
| 11 | 4.92                                 | 25.00        | -8.04       | -0.29                    | 0.01         | -0.37       |

Table 4.26: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current ( $I_p$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of GC electrode at different scan rate (2<sup>nd</sup> cycle)

| $v/\text{Vs}^{-1}$ | $E_{pa0}/\text{V}$ | $E_{pa1}/\text{V}$ | $E_{pa2}/\text{V}$ | $E_{pc1}/\text{V}$ | $\Delta E = E_{pc1} - E_{pa1}$ | $\Delta E_{1/2}/\text{V}$ | $I_{pa0}/\mu\text{A}$ | $I_{pa1}/\mu\text{A}$ | $I_{pa2}/\mu\text{A}$ | $I_{pc1}/\mu\text{A}$ | $I_{pa1}/I_{pc1}$ |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------------------|---------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------|
| 0.05               | 0.29               | 0.69               | 1.09               | 0.03               | 0.66                           | 0.36                      | 10.64                 | 30.65                 | 7.90                  | -12.27                | 2.49              |
| 0.10               | 0.37               | 0.75               | 1.14               | -0.02              | 0.77                           | 0.36                      | 12.56                 | 35.60                 | 10.86                 | -12.50                | 2.84              |
| 0.15               | 0.33               | 0.74               | 1.15               | -0.01              | 0.75                           | 0.36                      | 20.41                 | 40.14                 | 11.44                 | -13.10                | 2.90              |
| 0.20               | 0.34               | 0.78               | 1.18               | -0.04              | 0.82                           | 0.37                      | 20.77                 | 43.08                 | 13.84                 | -13.50                | 2.33              |
| 0.25               | 0.36               | 0.82               | 1.21               | -0.04              | 0.86                           | 0.39                      | 21.71                 | 45.87                 | 12.67                 | -15.56                | 2.02              |
| 0.30               | 0.37               | 0.83               | 1.21               | -0.05              | 0.88                           | 0.39                      | 22.74                 | 50.22                 | 13.98                 | -16.28                | 1.92              |
| 0.35               | 0.37               | 0.84               | 1.24               | -0.06              | 0.90                           | 0.39                      | 24.72                 | 55.18                 | 15.44                 | -18.50                | 1.91              |
| 0.40               | 0.35               | 0.82               | 1.22               | -0.07              | 0.89                           | 0.37                      | 26.35                 | 56.14                 | 14.91                 | -19.25                | 1.87              |
| 0.45               | 0.37               | 0.83               | 1.23               | -0.08              | 0.91                           | 0.37                      | 26.64                 | 60.93                 | 18.47                 | -21.54                | 1.91              |
| 0.50               | 0.35               | 0.82               | 1.22               | -0.08              | 0.90                           | 0.37                      | 28.71                 | 64.00                 | 18.78                 | -25.32                | 1.99              |



Table 4.27: Peak current  $I_p$  ( $\mu\text{A}$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Au electrode at different scan rate ( $2^{\text{nd}}$  cycle)

| $v/\text{Vs}^{-1}$ | $I_{pa0}/\mu\text{A}$ | $I_{pa1}/\mu\text{A}$ | $I_{pa2}/\mu\text{A}$ | $I_{pc0}/\mu\text{A}$ | $I_{pc1}/\mu\text{A}$ | $I_{pc2}/\mu\text{A}$ | $I_{pa1}/I_{pc1}$ | $I_{pa0}/I_{pa1}$ |
|--------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------|-------------------|
| 0.05               | 2.34                  | 11.60                 | 5.41                  | -4.18                 | -6.04                 | -7.24                 | 1.92              | 0.20              |
| 0.10               | 4.24                  | 12.99                 | 6.78                  | -4.49                 | -8.07                 | -7.15                 | 1.60              | 0.32              |
| 0.15               | 4.74                  | 13.51                 | 7.40                  | -4.85                 | -9.31                 | -12.15                | 1.45              | 0.35              |
| 0.20               | 6.21                  | 14.42                 | 7.09                  | -5.21                 | -9.87                 | -12.10                | 1.46              | 0.43              |
| 0.25               | 6.81                  | 14.83                 | 7.78                  | -5.58                 | -9.62                 | -12.06                | 1.54              | 0.45              |
| 0.30               | 7.16                  | 15.90                 | 7.93                  | -5.32                 | -11.27                | -14.25                | 1.41              | 0.45              |
| 0.35               | 8.13                  | 16.64                 | 8.09                  | -5.28                 | -11.95                | -15.11                | 1.39              | 0.48              |
| 0.40               | 7.06                  | 17.39                 | 8.44                  | -5.09                 | -12.60                | -13.90                | 1.38              | 0.40              |
| 0.45               | 8.33                  | 18.27                 | 8.61                  | -4.30                 | -                     | -12.88                | -                 | -                 |
| 0.50               | 8.09                  | 19.83                 | -                     | -4.86                 | -                     | -13.98                | -                 | -                 |

Table 4.28: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Au electrode at different scan rate ( $2^{\text{nd}}$  cycle)

| $v/\text{Vs}^{-1}$ | $E_{pa0}/\text{V}$ | $E_{pa1}/\text{V}$ | $E_{pa2}/\text{V}$ | $E_{pc0}/\text{V}$ | $E_{pc1}/\text{V}$ | $E_{pc2}/\text{V}$ | $\Delta E_1 = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2} (\text{V})$ |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|----------------------------------|-----------------------------|
| 0.05               | 0.25               | 0.54               | 1.09               | 0.08               | 0.31               | 0.70               | 0.23                             | 0.42                        |
| 0.10               | 0.27               | 0.56               | 1.12               | 0.07               | 0.28               | 0.67               | 0.28                             | 0.42                        |
| 0.15               | 0.28               | 0.58               | 1.12               | 0.05               | 0.26               | 0.66               | 0.32                             | 0.42                        |
| 0.20               | 0.29               | 0.63               | 1.13               | 0.04               | 0.25               | 0.64               | 0.38                             | 0.44                        |
| 0.25               | 0.29               | 0.70               | 1.13               | 0.03               | 0.23               | 0.65               | 0.47                             | 0.46                        |
| 0.30               | 0.31               | 0.71               | 1.14               | 0.04               | 0.23               | 0.62               | 0.48                             | 0.47                        |
| 0.35               | 0.31               | 0.72               | 1.15               | 0.02               | 0.22               | 0.61               | 0.50                             | 0.47                        |
| 0.40               | 0.32               | 0.75               | 1.18               | -0.02              | 0.21               | 0.61               | 0.54                             | 0.48                        |
| 0.45               | 0.33               | 0.76               | 1.18               | -0.02              | -                  | 0.61               | 0.76                             | -                           |
| 0.50               | 0.32               | 0.75               | -                  | -0.02              | -                  | 0.61               | 0.75                             | -                           |

Table 4.29: Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current  $I_p$  ( $\mu A$ ), corresponding peak current ratio ( $I_{pa}/I_{pc}$ ) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) of Pt electrode at different scan rate ( $2^{nd}$  cycle)

| $v/Vs^{-1}$ | $E_{pa0}/V$ | $E_{pa1}/V$ | $E_{pc1}/V$ | $\Delta E = E_{pa1} - E_{pc1}$ | $\Delta E_{1/2}/V$ | $I_{pa0}/\mu A$ | $I_{pa1}/\mu A$ | $I_{pc1}/\mu A$ | $I_{pa1}/I_{pc1}$ |
|-------------|-------------|-------------|-------------|--------------------------------|--------------------|-----------------|-----------------|-----------------|-------------------|
| 0.05        | 0.27        | 0.71        | 0.03        | 0.68                           | 0.37               | 2.54            | 10.67           | -3.02           | 3.53              |
| 0.10        | 0.29        | 0.76        | -0.01       | 0.77                           | 0.37               | 2.86            | 12.62           | -4.51           | 2.79              |
| 0.15        | 0.30        | 0.80        | -0.04       | 0.84                           | 0.38               | 3.11            | 15.92           | -4.23           | 3.76              |
| 0.20        | 0.31        | 0.81        | -0.05       | 0.86                           | 0.38               | 2.53            | 15.44           | -3.00           | 5.14              |
| 0.25        | 0.31        | 0.84        | -0.06       | 0.9                            | 0.39               | 2.21            | 19.24           | -5.08           | 3.78              |
| 0.30        | 0.32        | 0.85        | -0.07       | 0.92                           | 0.39               | 3.74            | 18.06           | -3.48           | 5.18              |
| 0.35        | 0.32        | 0.86        | -0.07       | 0.93                           | 0.39               | 3.52            | 19.68           | -1.87           | 10.52             |
| 0.40        | 0.33        | 0.89        | -0.09       | 0.98                           | 0.40               | 4.39            | 21.9            | 2.93            | 7.47              |
| 0.45        | 0.33        | 0.88        | -0.09       | 0.97                           | 0.39               | 3.40            | 22.06           | -2.07           | 10.65             |
| 0.50        | 0.33        | 0.89        | -0.10       | 0.99                           | 0.39               | 3.32            | 19.77           | -2.23           | 8.86              |

Table 4.30: Peak Current  $I_p$  ( $\mu A$ ) and Peak potential  $E_p$  (V) of pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s ( $2^{nd}$  cycle),  $A_0$ = appeared anodic peak and  $A_1$ = 1<sup>st</sup> anodic peak

| pH | Peak Current $I_p$ ( $\mu A$ ) |       | Peak potential $E_p$ (V) |       |
|----|--------------------------------|-------|--------------------------|-------|
|    | $A_0$                          | $A_1$ | $A_0$                    | $A_1$ |
| 2  | 12.90                          | 35.50 | 0.33                     | 0.66  |
| 3  | 15.71                          | 41.35 | 0.37                     | 0.75  |
| 5  | 9.79                           | 37.92 | 0.22                     | 0.56  |
| 7  | 3.31                           | 36.46 | 0.14                     | 0.43  |
| 9  | -                              | 24.9  | -                        | 0.50  |



Table 4.31: Peak Current  $I_p$  ( $\mu\text{A}$ ) and Peak potential  $E_p$  (V) of pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle),  $A_2=2^{\text{nd}}$  anodic peak

| pH | Peak Current $I_p$ ( $\mu\text{A}$ ) |       |       | Peak potential $E_p$ (V) |       |       |
|----|--------------------------------------|-------|-------|--------------------------|-------|-------|
|    | $A_0$                                | $A_1$ | $A_2$ | $A_0$                    | $A_1$ | $A_2$ |
| 2  | 3.60                                 | 15.47 | -     | 0.31                     | 0.65  | -     |
| 3  | 5.32                                 | 12.45 | 9.39  | 0.16                     | 0.41  | 1.18  |
| 5  | 4.24                                 | 10.99 | 6.78  | 0.27                     | 0.56  | 1.12  |
| 7  | 1.39                                 | 14.17 | 13.36 | 0.03                     | 0.25  | 1.00  |
| 9  | -                                    | 5.11  | 9.80  | -                        | 0.39  | 1.01  |

Table 4.32: Peak Current  $I_p$  ( $\mu\text{A}$ ) and Peak potential  $E_p$  (V) of pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

| pH | Peak Current $I_p$ ( $\mu\text{A}$ ) |       | Peak potential $E_p$ (V) |       |
|----|--------------------------------------|-------|--------------------------|-------|
|    | $A_0$                                | $A_1$ | $A_0$                    | $A_1$ |
| 2  | 2.96                                 | 11.08 | 0.33                     | 0.67  |
| 3  | 4.86                                 | 12.11 | 0.19                     | 0.63  |
| 5  | 4.04                                 | 11.77 | 0.28                     | 0.64  |
| 7  | 0.90                                 | 10.79 | 0.11                     | 0.50  |

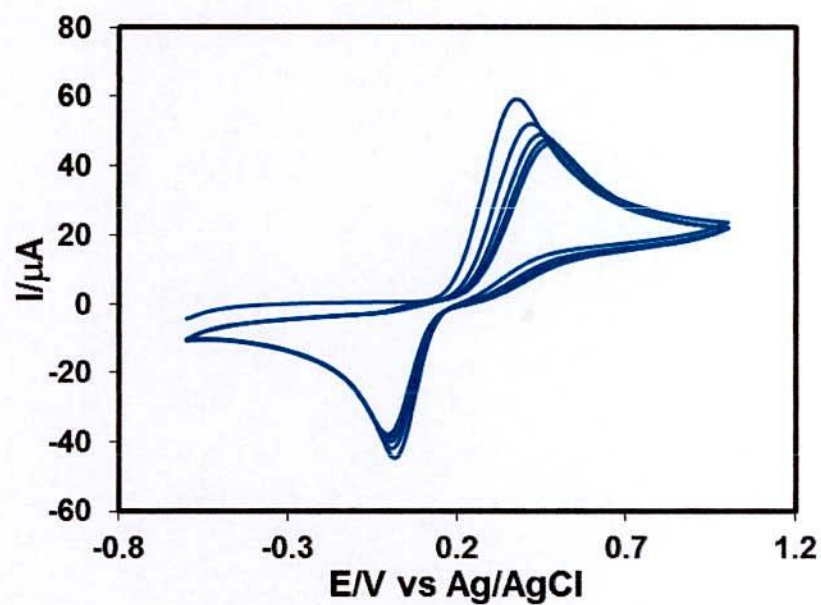


Fig. 4.1: Cyclic voltammogram (CV) of 5 cycles of 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s

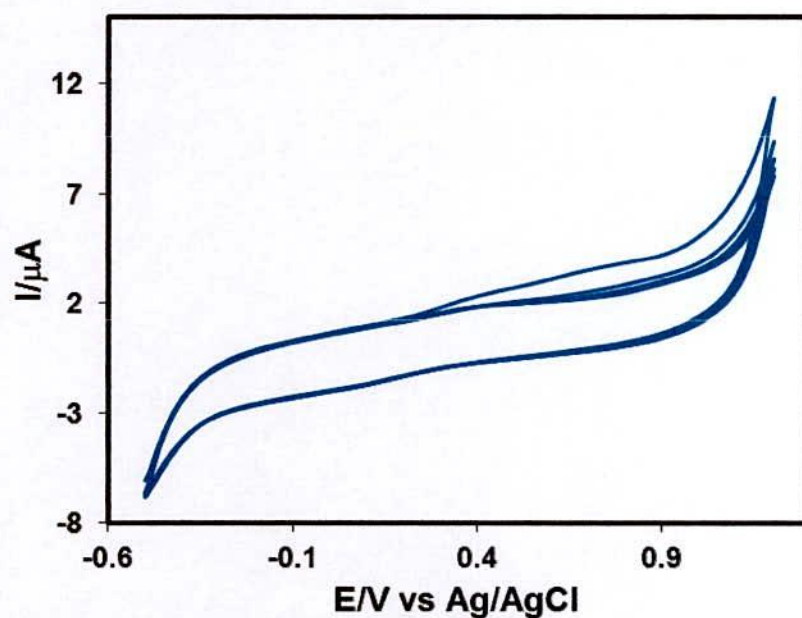


Fig. 4.2: Cyclic voltammogram of 5 cycles of 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s



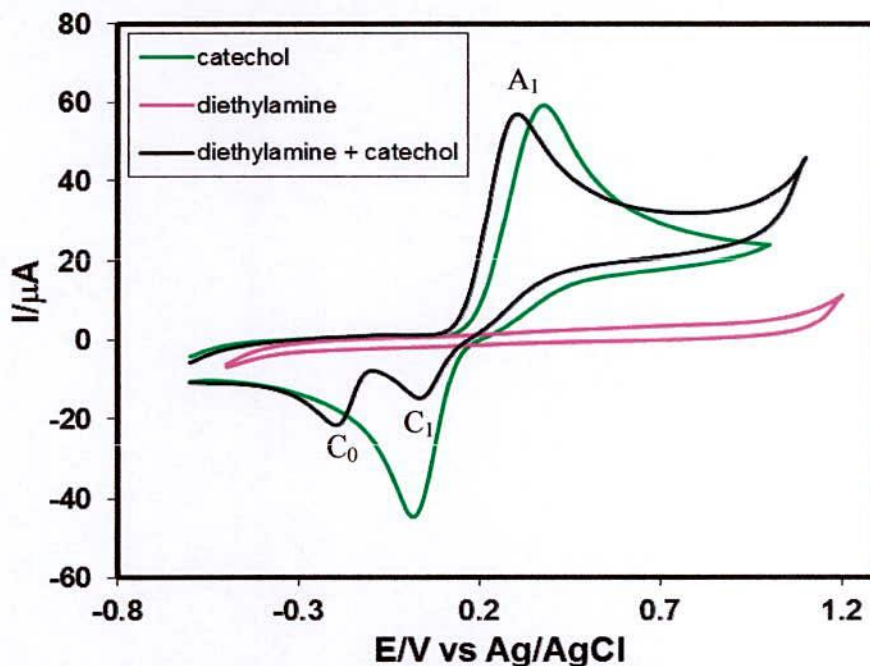


Fig. 4.3: Comparison of cyclic voltammograms of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle) (Where A<sub>1</sub>= 1<sup>st</sup> oxidation peak, C<sub>0</sub>= Appeared reduction peak and C<sub>1</sub>= 1<sup>st</sup> reduction peak)

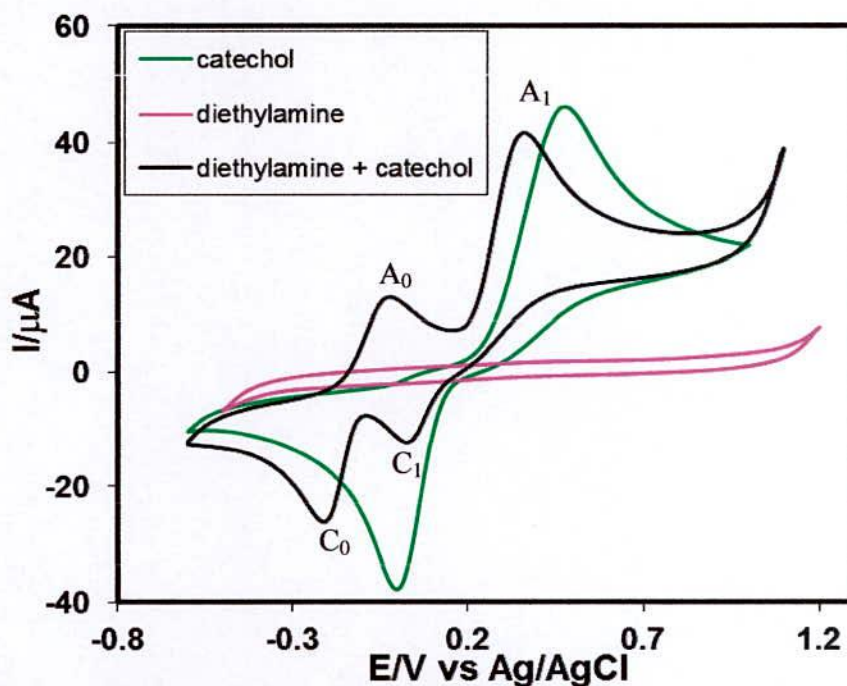


Fig. 4.4: Comparison of cyclic voltammograms of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle) (A<sub>0</sub> = Appeared oxidation peak)

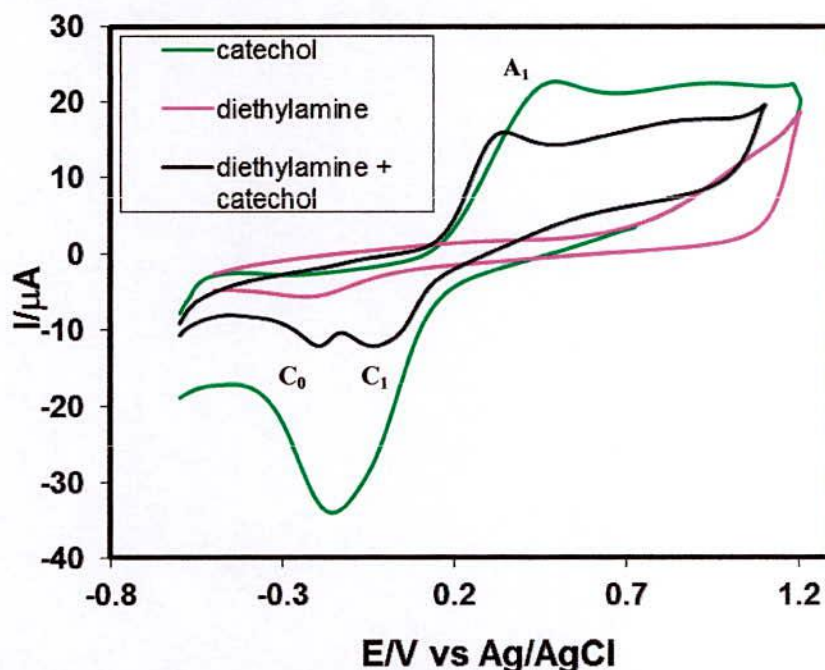


Fig. 4.5: Comparison of cyclic voltammograms of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle)

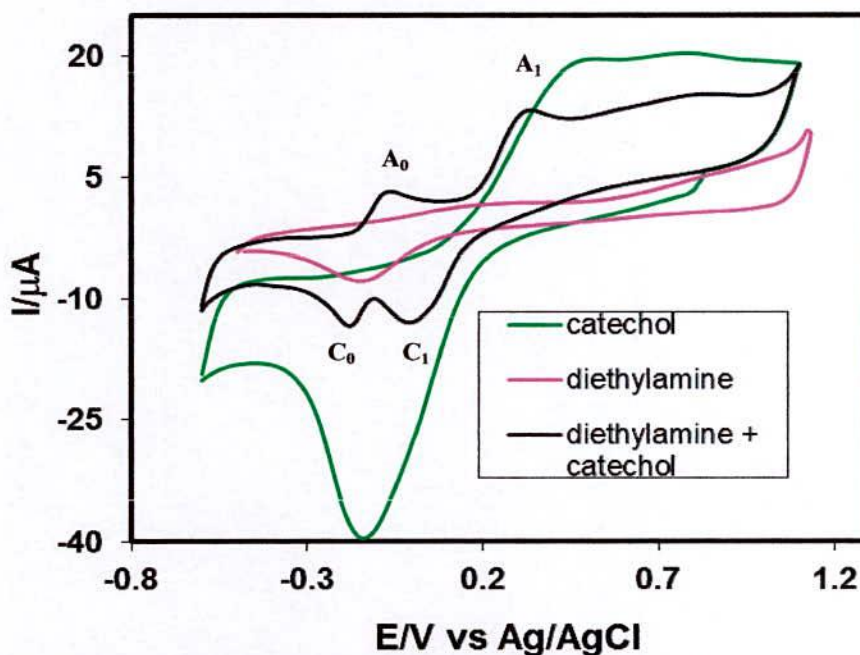


Fig. 4.6: Comparison of cyclic voltammograms of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)



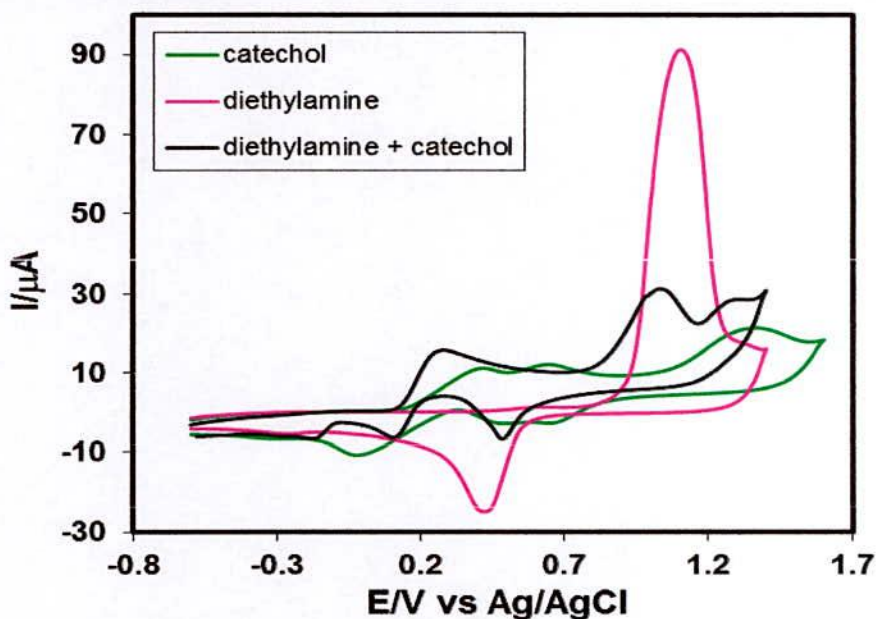


Fig. 4.7: Comparison of cyclic voltammograms of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle)

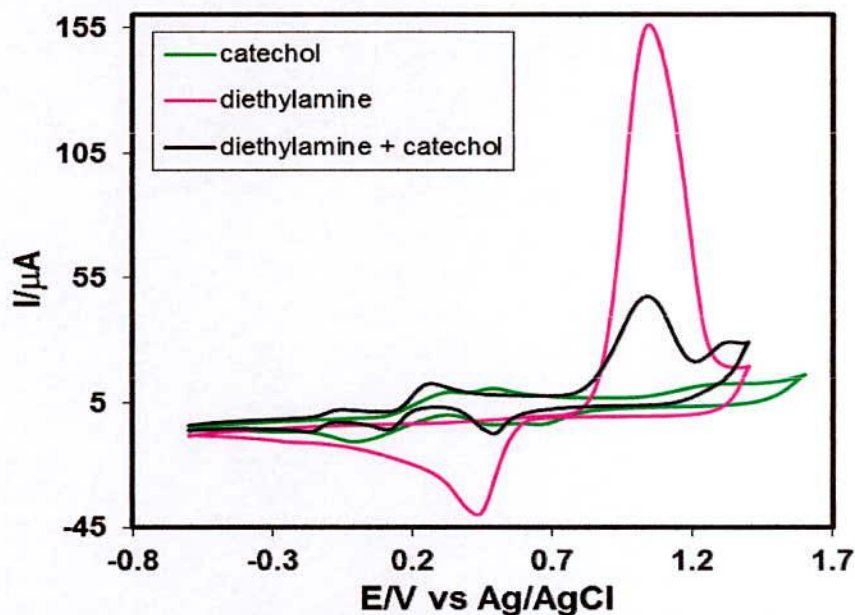


Fig. 4.8: Comparison of cyclic voltammograms of only 2mM catechol, only 250mM diethylamine and 2mM catechol + 250mM diethylamine of Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

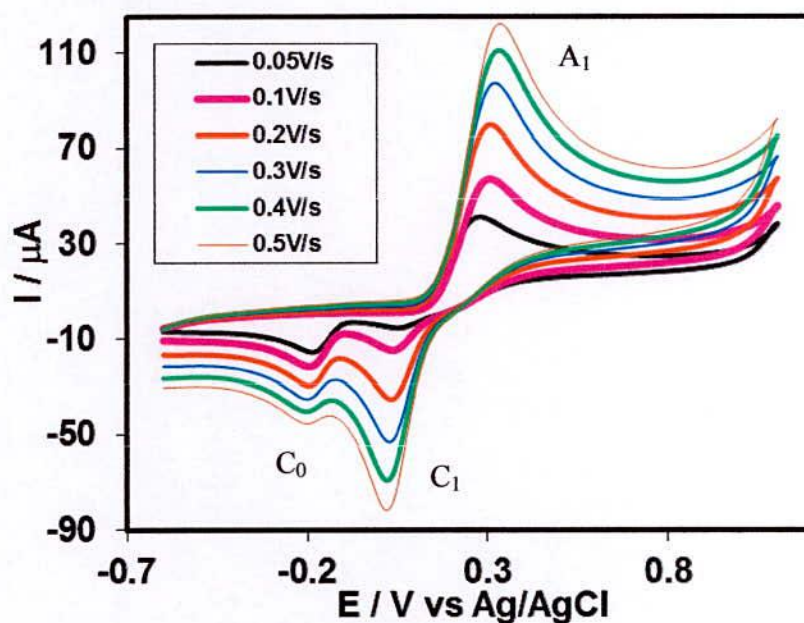


Fig. 4.9: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle) (Where  $A_1$  = 1<sup>st</sup> oxidation peak,  $C_0$  = Appeared reduction peak and  $C_1$  = 1<sup>st</sup> reduction peak)

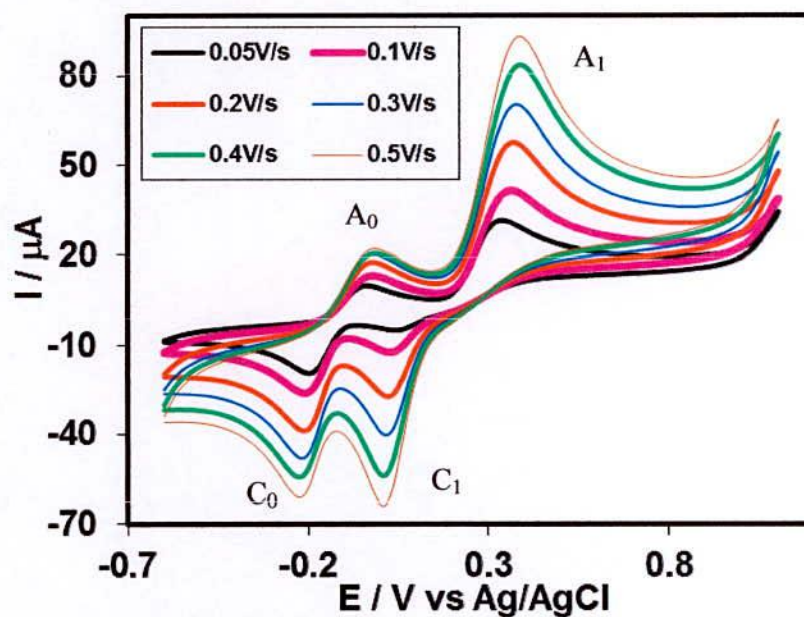


Fig. 4.10: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle),  $A_0$  = Appeared oxidation peak



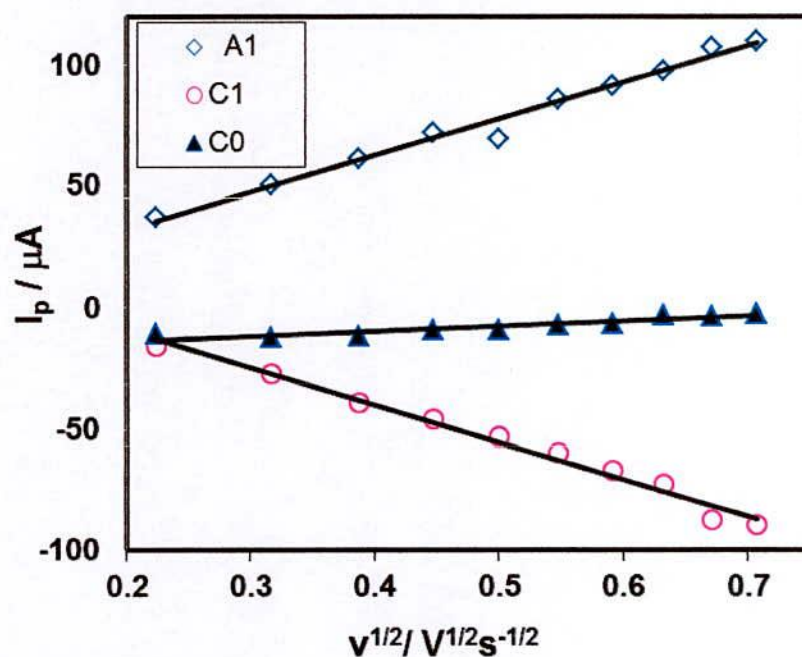


Fig. 4.11: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1<sup>st</sup> cycle)

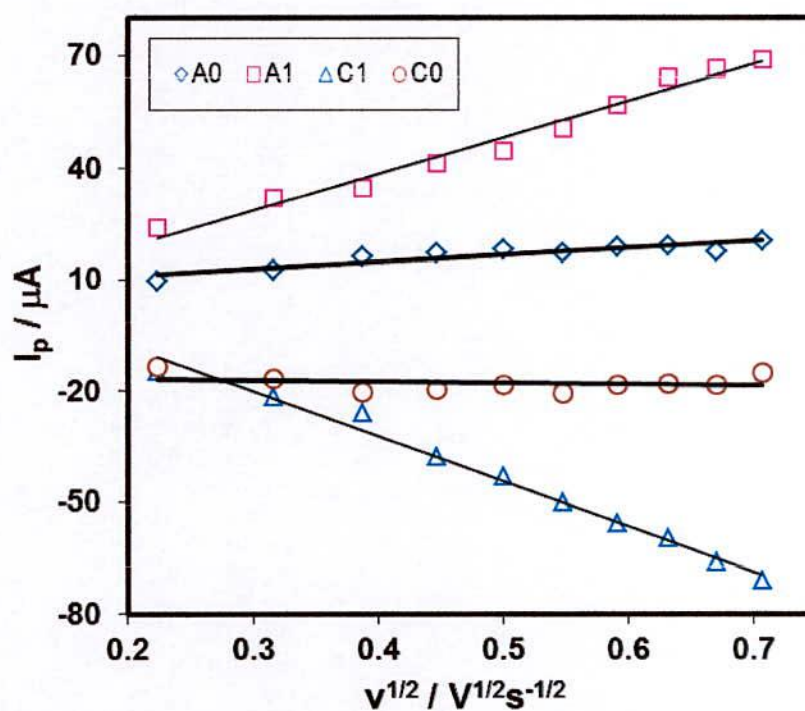


Fig. 4.12: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (2<sup>nd</sup> cycle)

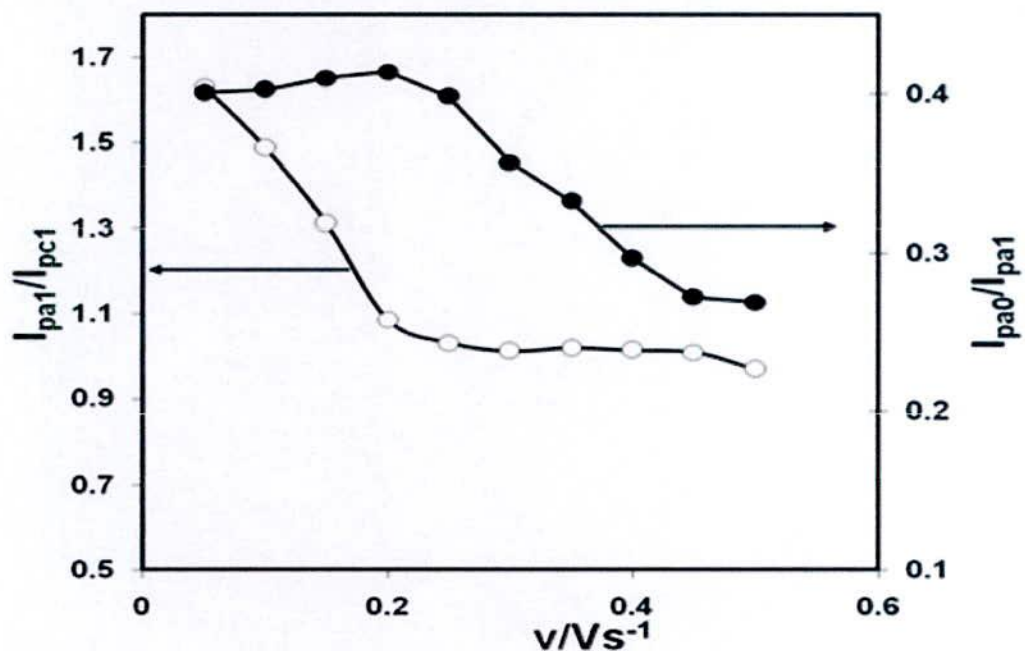


Fig. 4.13: Variation of peak current ratio of corresponding peak ( $I_{pa1}/I_{pc1}$ ) and anodic peak ( $I_{pa0}/I_{pa1}$ ) vs scan rate ( $v$ ) of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate 0.1 V/s in the second scan of potential

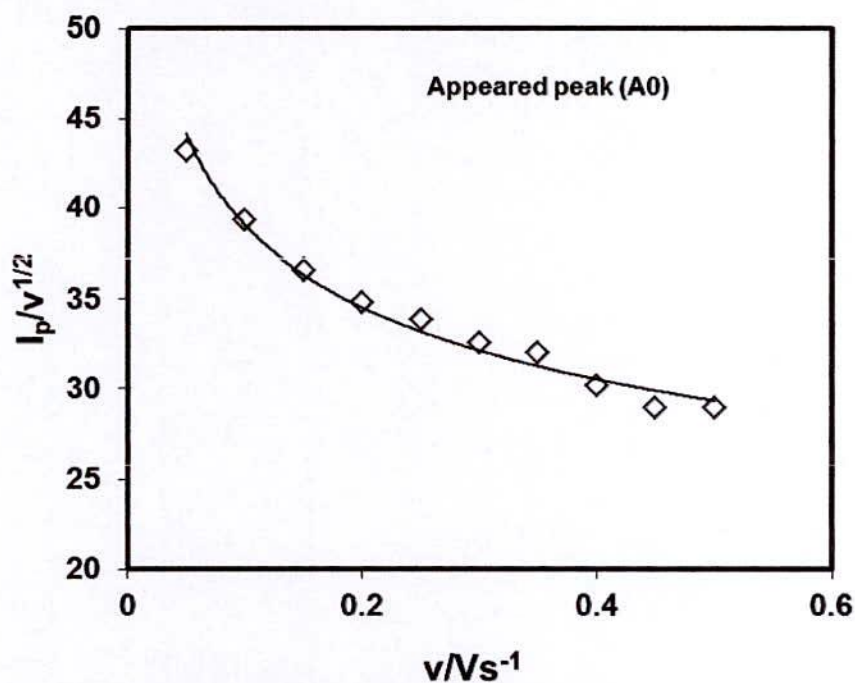


Fig. 4.14: Plots of current function ( $I_p/v^{1/2}$ ) versus scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) of the Appeared anodic peak ( $A_0$ )



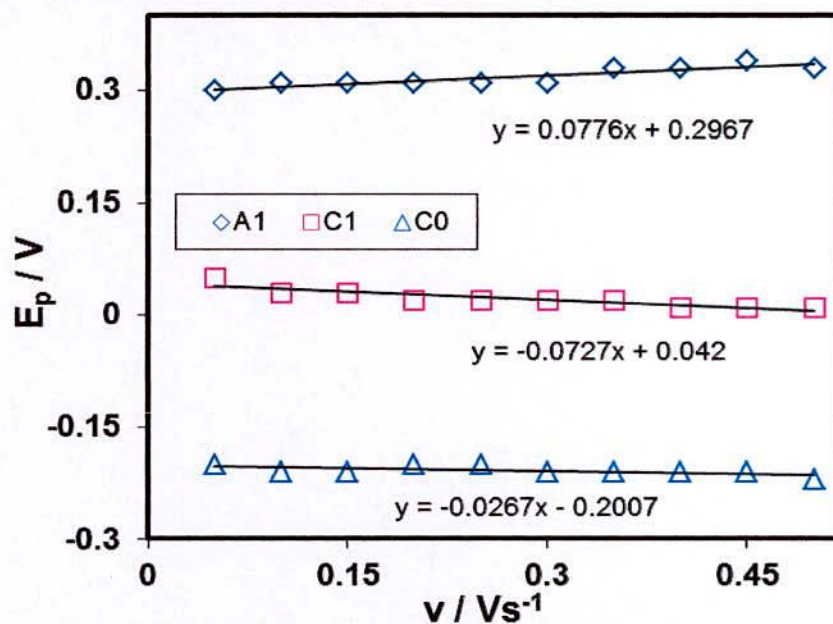


Fig. 4.15: Plots of peak potential ( $E_p$ ) versus scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) (1<sup>st</sup> cycle)

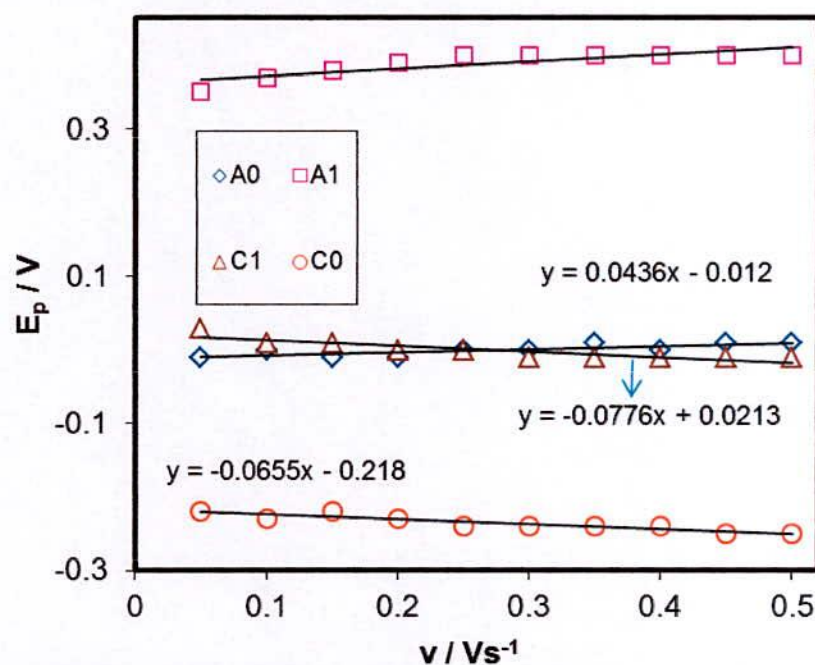


Fig. 4.16: Plots of peak potential ( $E_p$ ) versus scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle

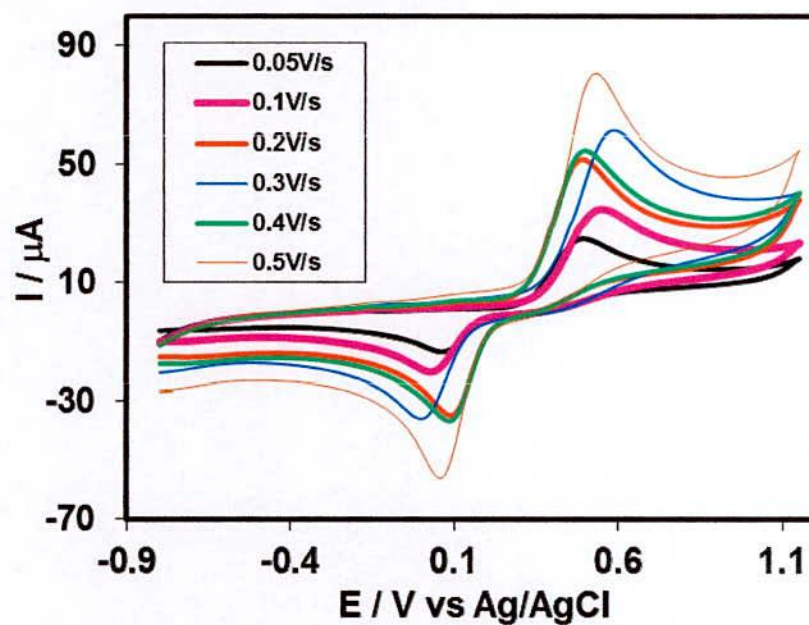


Fig. 4.17: Cyclic voltammogram of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 3) at different scan rate (1<sup>st</sup> cycle)

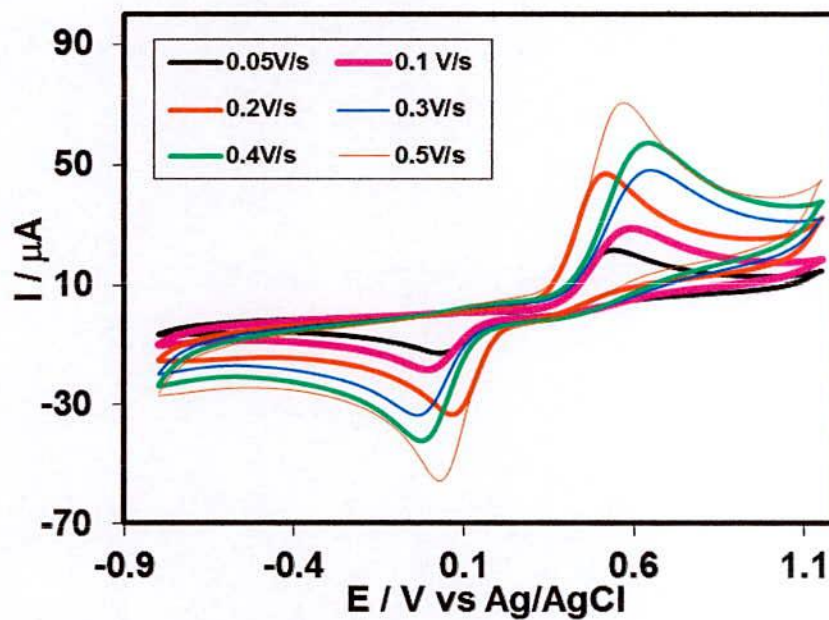


Fig. 4.18: Cyclic voltammogram of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 3) at different scan rate (2<sup>nd</sup> cycle)



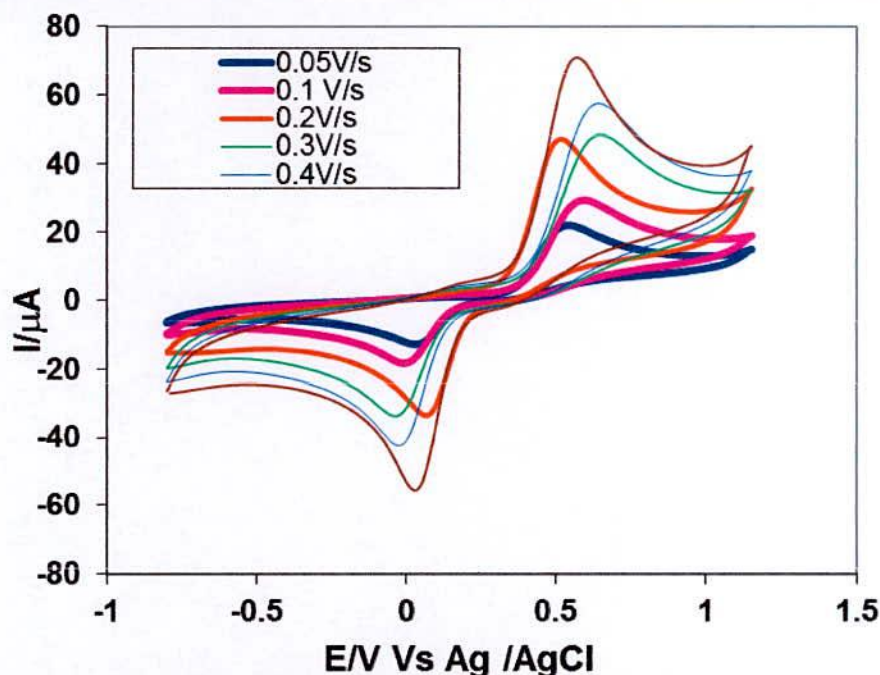


Fig. 4.19: Cyclic voltammogram of 2mM catechol + 250mM diethylamine at GC electrode in buffer solution (pH 5) at different scan rate (2<sup>nd</sup> cycle)

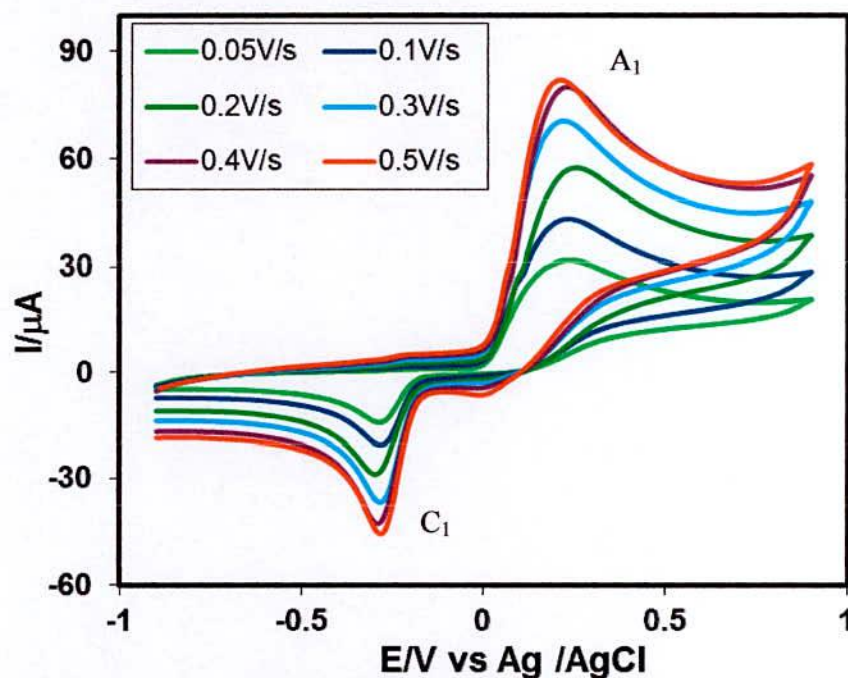


Fig. 4.20: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 9) at different scan rate (1<sup>st</sup> cycle)

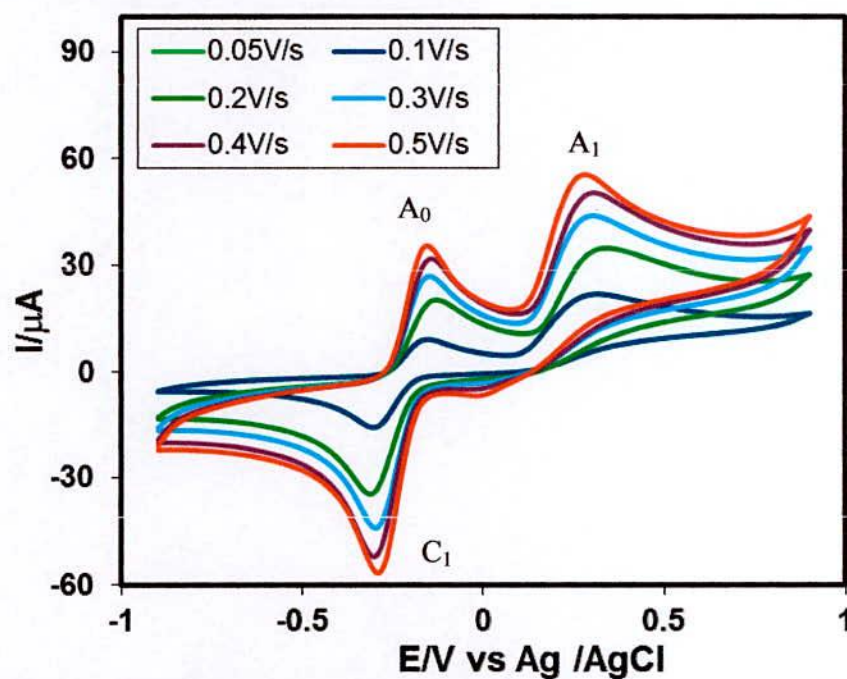


Fig. 4.21: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 9) at different scan rate (2<sup>nd</sup> cycle)

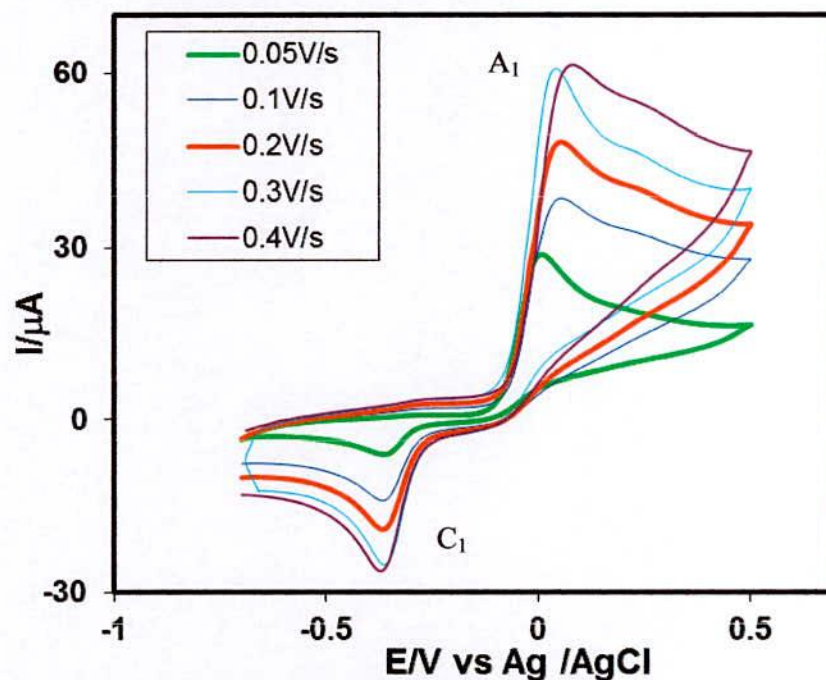


Fig. 4.22: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) at different scan rate (1<sup>st</sup> cycle)



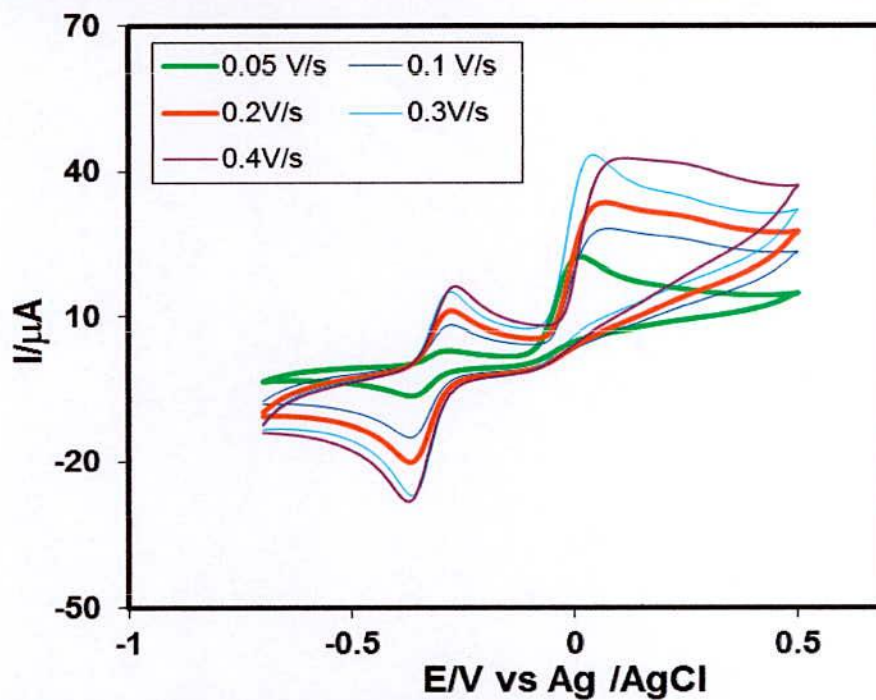


Fig. 4.23: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) at different scan rate (2<sup>nd</sup> cycle)

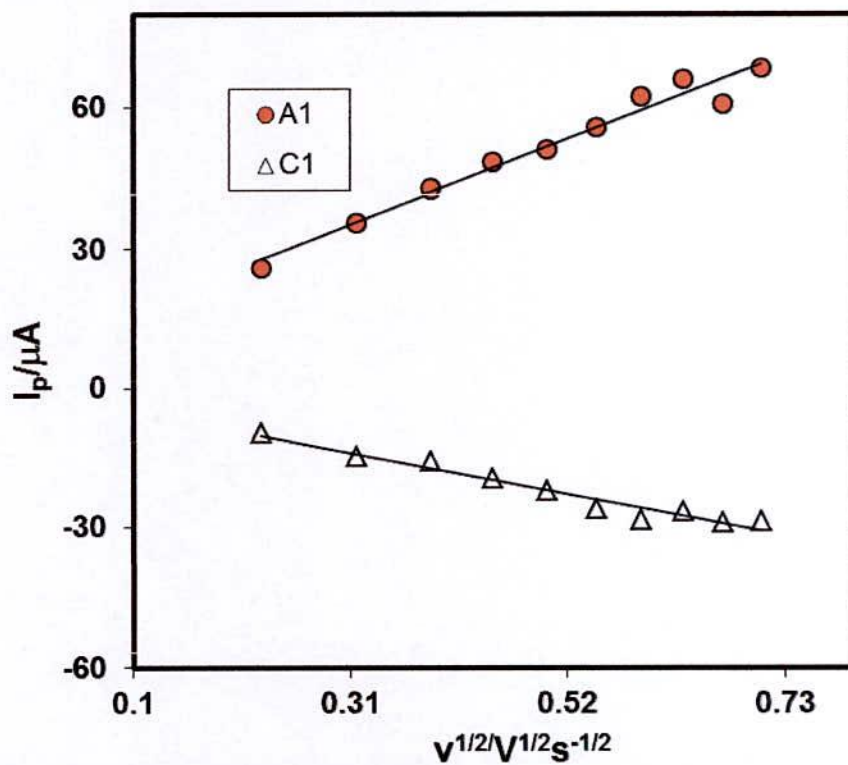


Fig. 4.24: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 3) at 1<sup>st</sup> cycle

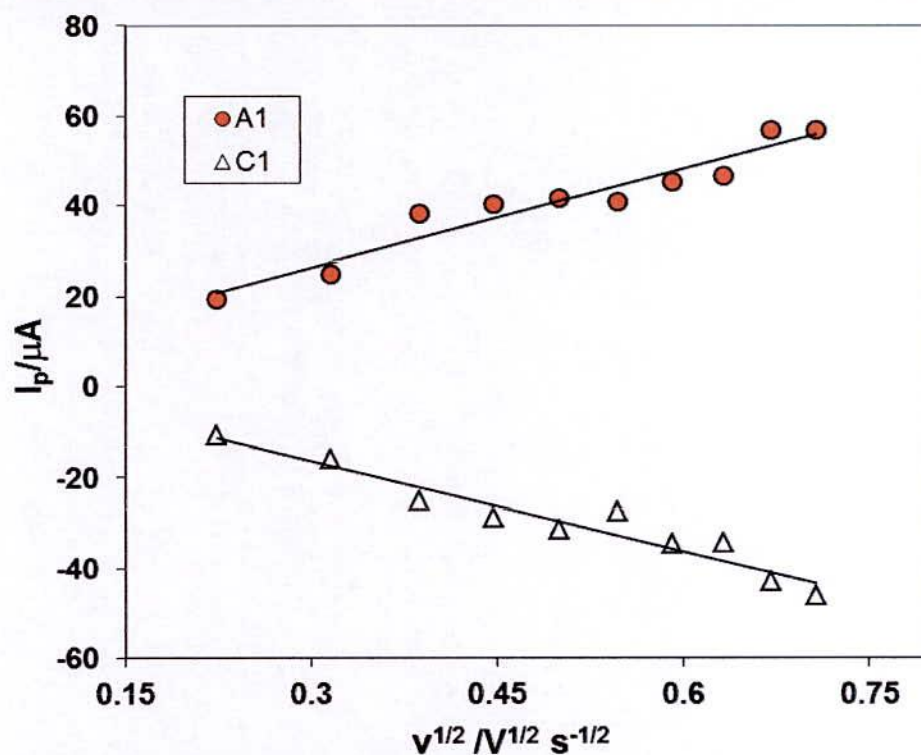


Fig. 4.25: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle

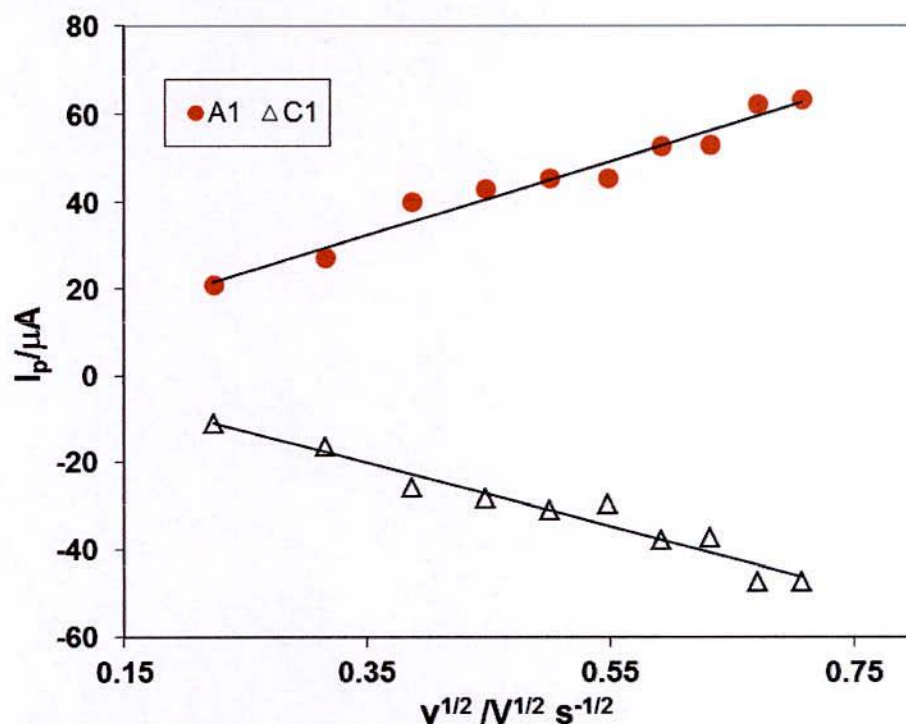


Fig. 4.26: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 5) at 2<sup>nd</sup> cycle



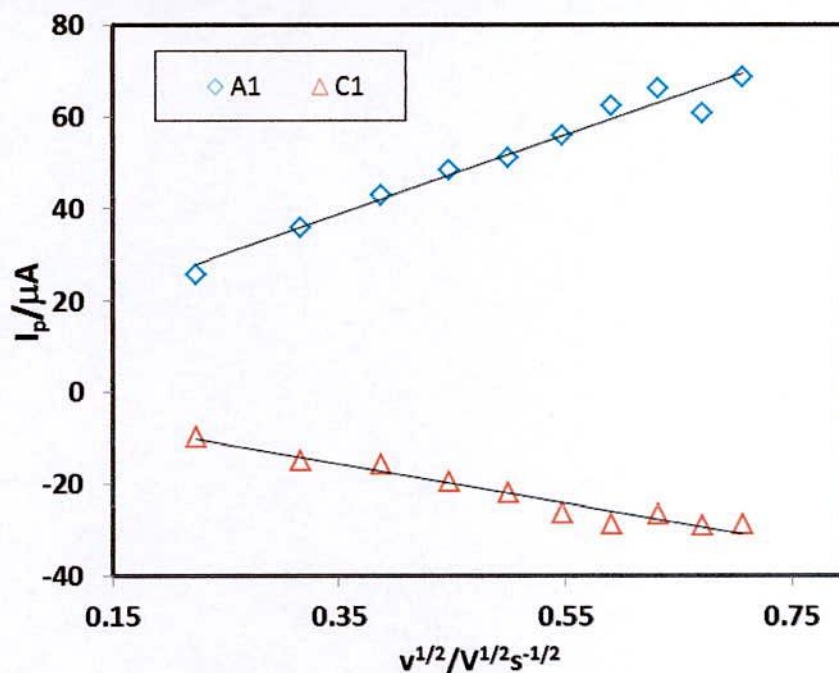


Fig. 4.27: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 9) at 1<sup>st</sup> cycle

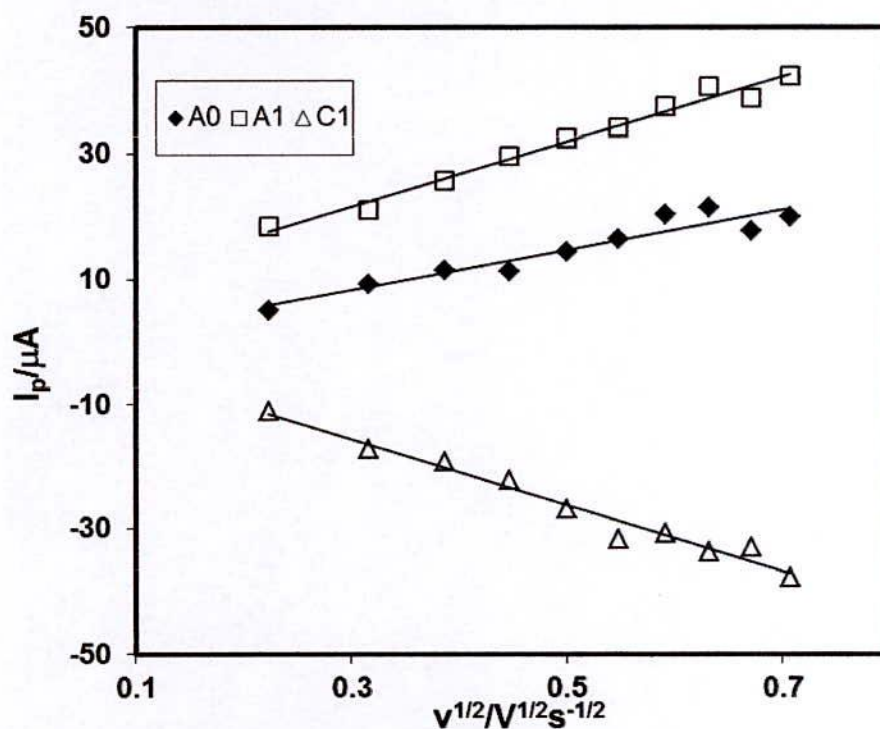


Fig. 4.28: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM catechol + 250mM diethylamine of GC electrode in buffer solution (pH 9) at 2<sup>nd</sup> cycle

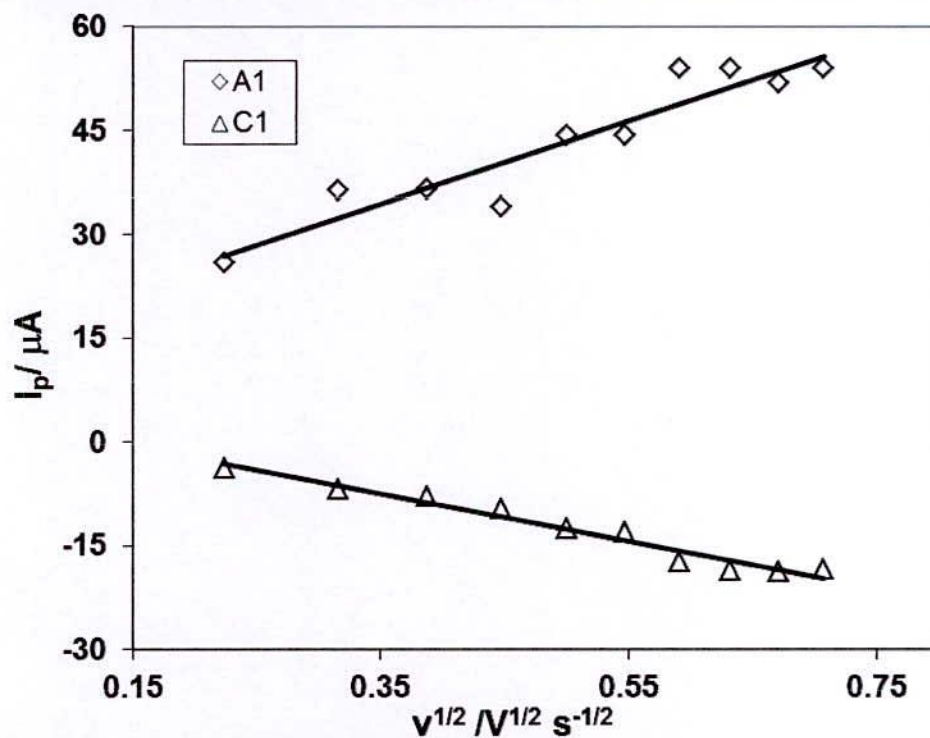


Fig. 4.29: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) at 1<sup>st</sup> cycle

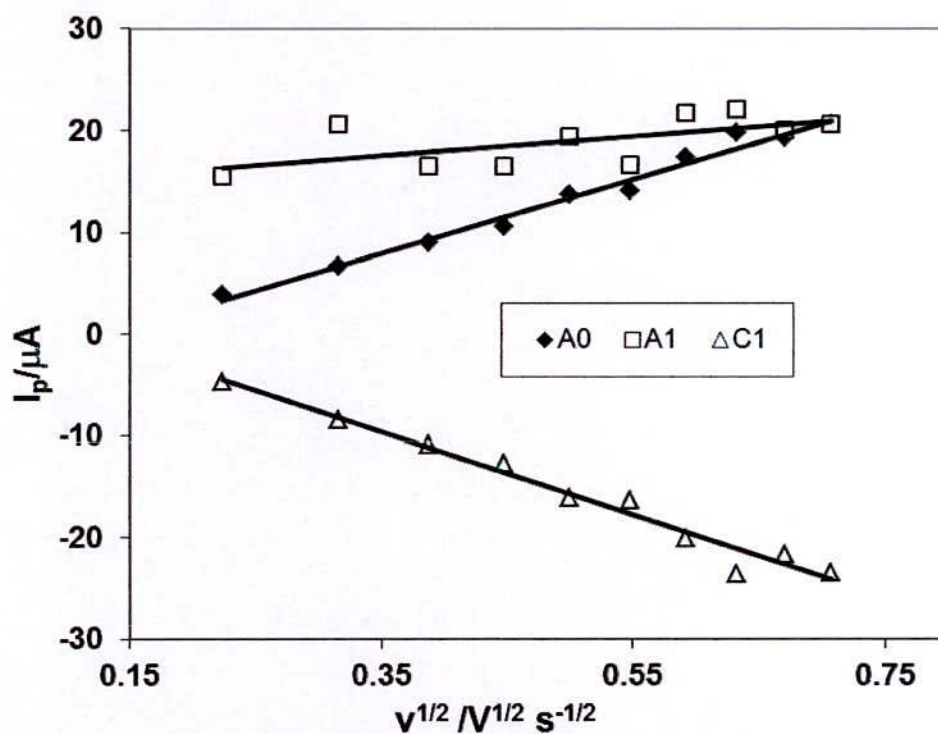


Fig. 4.30: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 11) at 2<sup>nd</sup> cycle



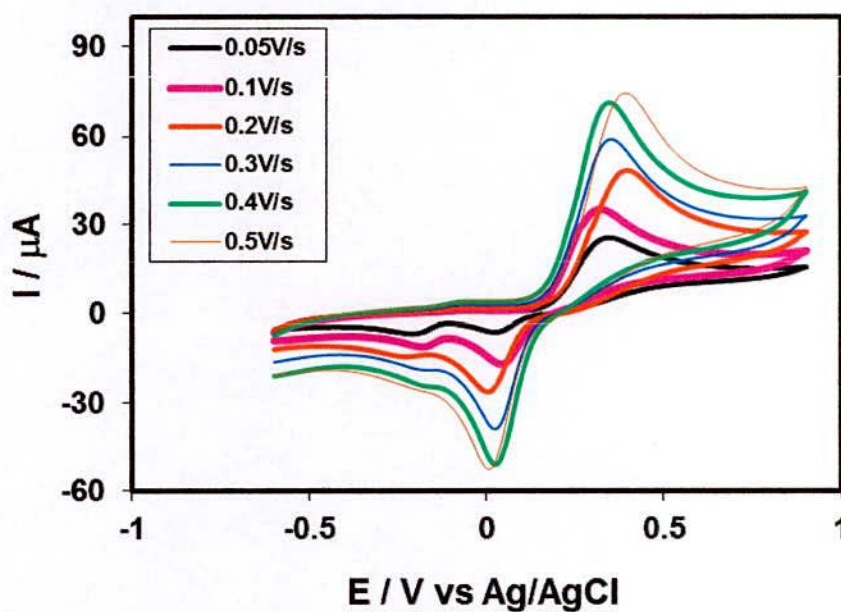


Fig. 4.31: Cyclic voltammogram of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

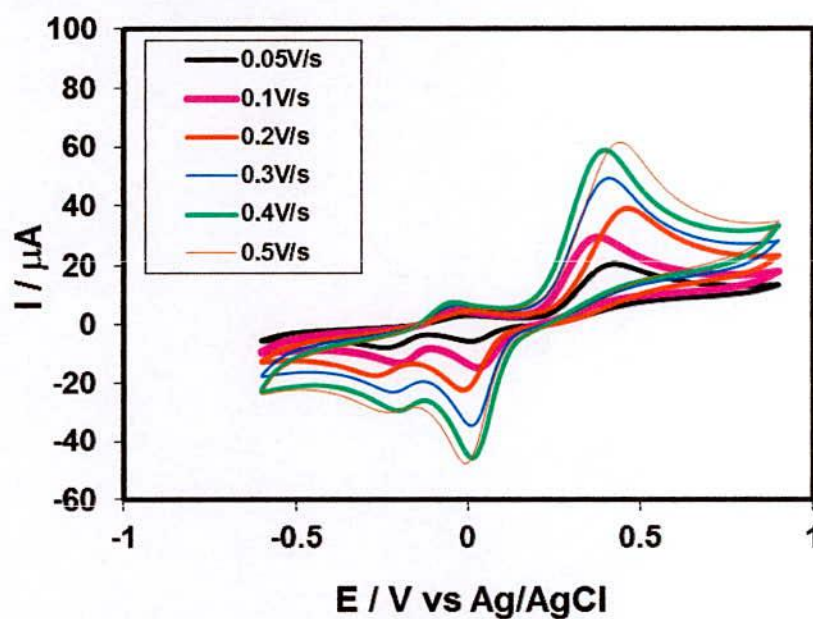


Fig. 4.32: Cyclic voltammogram of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)

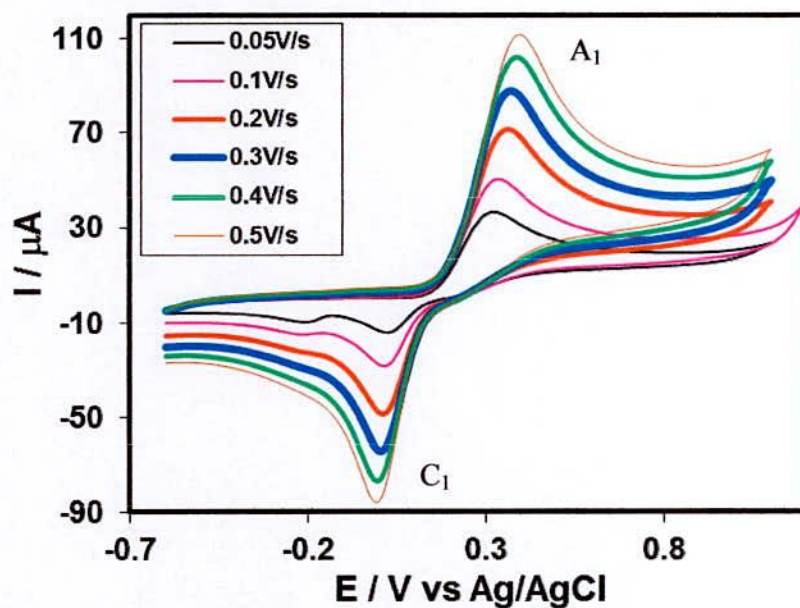


Fig. 4.33: Cyclic voltammogram of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

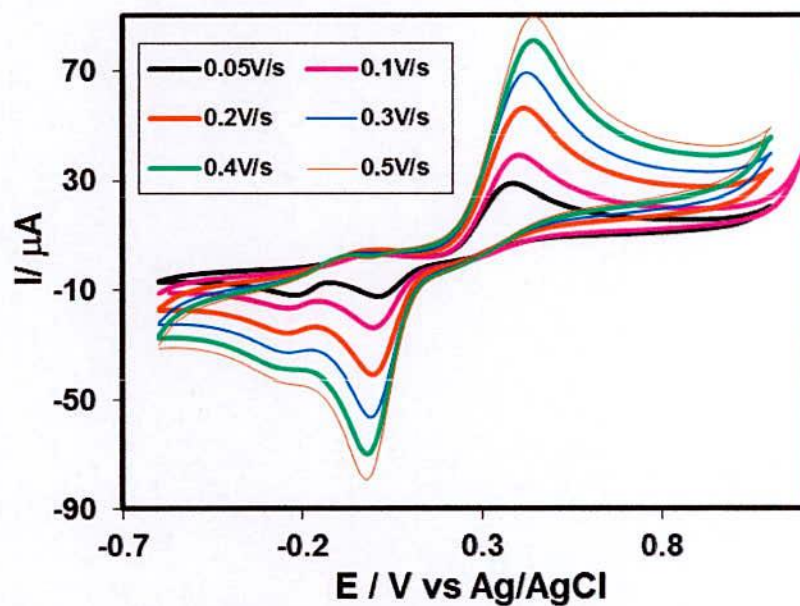


Fig. 4.34: Cyclic voltammogram of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)



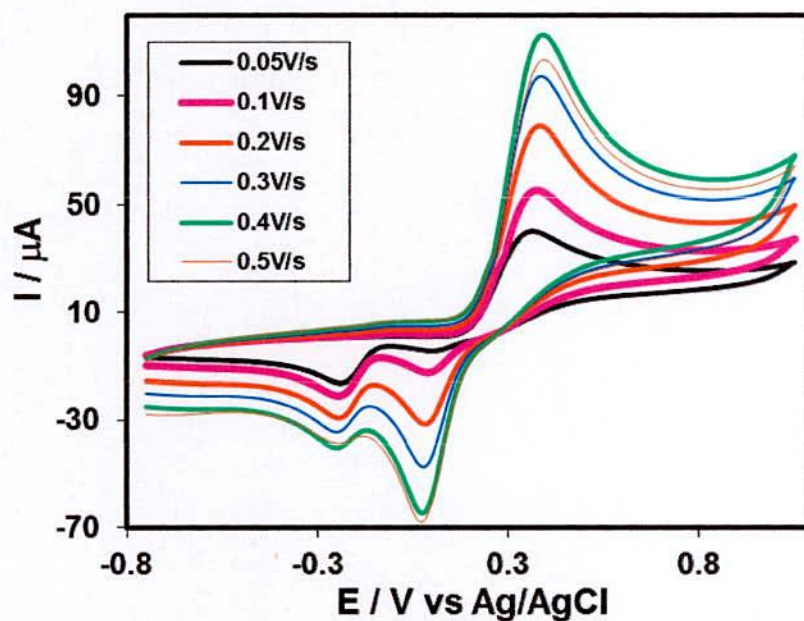


Fig. 4.35: Cyclic voltammogram of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

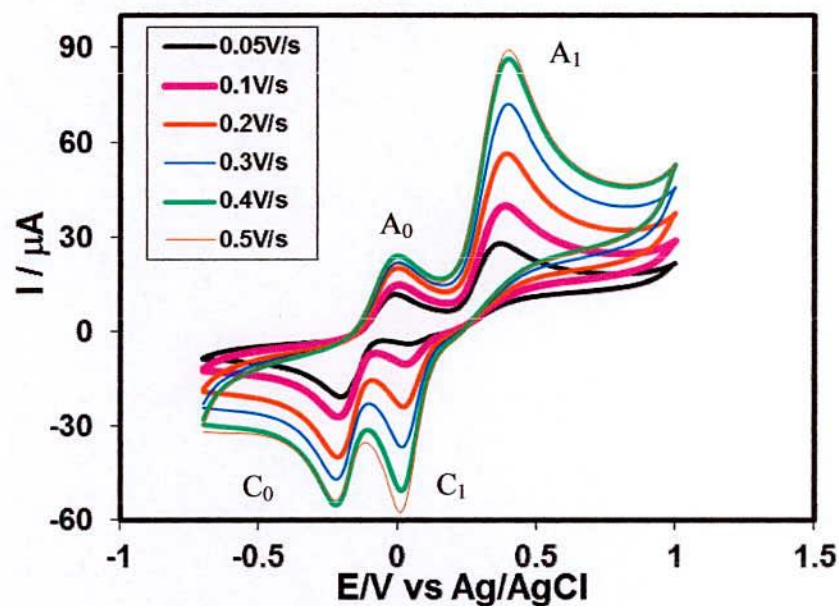


Fig. 4.36: Cyclic voltammogram of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)

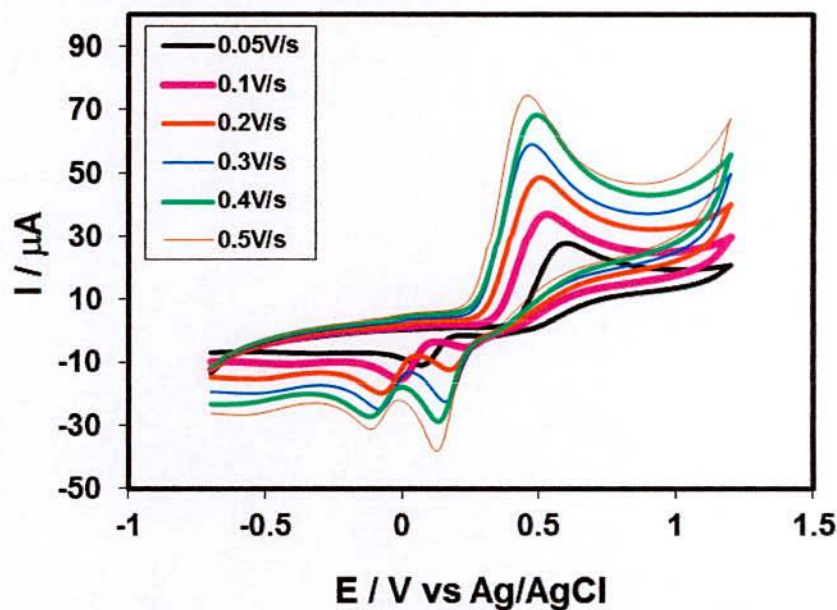


Fig. 4.37: Cyclic voltammogram of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

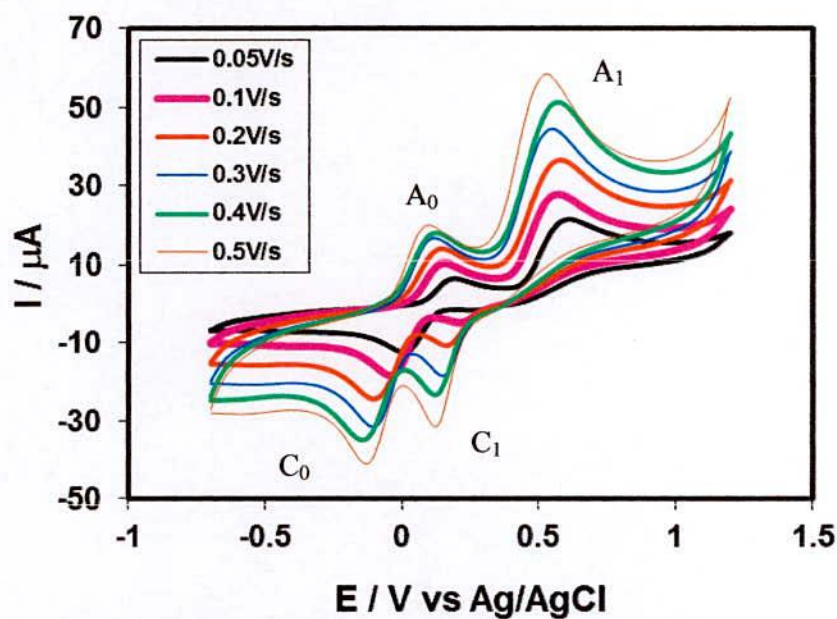


Fig. 4.38: Cyclic voltammogram of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)



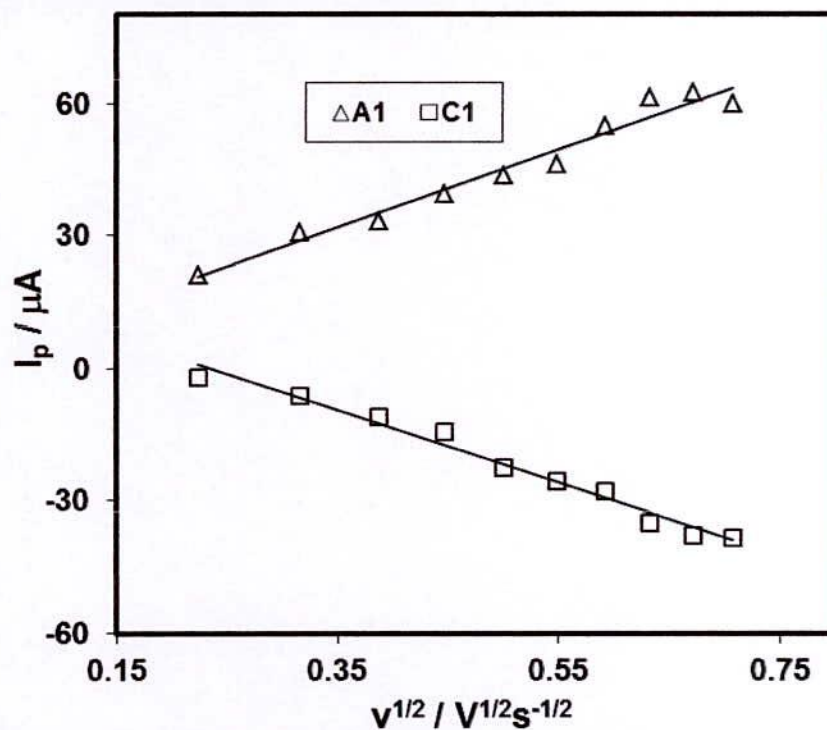


Fig. 4.39: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

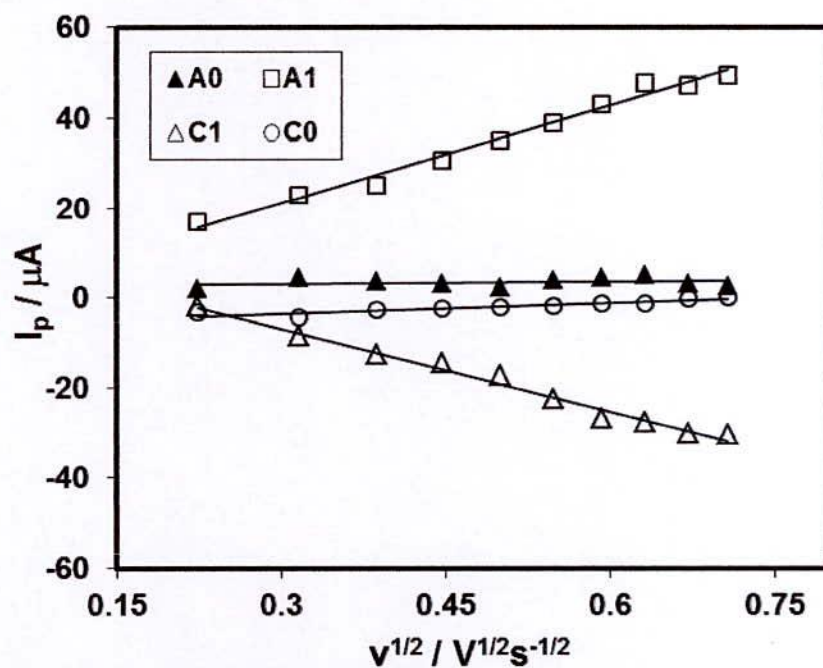


Fig. 4.40: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle

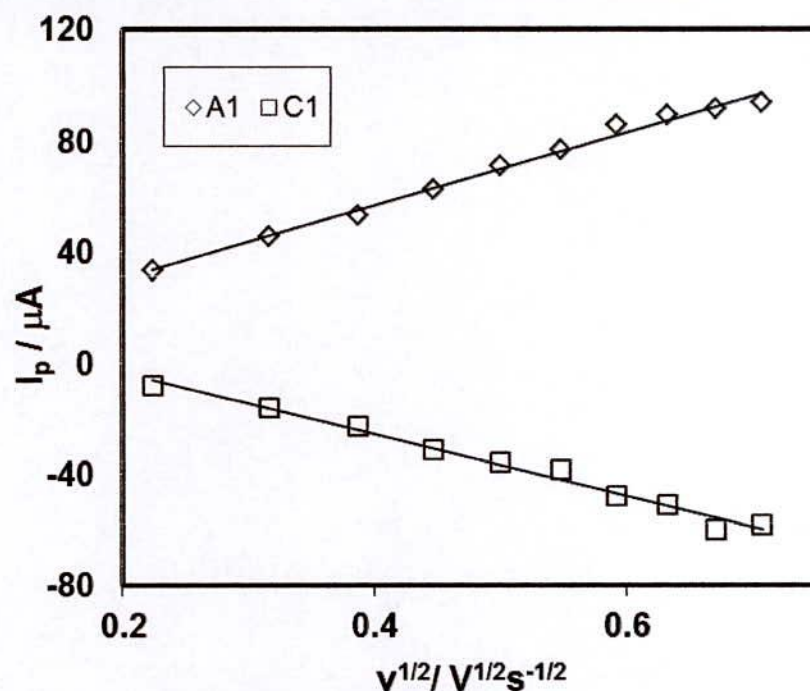


Fig. 5.41: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

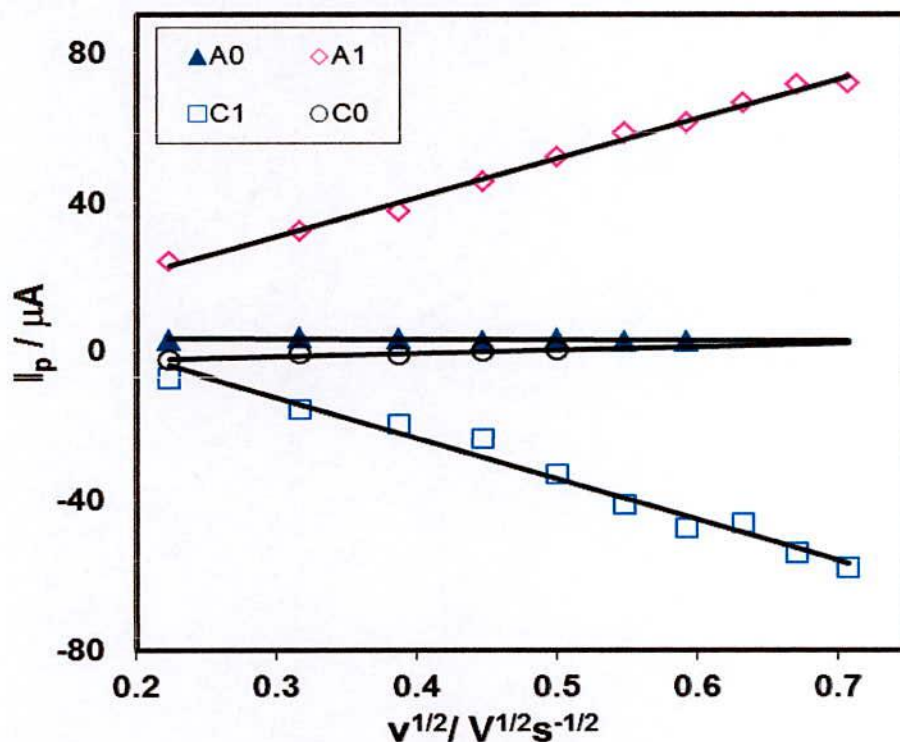


Fig. 4.42: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle



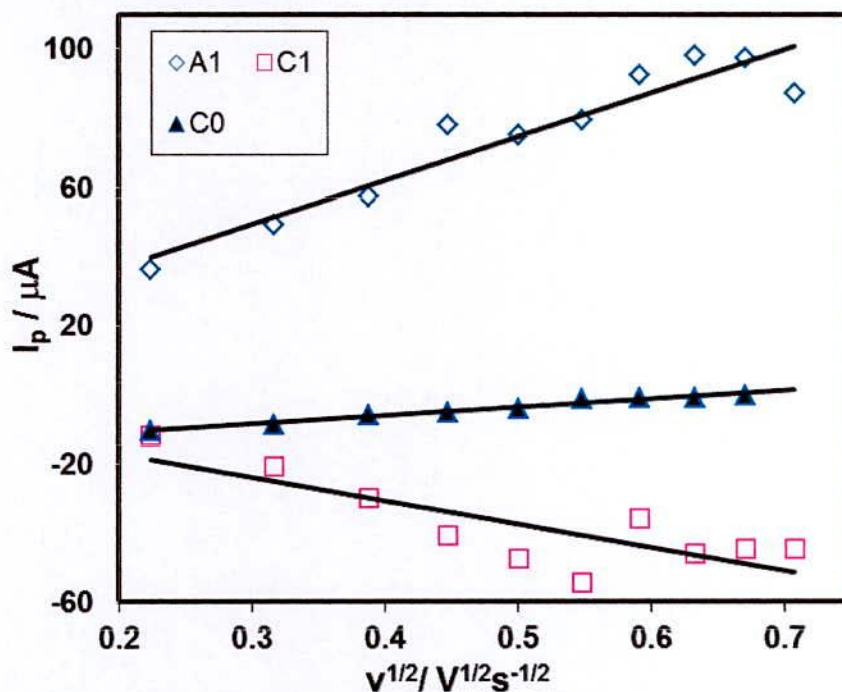


Fig. 4.43: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

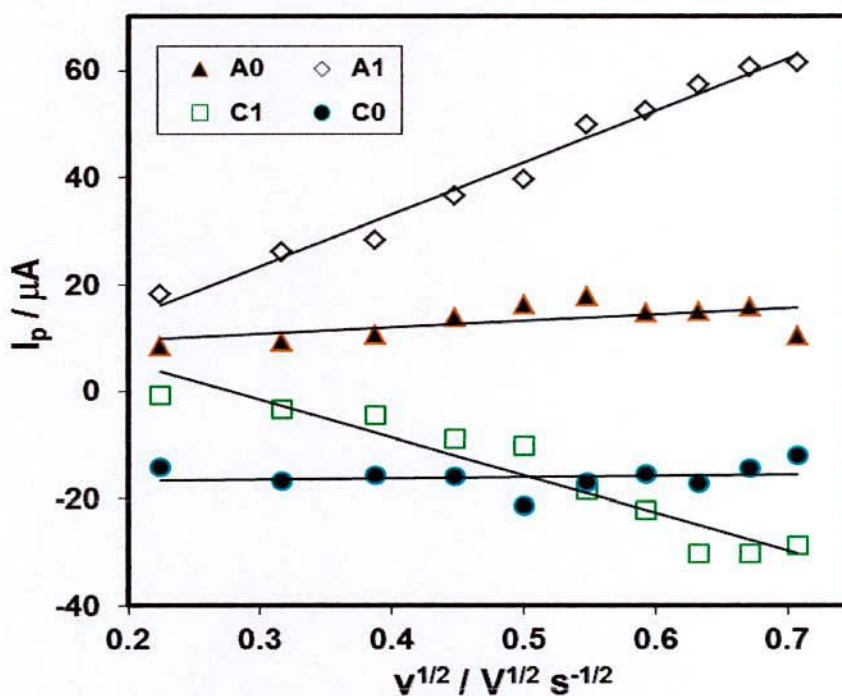


Fig. 4.44: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle

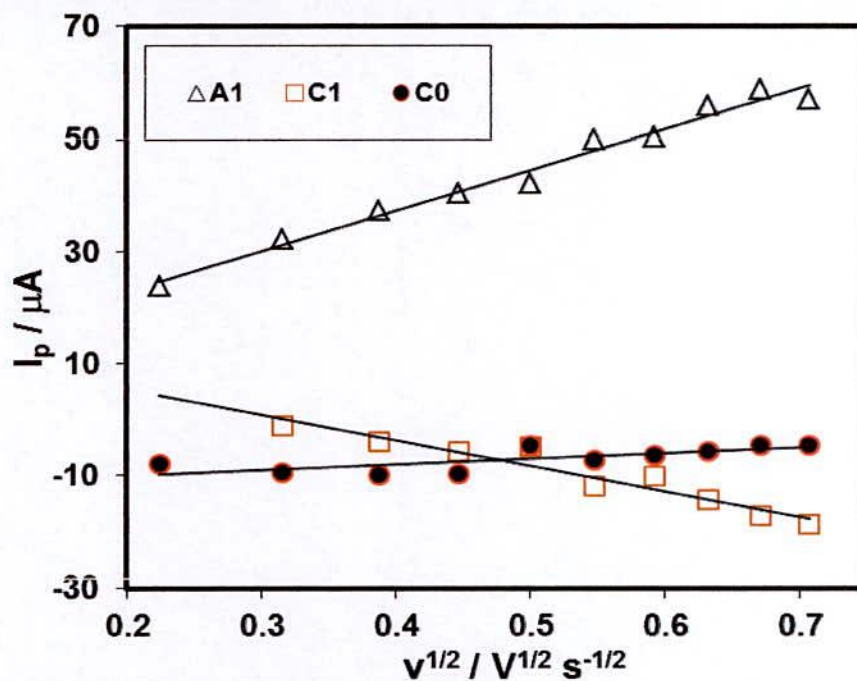


Fig. 4.45: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

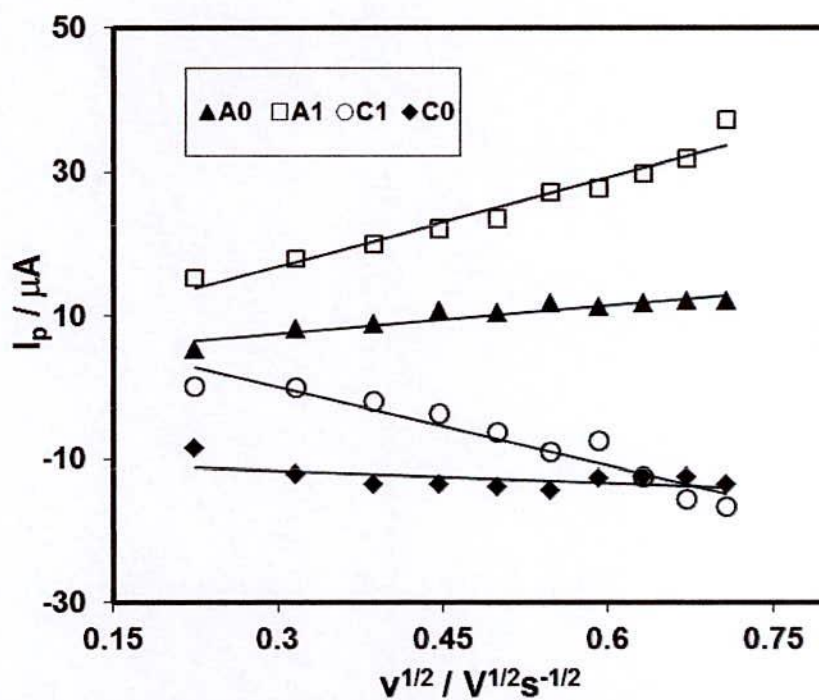


Fig. 4.46: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 350mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle



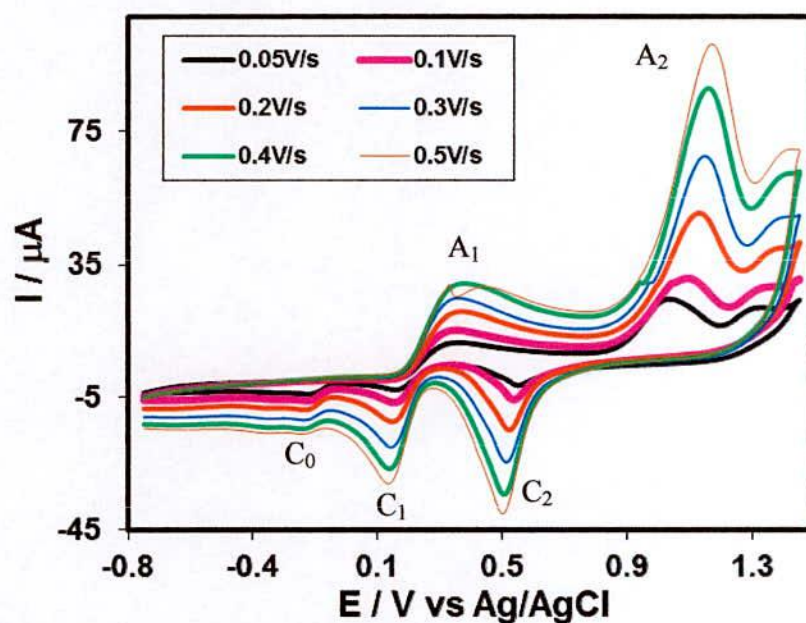


Fig. 4.47: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle) (Where  $A_1$ = 1<sup>st</sup> oxidation peak,  $A_2$ = 2<sup>nd</sup> oxidation peak,  $C_0$ = Apparent reduction peak,  $C_1$ = 1<sup>st</sup> reduction peak and  $C_2$ = 2<sup>nd</sup> reduction peak)

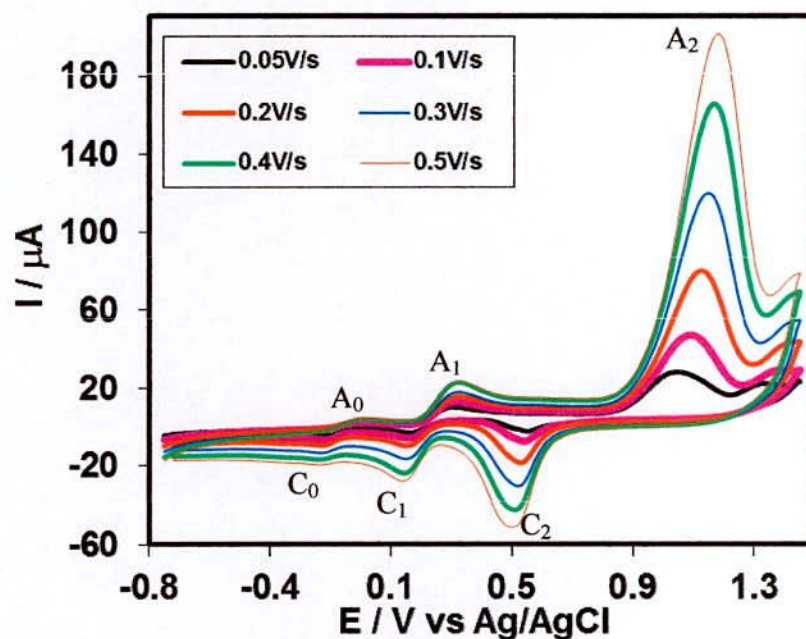


Fig. 4.48: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle),  $A_0$ = Apparent oxidation peak

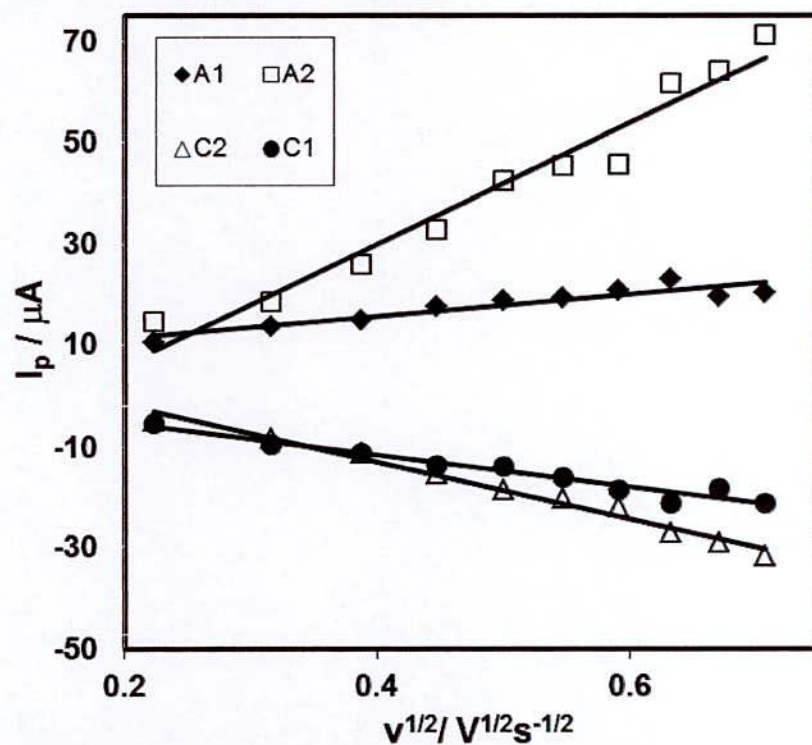


Fig. 4.49: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

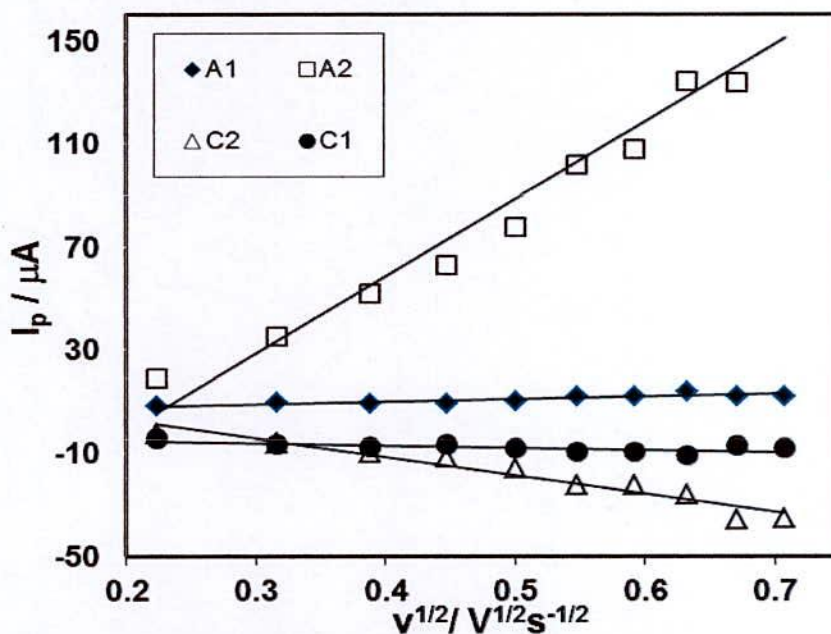


Fig. 4.50: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle



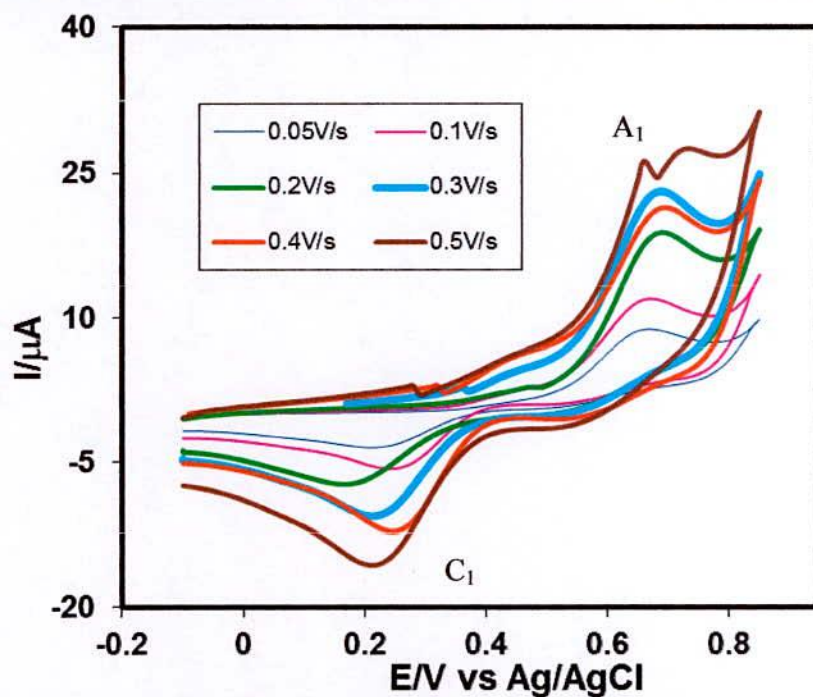


Fig. 4.51: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) at different scan rate (1<sup>st</sup> cycle)

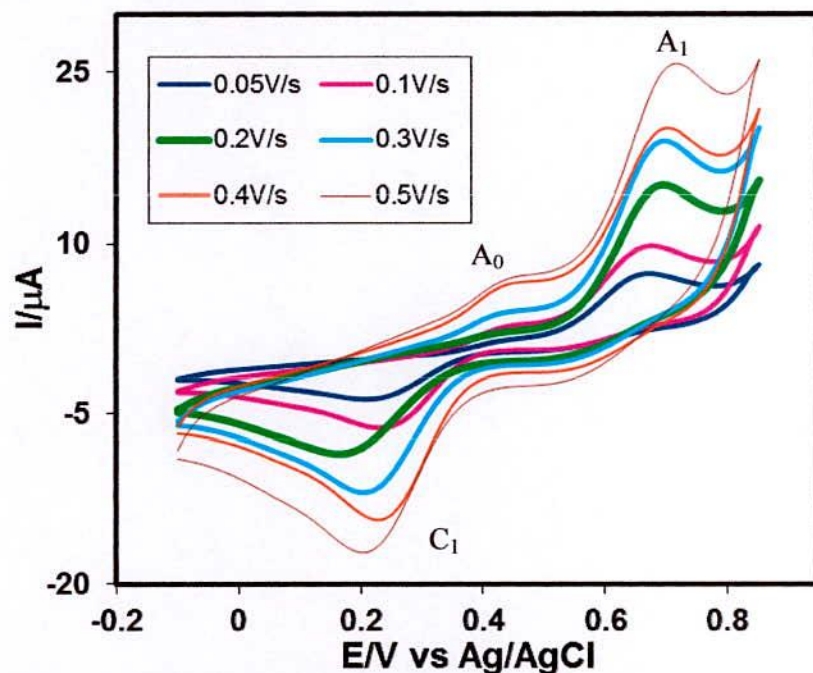


Fig. 4.52: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) at different scan rate (2<sup>nd</sup> cycle)

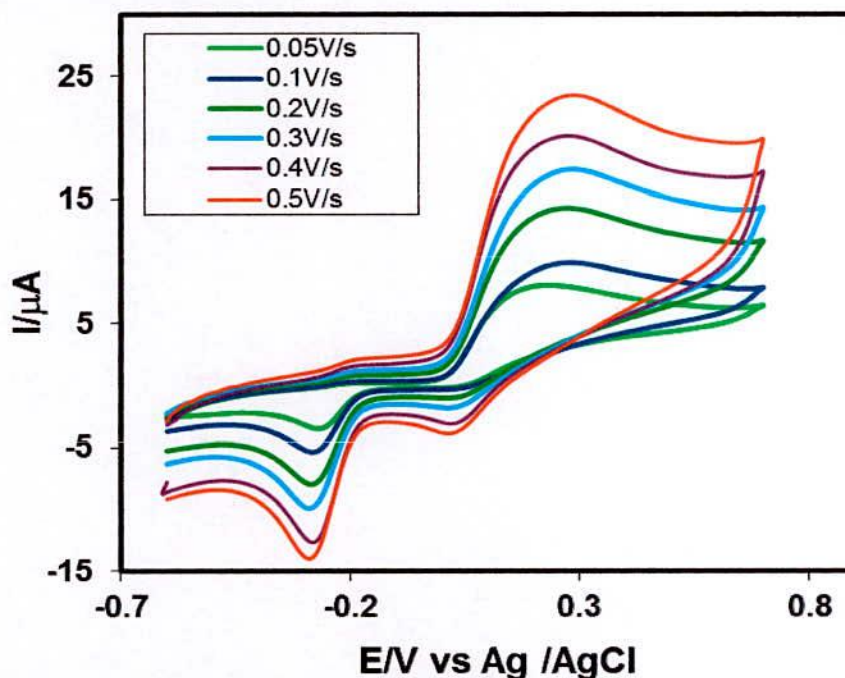


Fig. 4.53: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 9) at different scan rate (1<sup>st</sup> cycle)

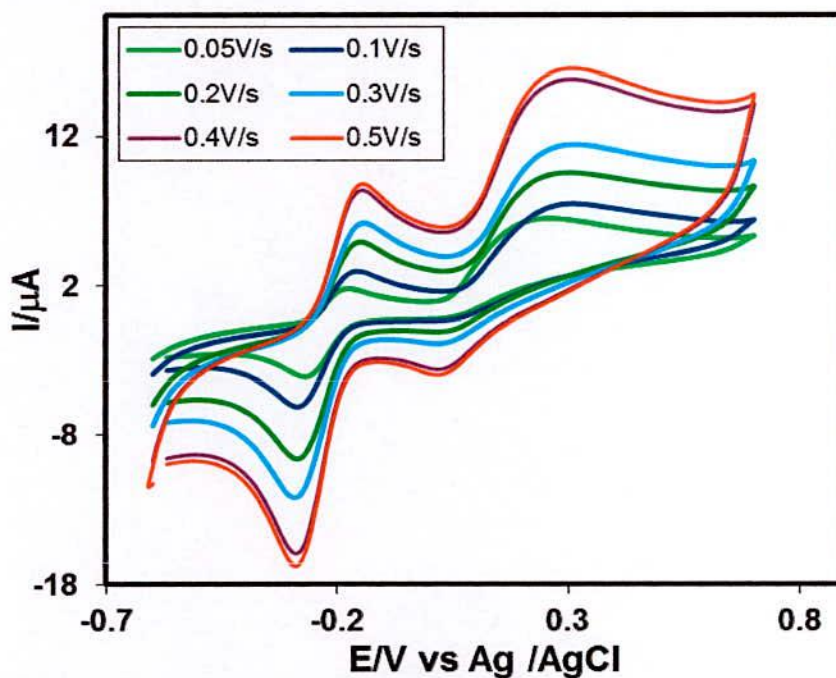


Fig. 4.54: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 9) at different scan rate (2<sup>nd</sup> cycle)



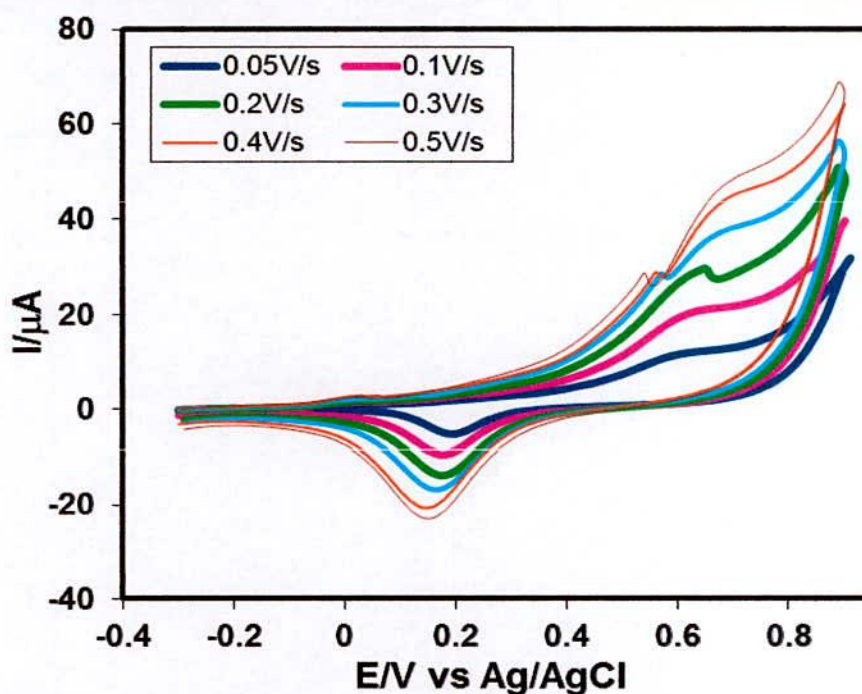


Fig. 4.55: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 11) at different scan rate (1<sup>st</sup> cycle)

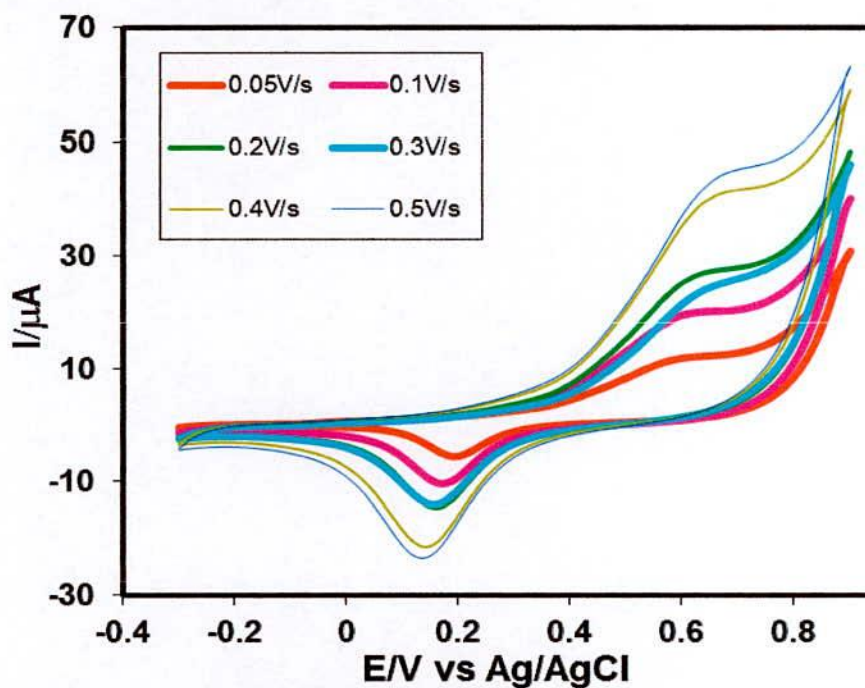


Fig. 4.56: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 11) at different scan rate (2<sup>nd</sup> cycle)

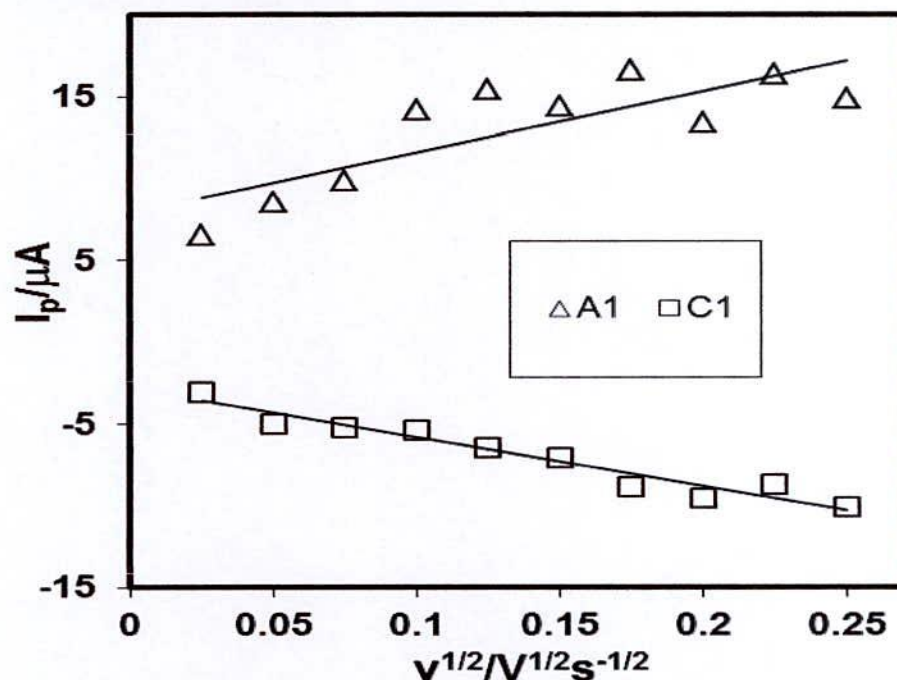


Fig. 4.57: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) at 1<sup>st</sup> cycle

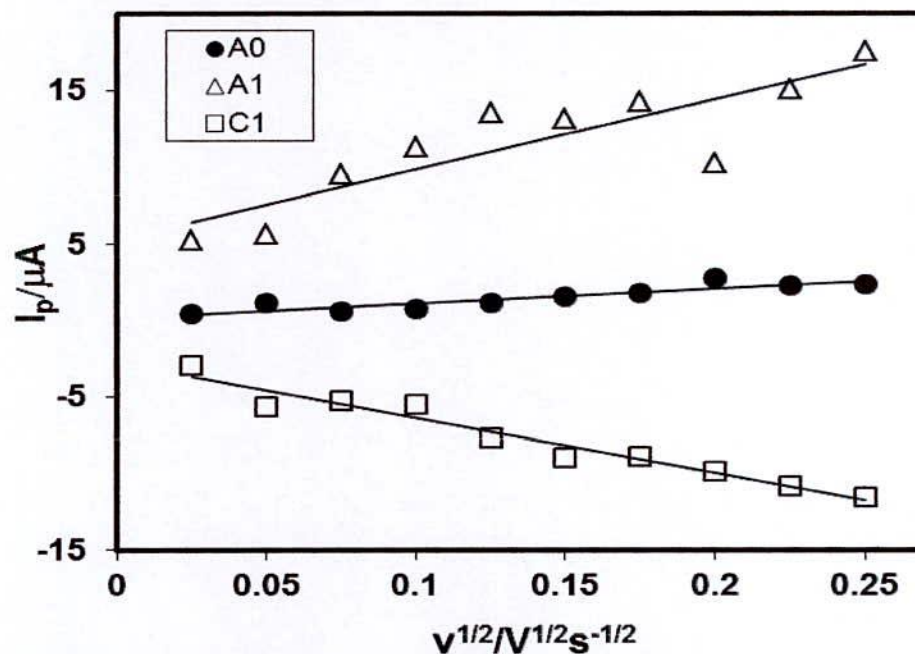


Fig. 4.58: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle



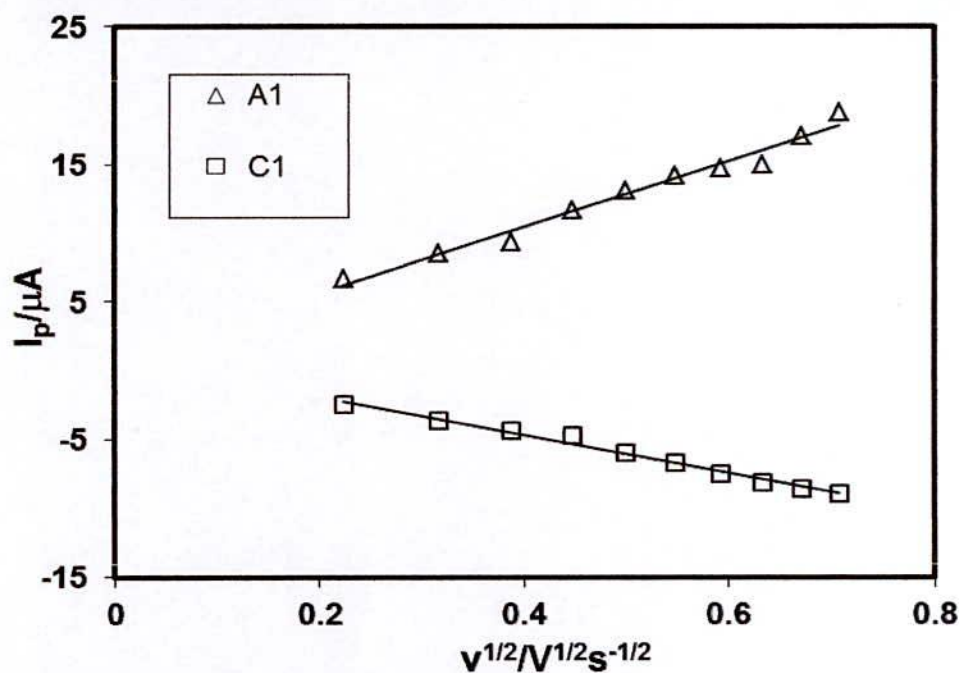


Fig. 4.59: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 9) at 1<sup>st</sup> cycle

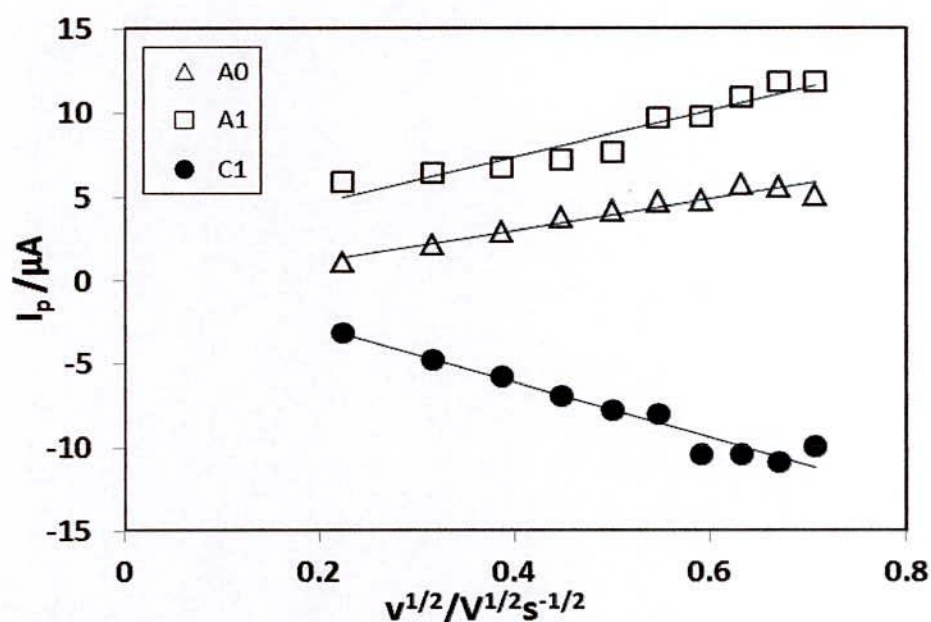


Fig. 4.60: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 9) at 2<sup>nd</sup> cycle

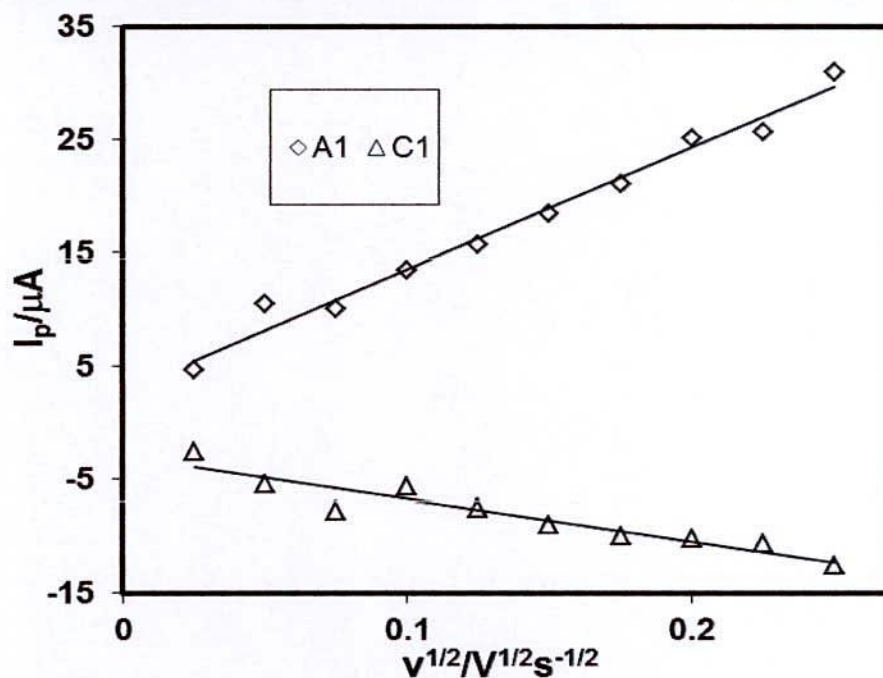


Fig. 4.61: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 11) at 1<sup>st</sup> cycle

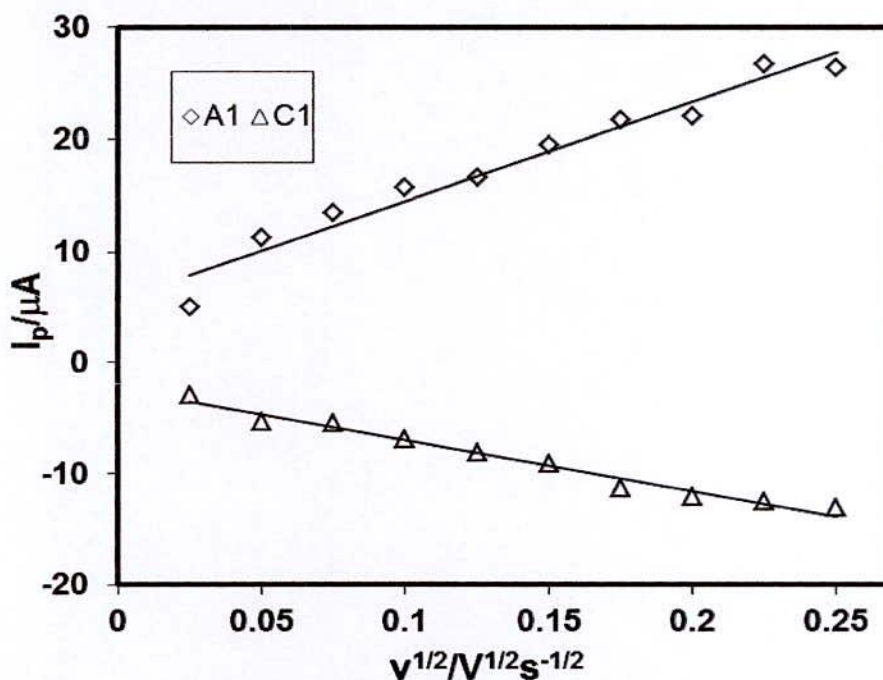


Fig. 4.62: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 11) at 2<sup>nd</sup> cycle



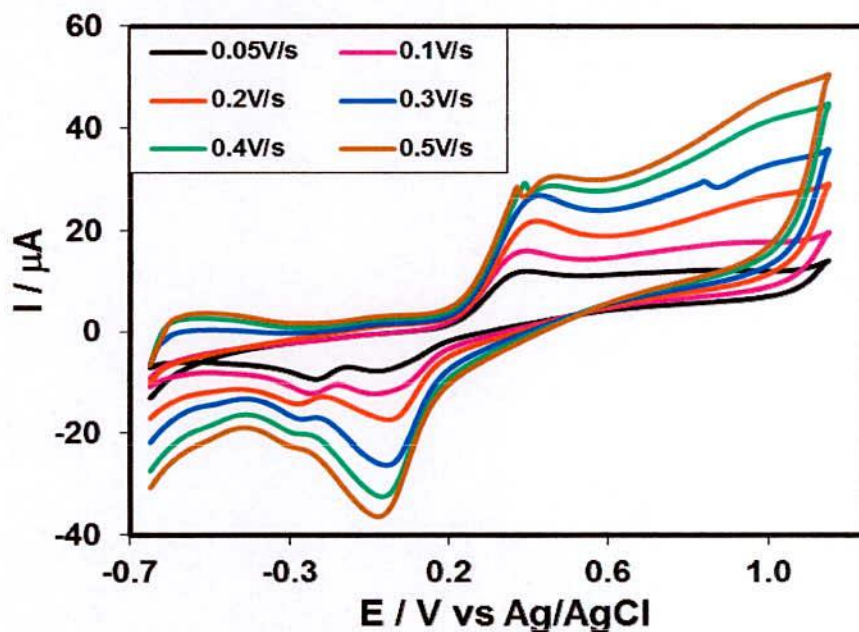


Fig. 4.63: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

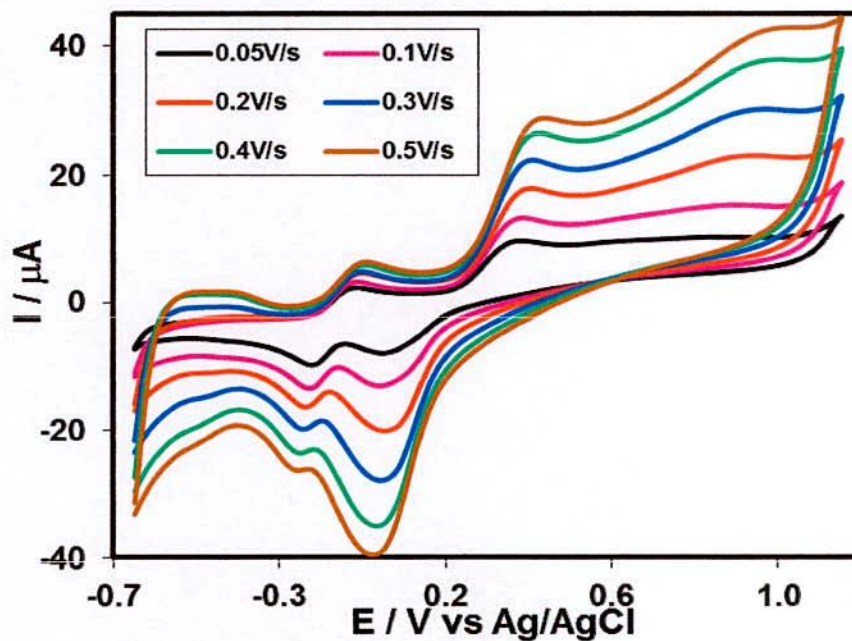


Fig. 4.64: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)

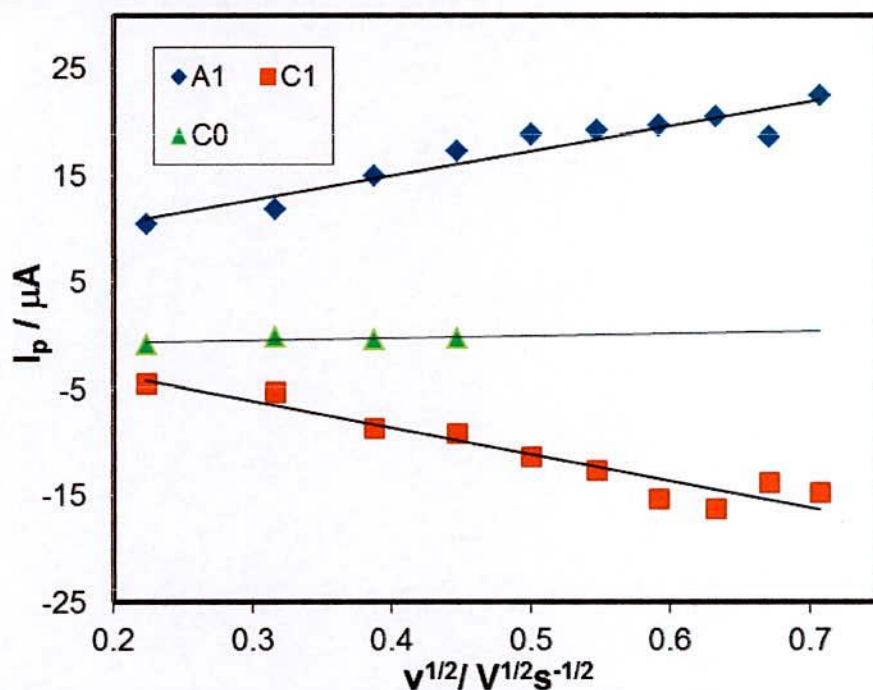


Fig. 4.65: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

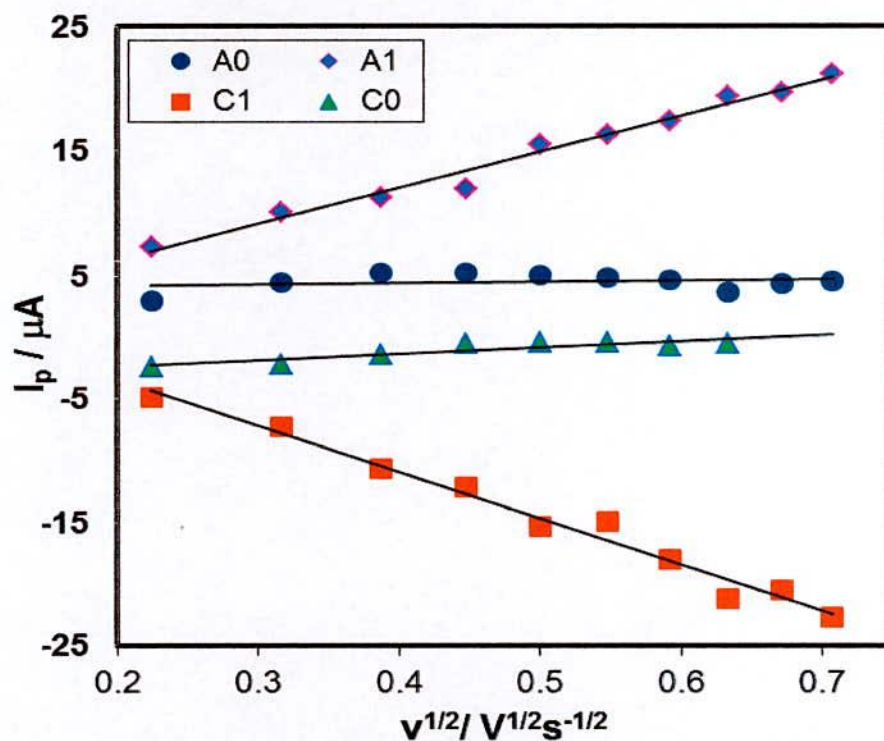


Fig. 4.66: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle



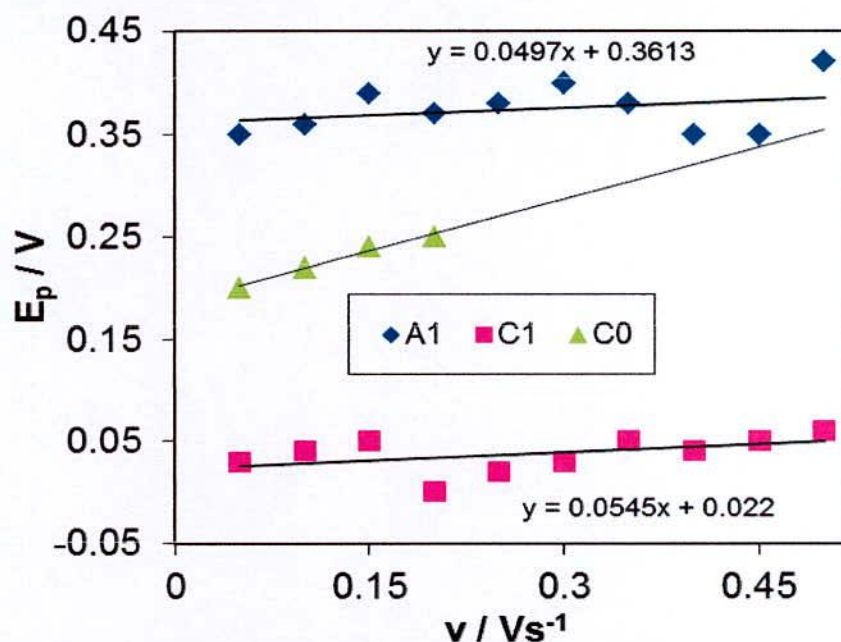


Fig. 4.67: Plots of peak potential ( $E_p$ ) versus different scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

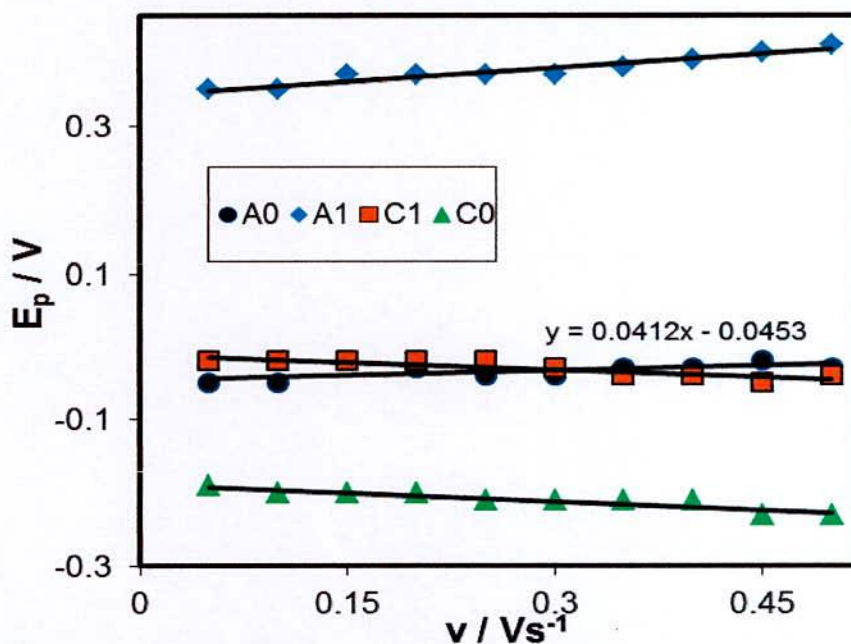


Fig. 4.68: Plots of peak potential ( $E_p$ ) versus different scan rate ( $v$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle

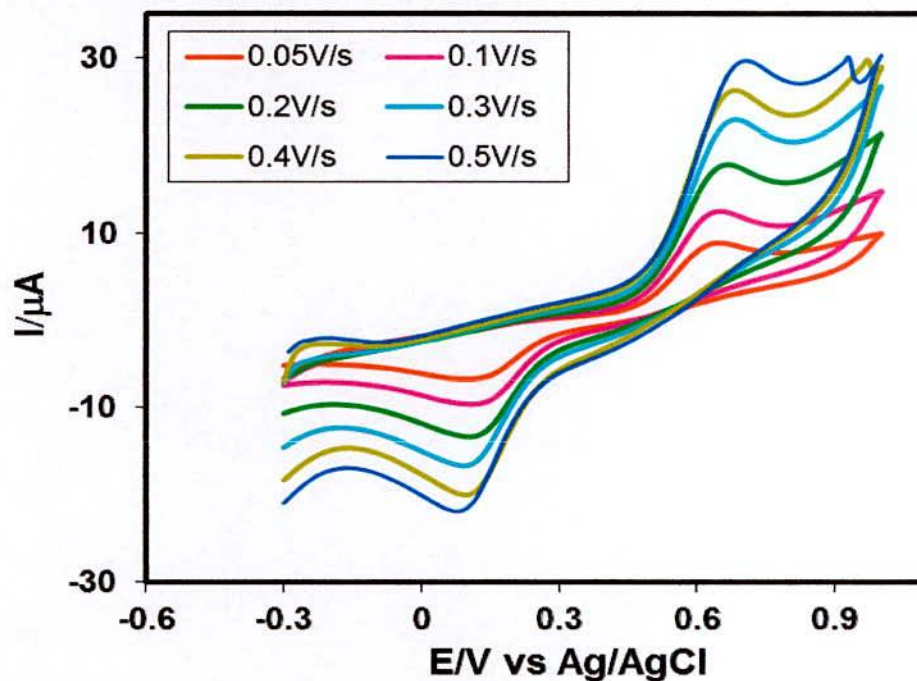


Fig. 4.69: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 3) at different scan rate (1<sup>st</sup> cycle)

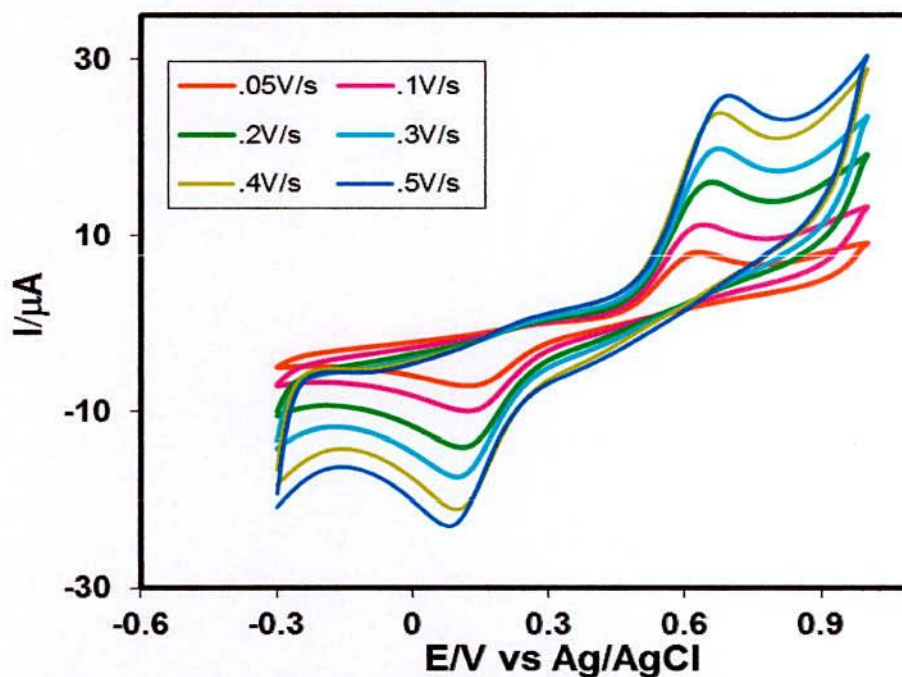


Fig. 4.70: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 3) at different scan rate (2<sup>nd</sup> cycle)



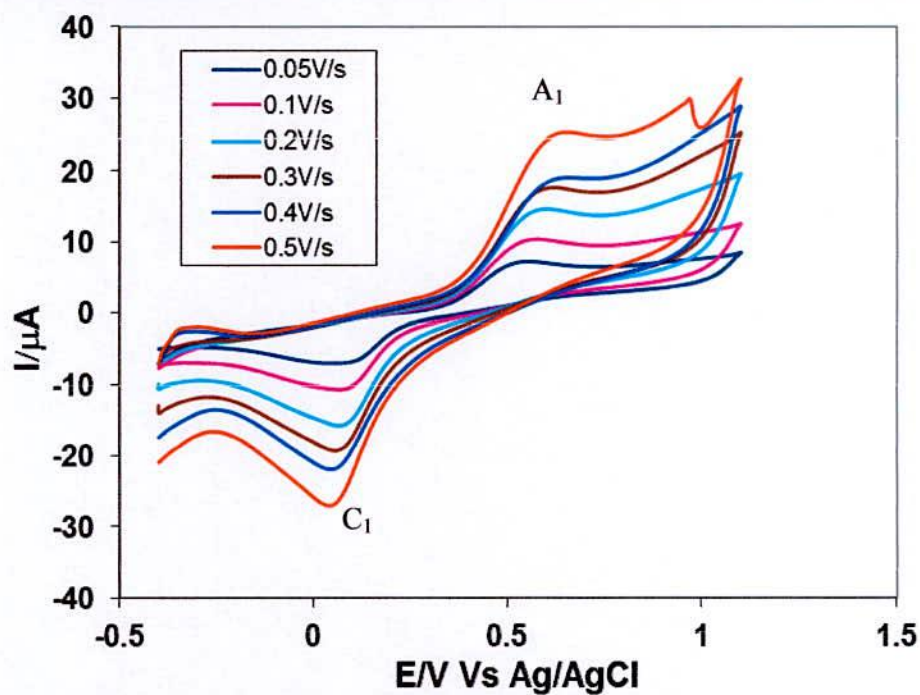


Fig. 4.71: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 5) at different scan rate (1<sup>st</sup> cycle)

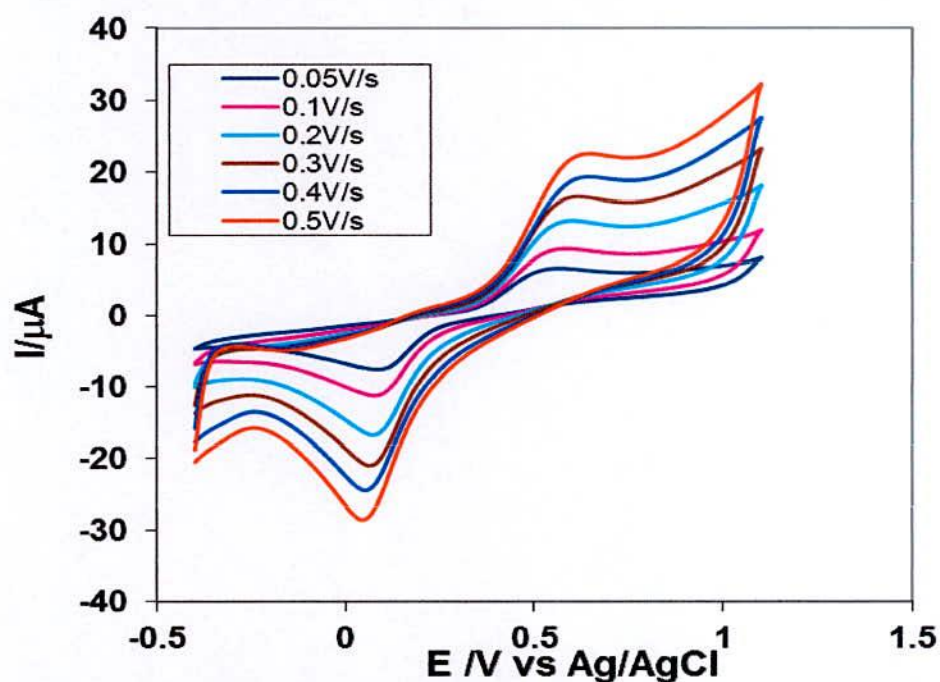


Fig. 4.72: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 5) at different scan rate (2<sup>nd</sup> cycle)

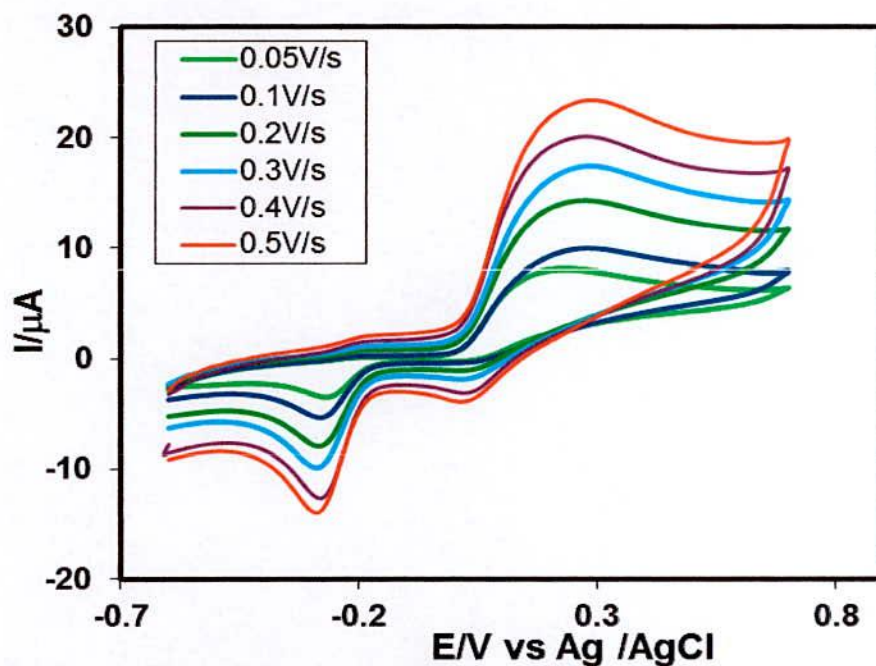


Fig. 4.73: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 9) at different scan rate (1<sup>st</sup> cycle)

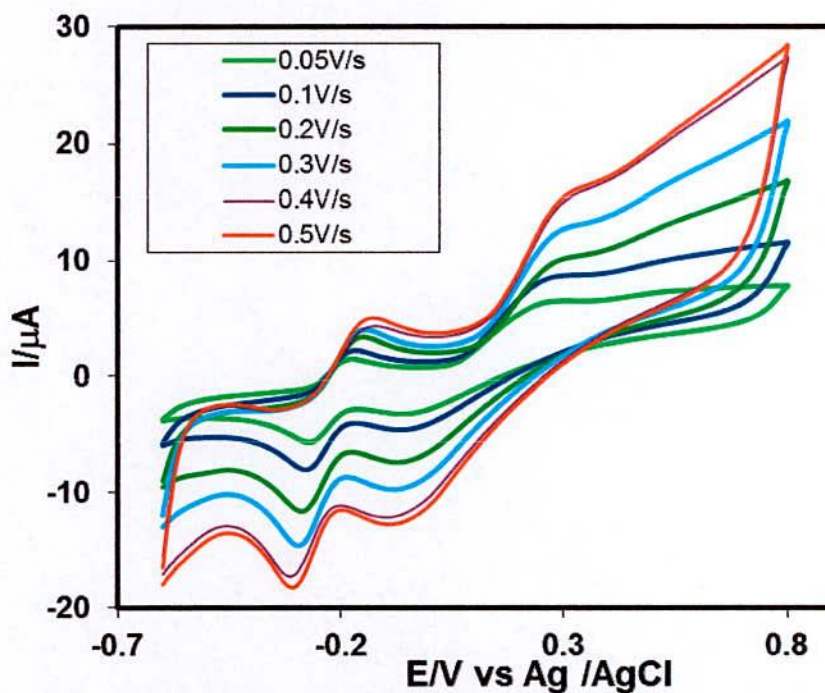


Fig. 4.74: Cyclic voltammogram of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 9) at different scan rate (2<sup>nd</sup> cycle)



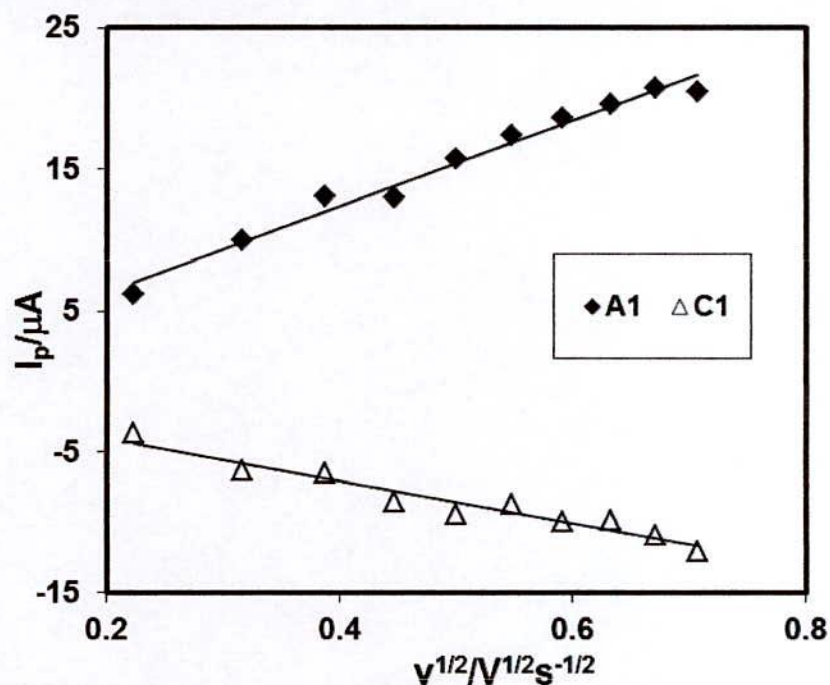


Fig. 4.75: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 3) at 1<sup>st</sup> cycle

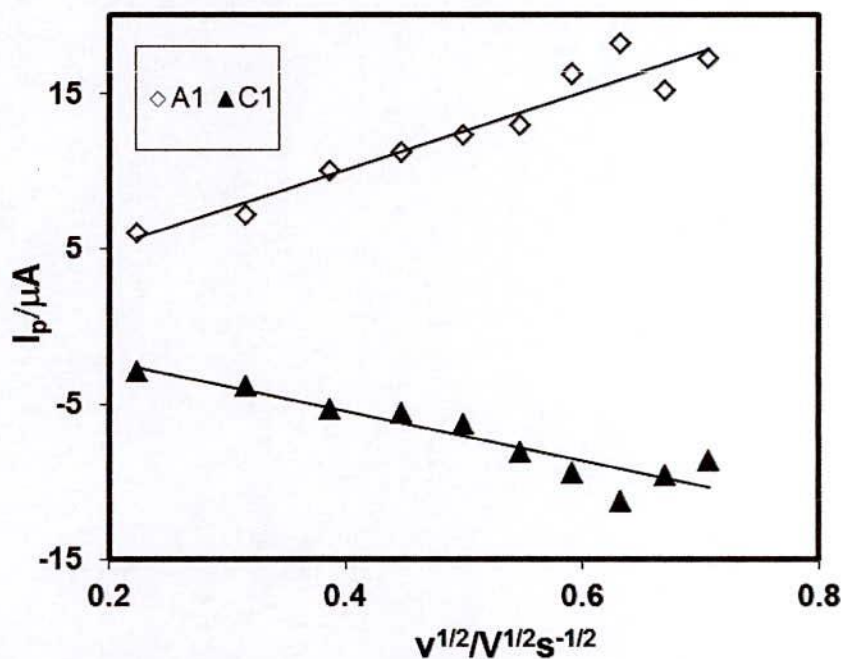


Fig. 4.76: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle

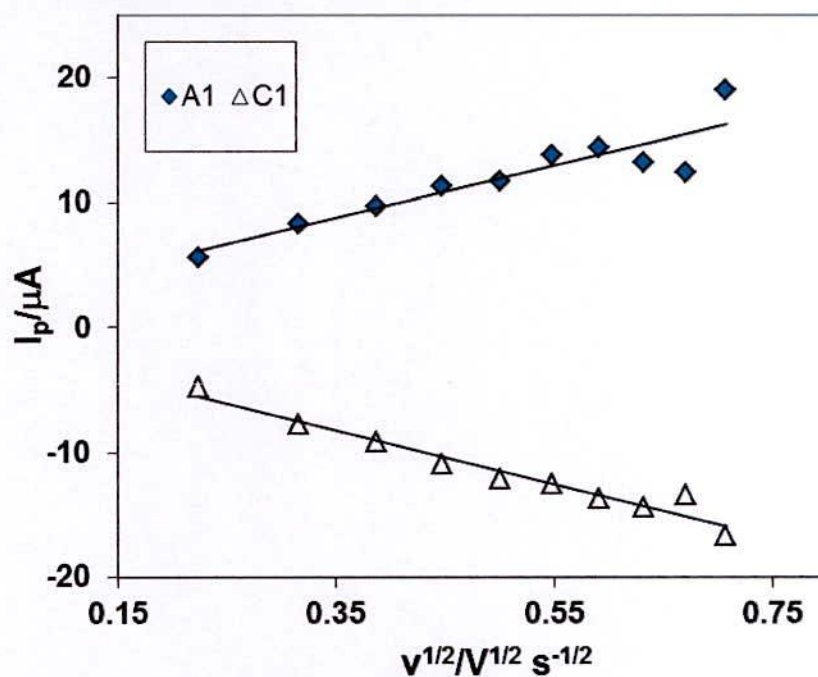


Fig. 4.77: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 5) at 1<sup>st</sup> cycle

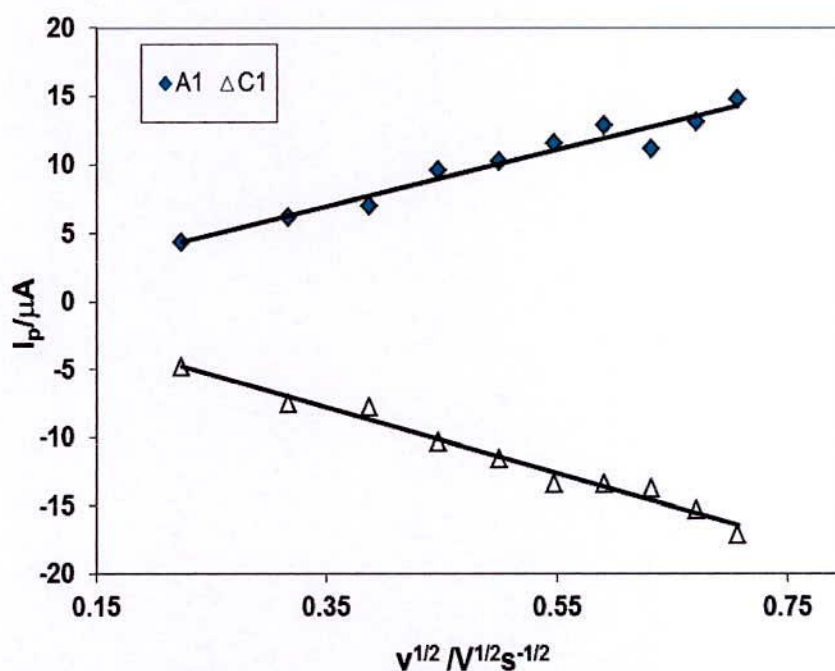


Fig. 4.78: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 5) at 2<sup>nd</sup> cycle



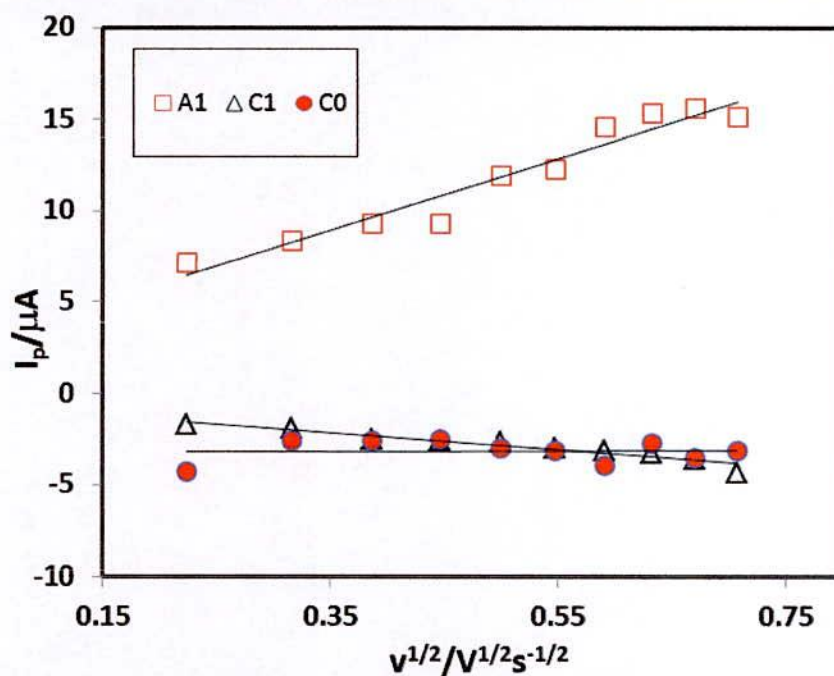


Fig. 4.79: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 9) at 1<sup>st</sup> cycle

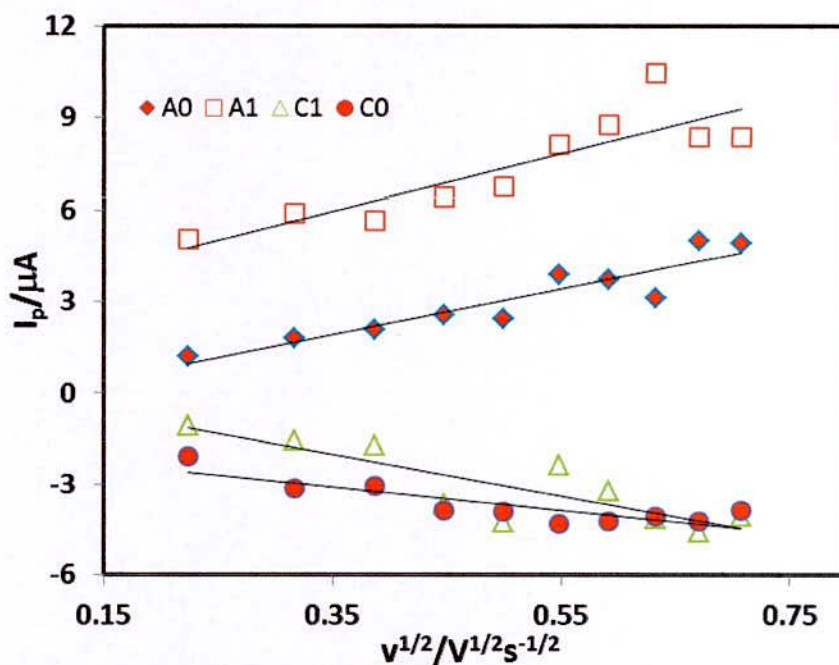


Fig. 4.80: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 9) at 2<sup>nd</sup> cycle

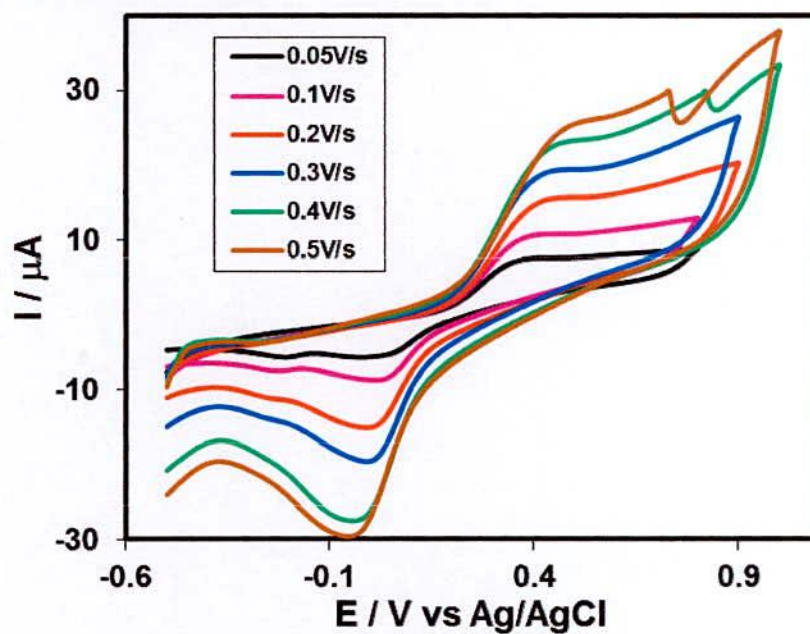


Fig. 4.81: Cyclic voltammogram of 150mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

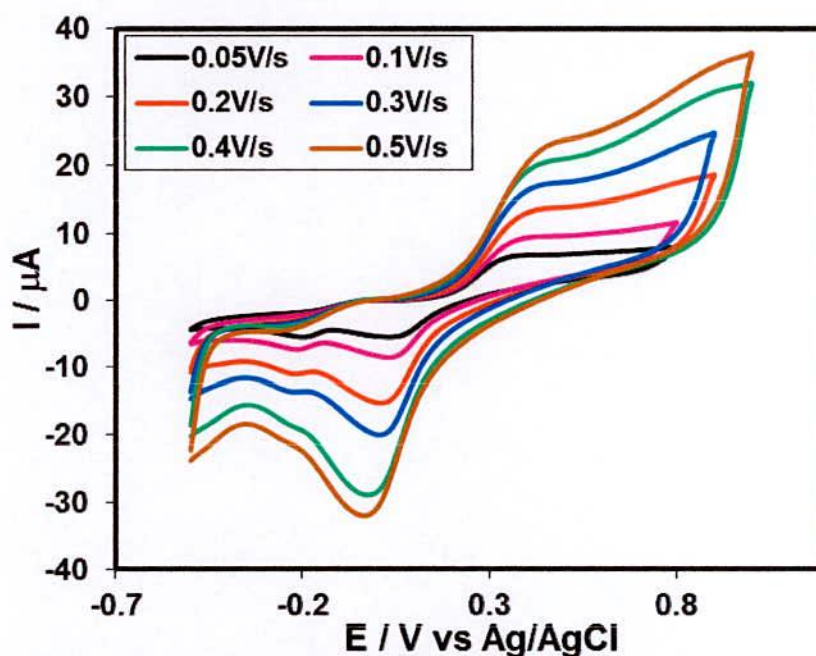


Fig. 4.82: Cyclic voltammogram of 150mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)



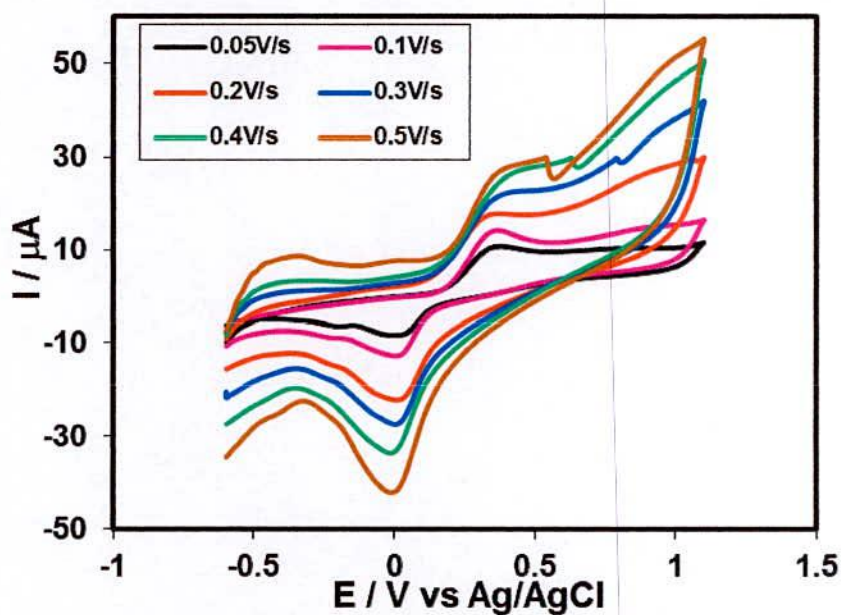


Fig. 4.83: Cyclic voltammogram of 200mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

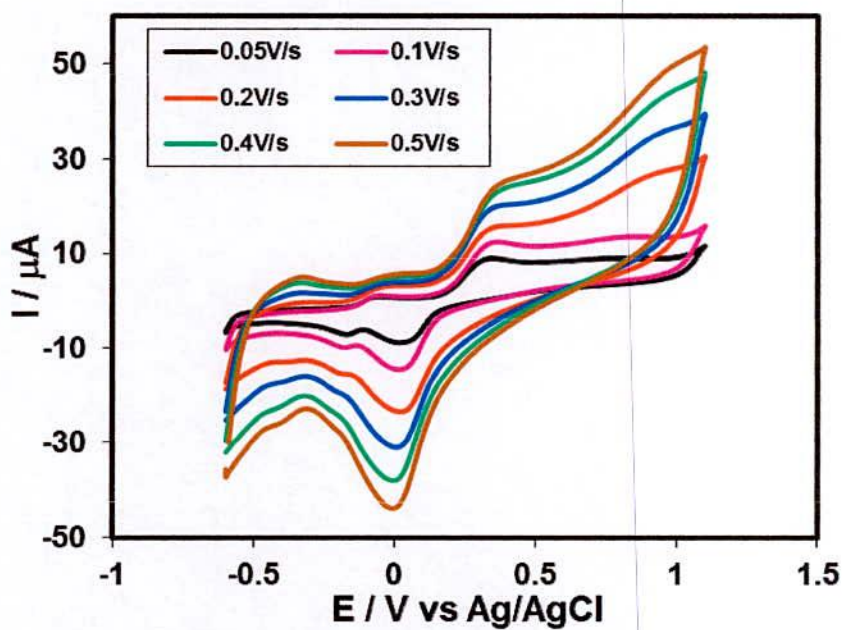


Fig. 4.84: Cyclic voltammogram of 200mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)

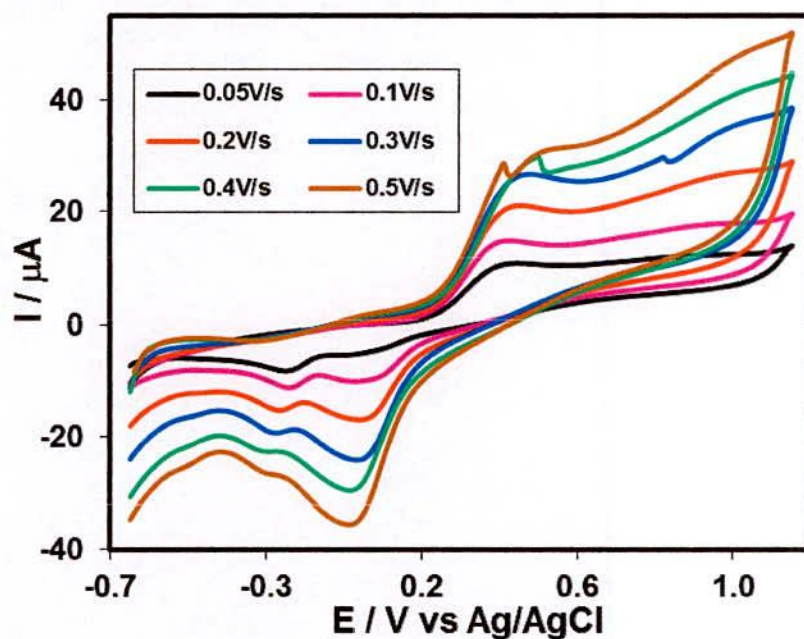


Fig. 4.85: Cyclic voltammogram of 300mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

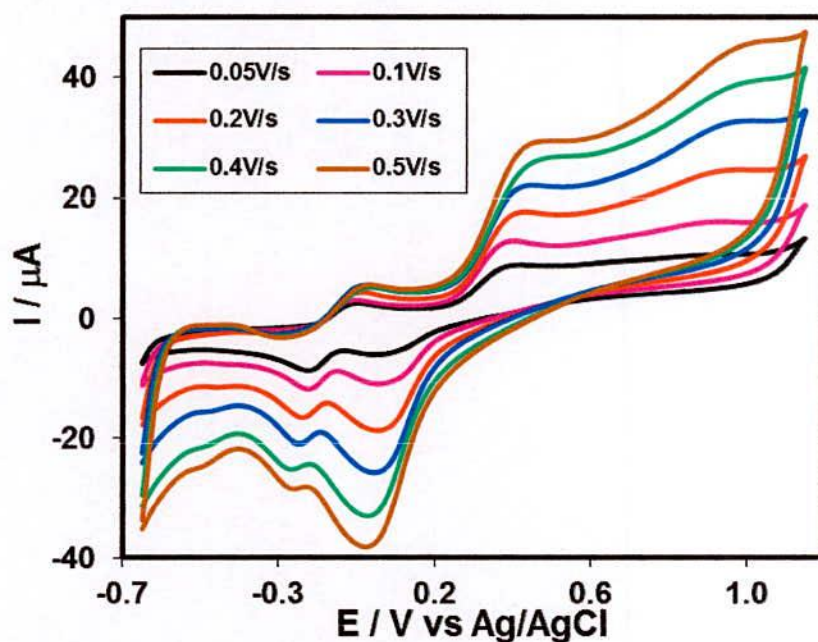


Fig. 4.86: Cyclic voltammogram of 300mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)



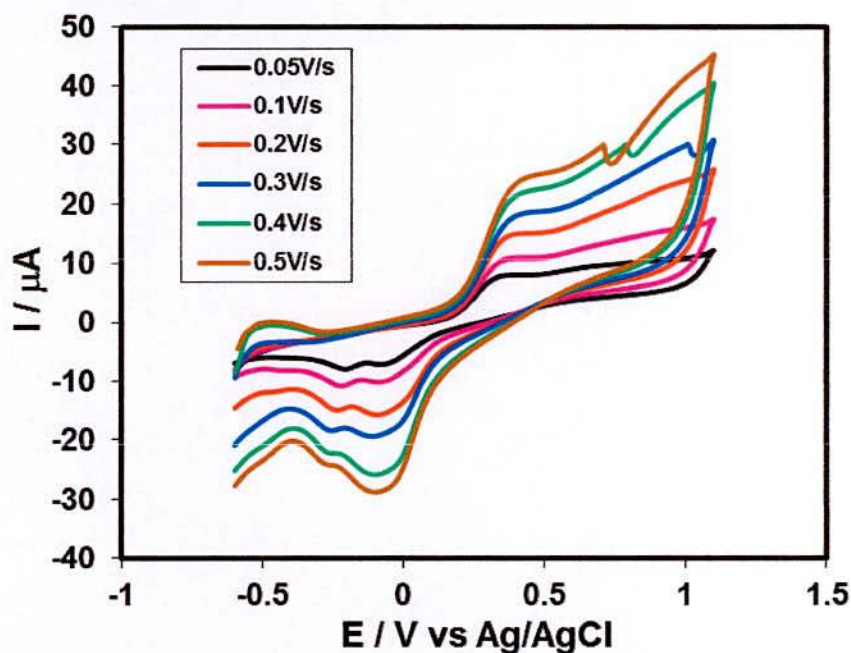


Fig. 4.87: Cyclic voltammogram of 350mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (1<sup>st</sup> cycle)

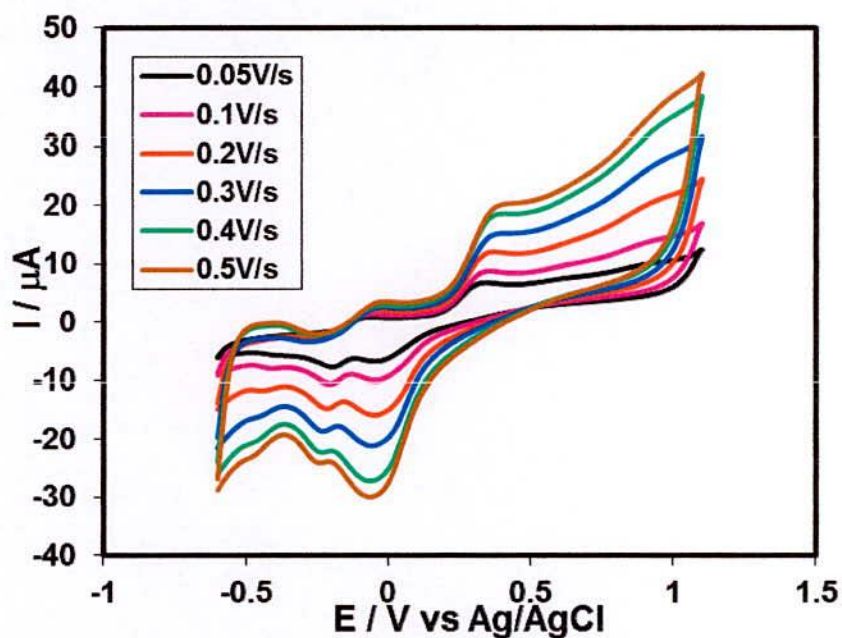


Fig. 4.88: Cyclic voltammogram of 350mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at different scan rate (2<sup>nd</sup> cycle)

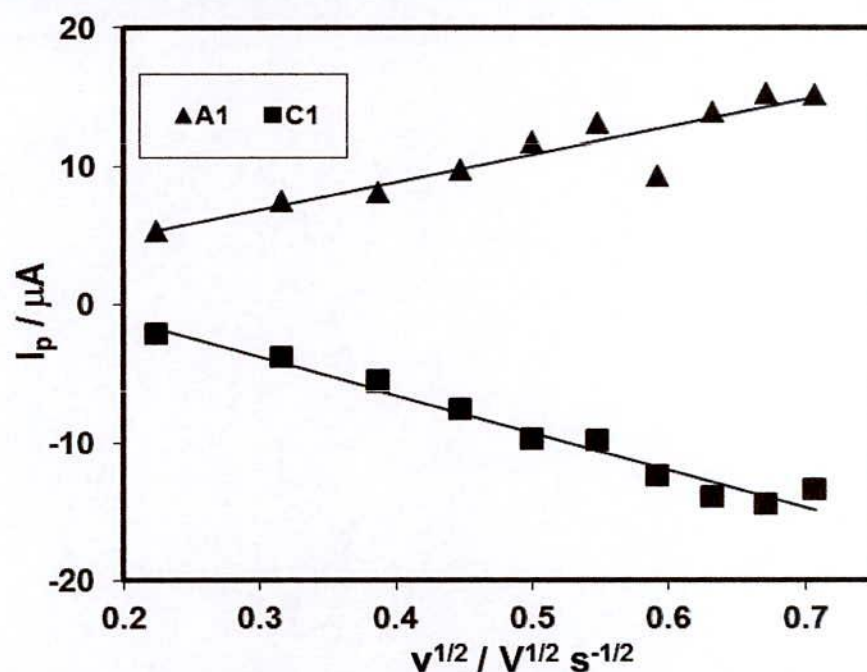


Fig. 4.89: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

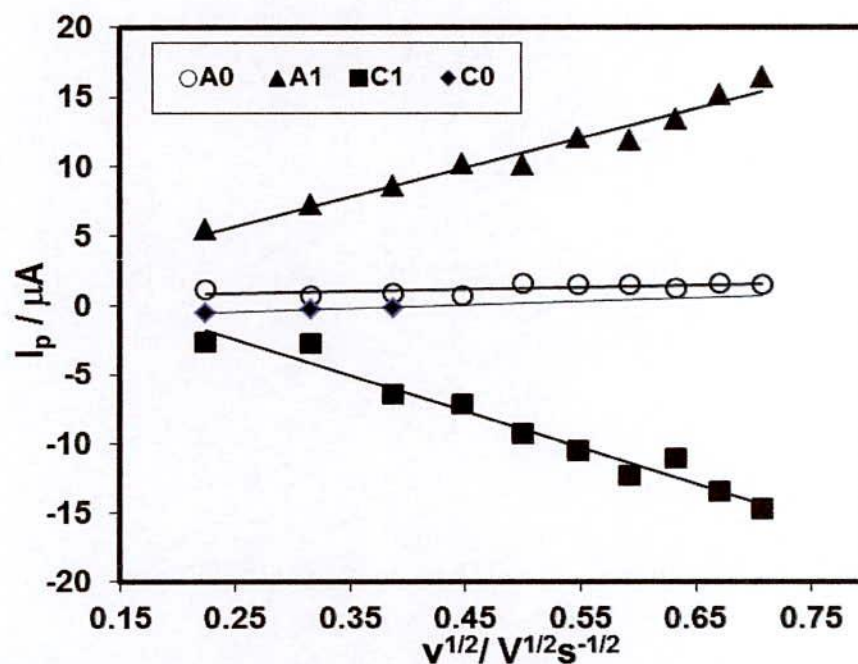


Fig. 4.90: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 150mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle



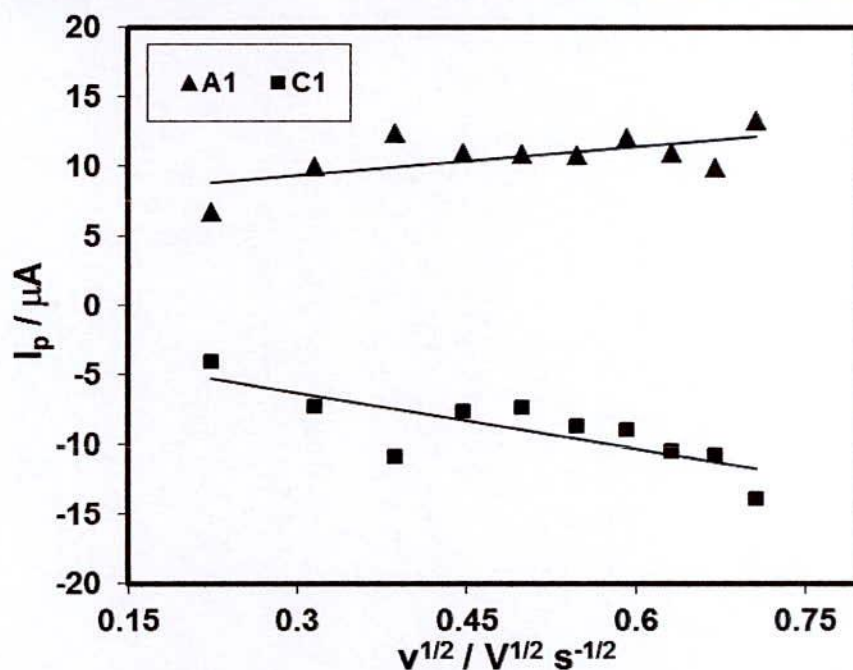


Fig. 4.91: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

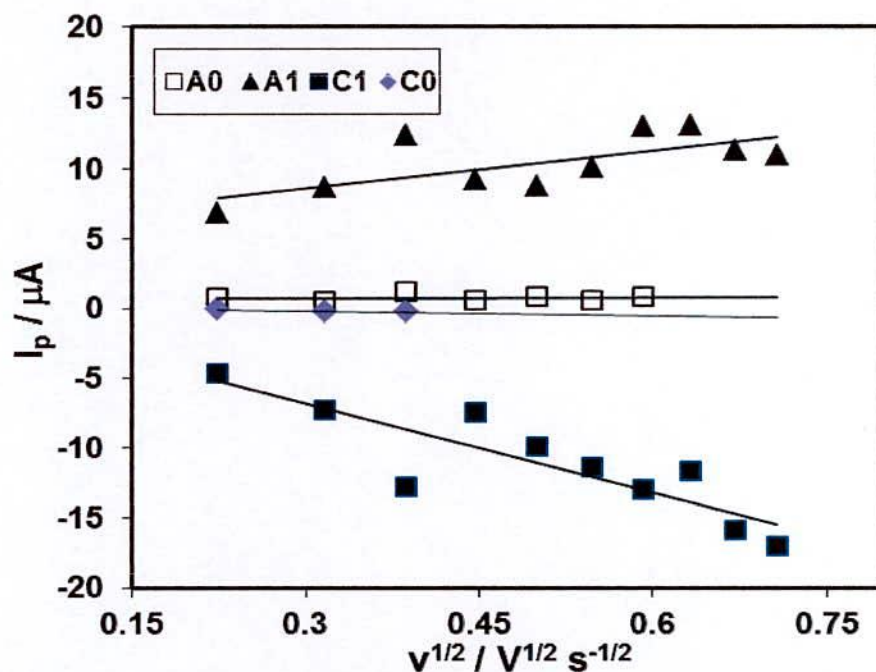


Fig. 4.92: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 200mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle

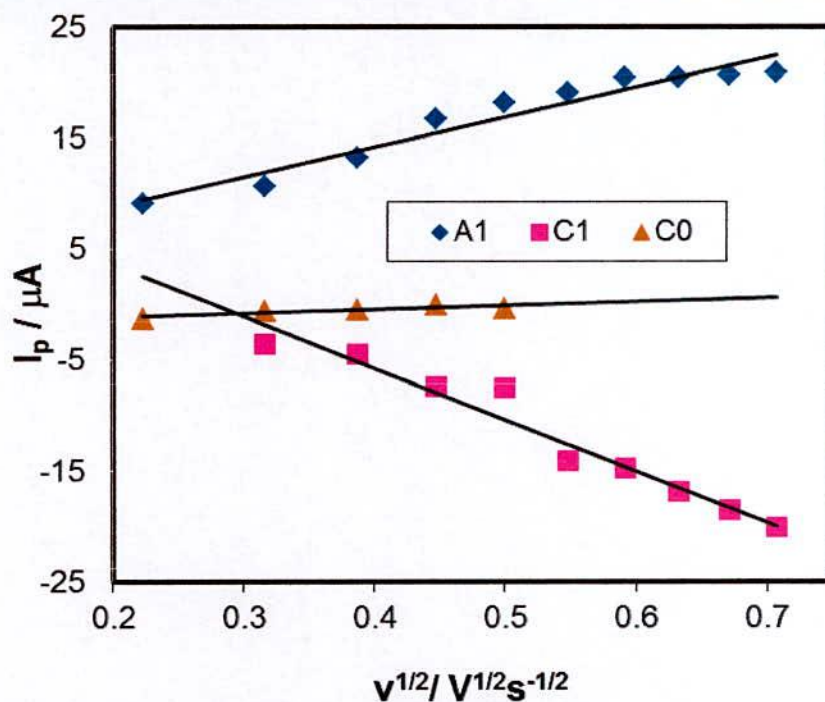


Fig. 4.93: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

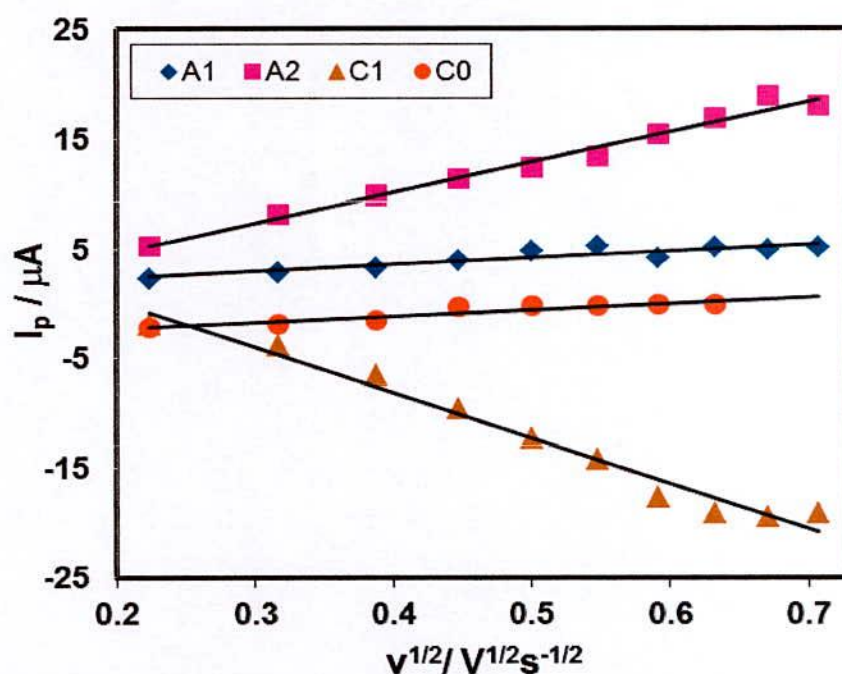


Fig. 4.94: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 300mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle



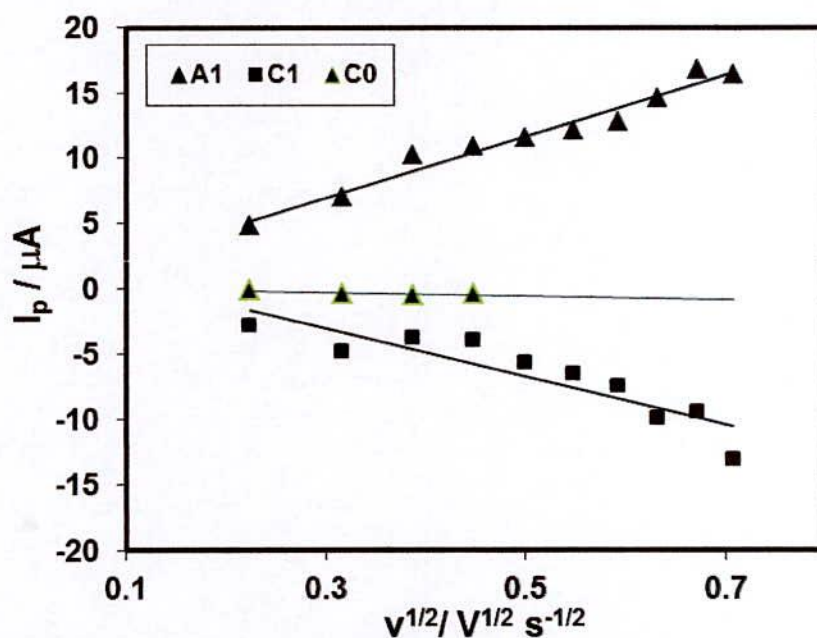


Fig. 4.95: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 350mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 1<sup>st</sup> cycle

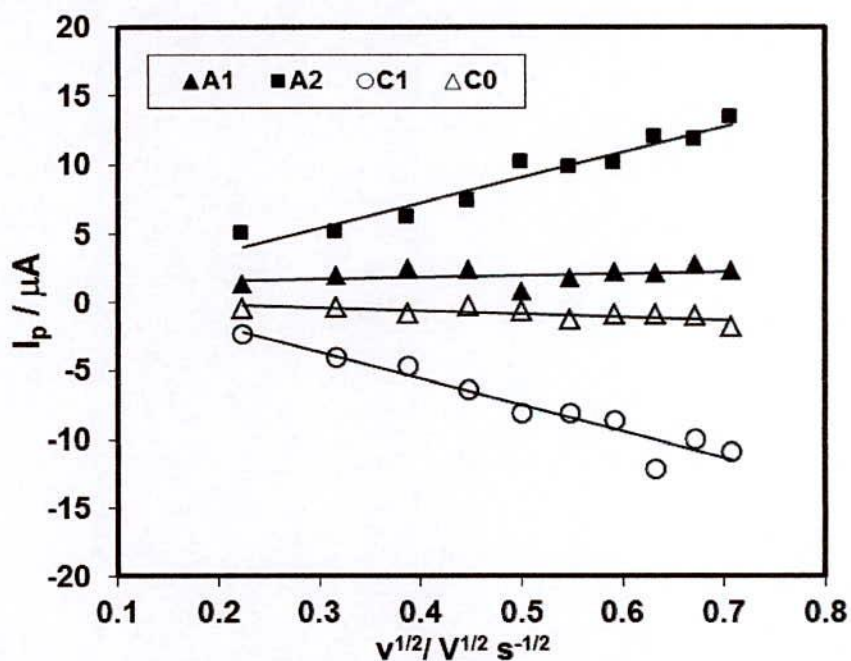


Fig. 4.96: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 350mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at 2<sup>nd</sup> cycle

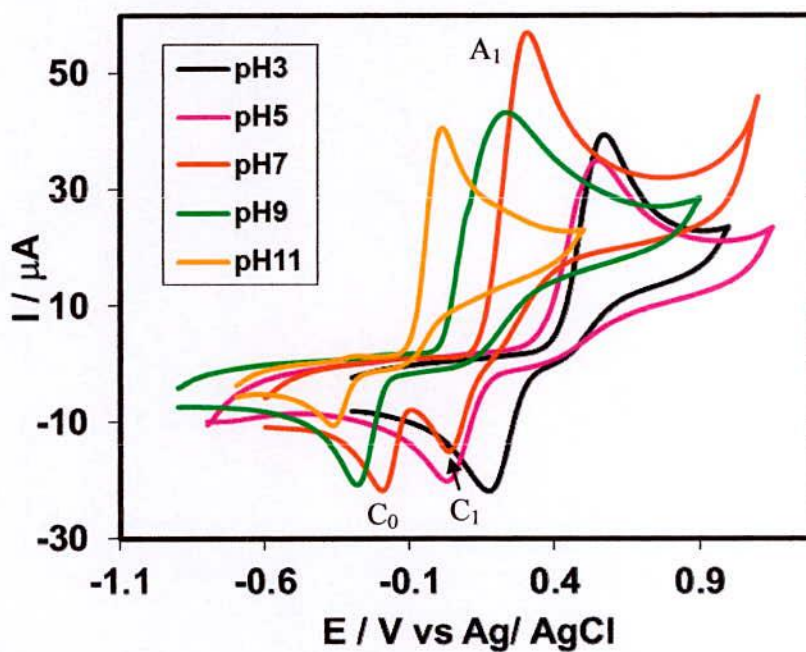


Fig. 4.97: Comparison of cyclic voltammogram of different pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1<sup>st</sup> cycle)

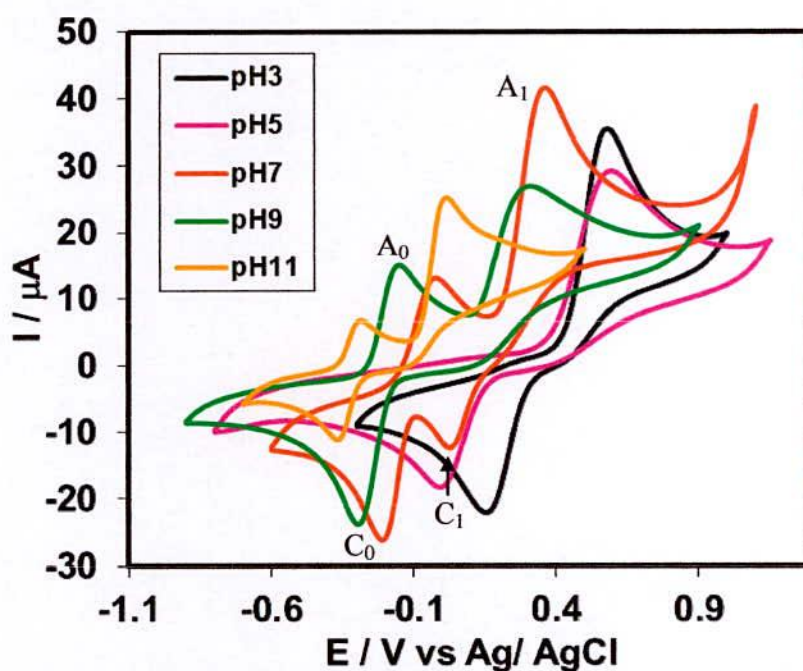


Fig. 4.98: Comparison of cyclic voltammogram of different pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)



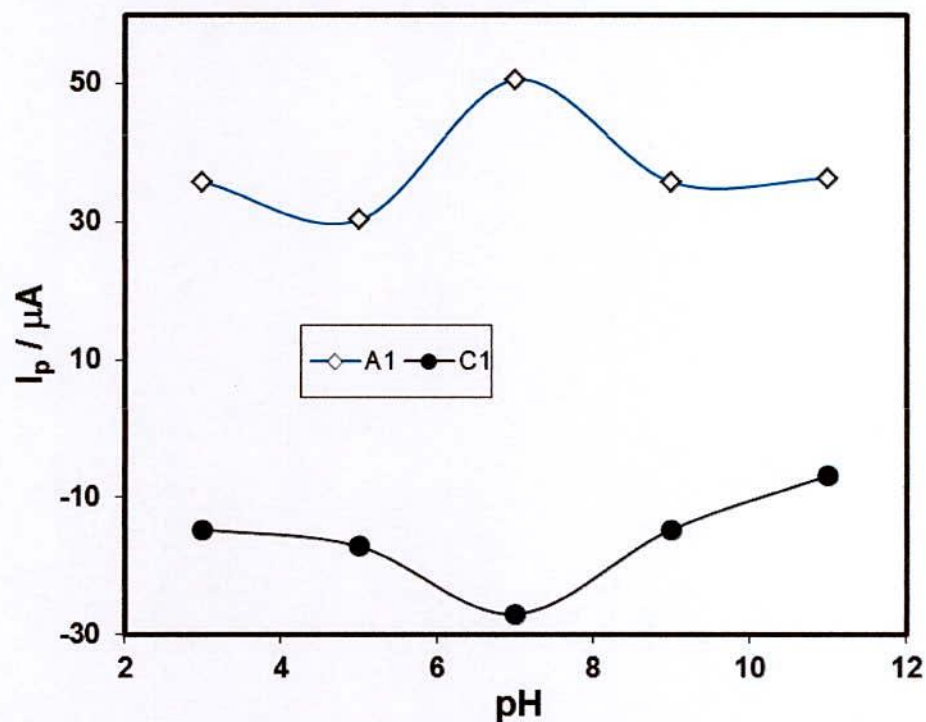


Fig. 4.99: Plots of peak current ( $I_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1<sup>st</sup> cycle)

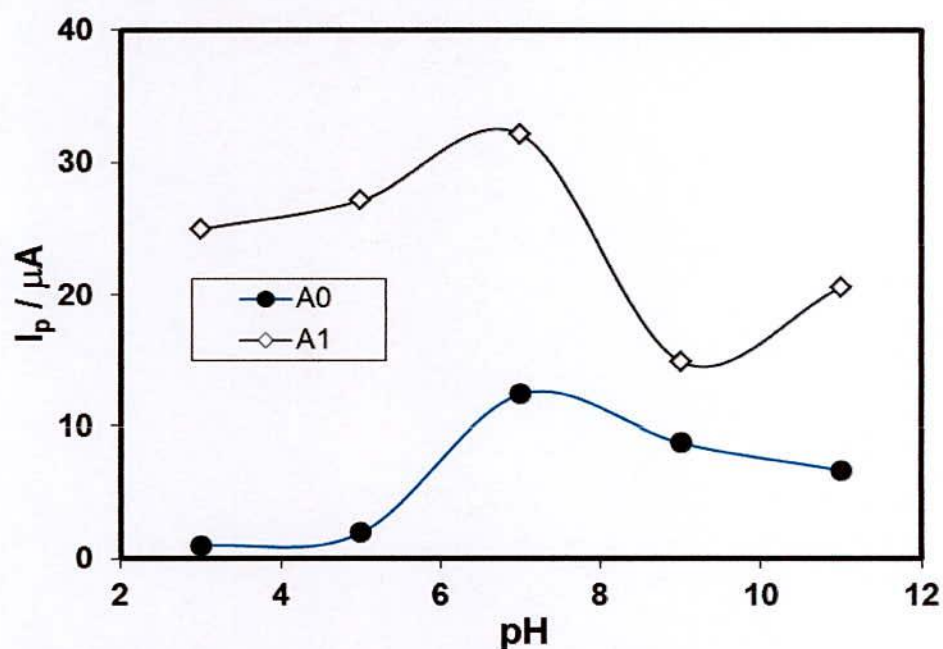


Fig. 4.100: Plots of peak current ( $I_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

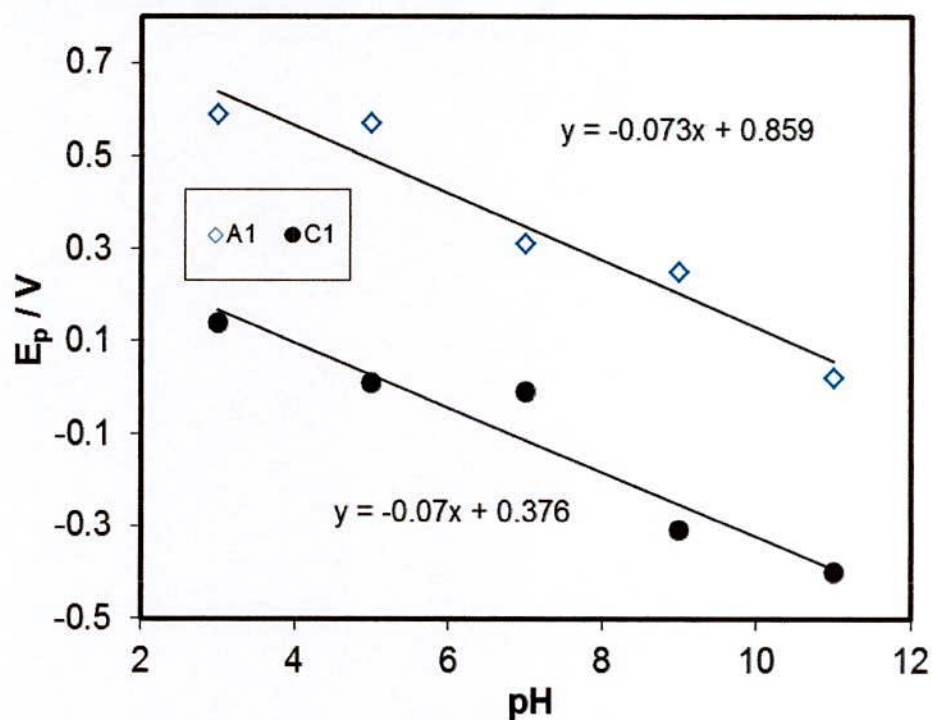


Fig. 4.101: Plots of peak potential ( $E_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1<sup>st</sup> cycle)

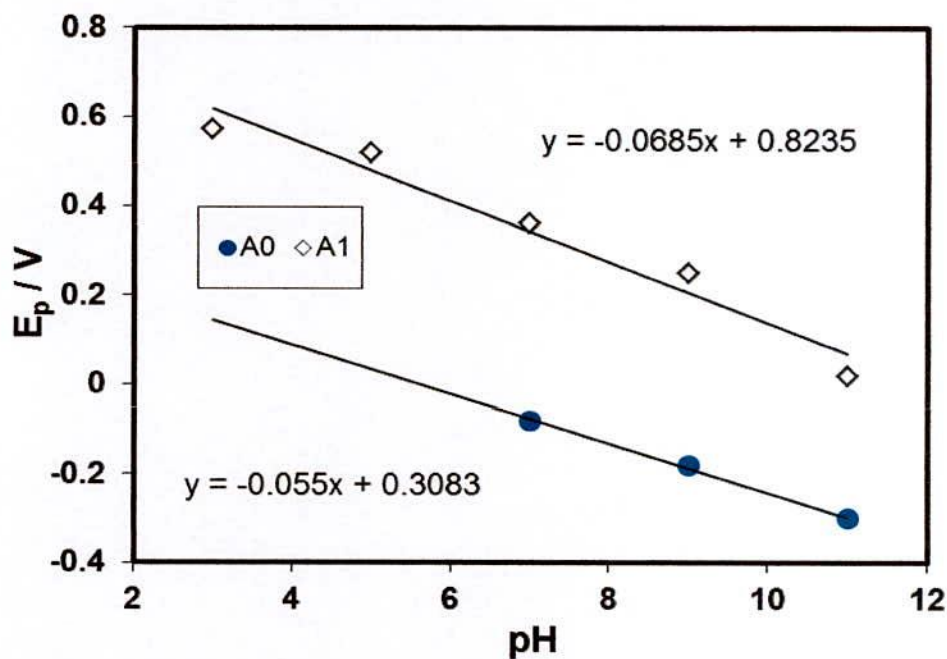


Fig. 4.102: Plots of peak potential ( $E_p$ ) versus pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)



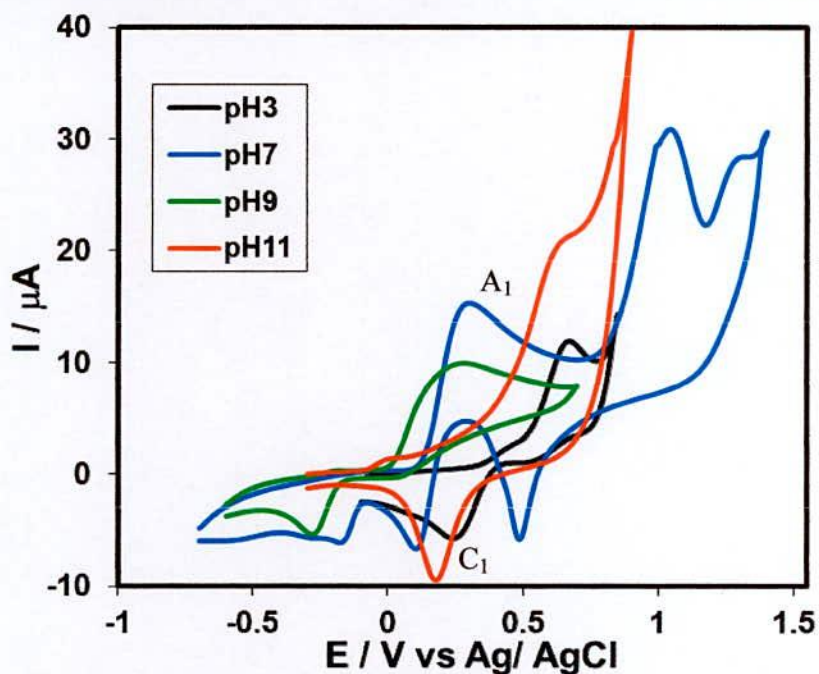


Fig. 4.103: Comparison of cyclic voltammogram of different pH (3, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1 V/s (1<sup>st</sup> cycle)

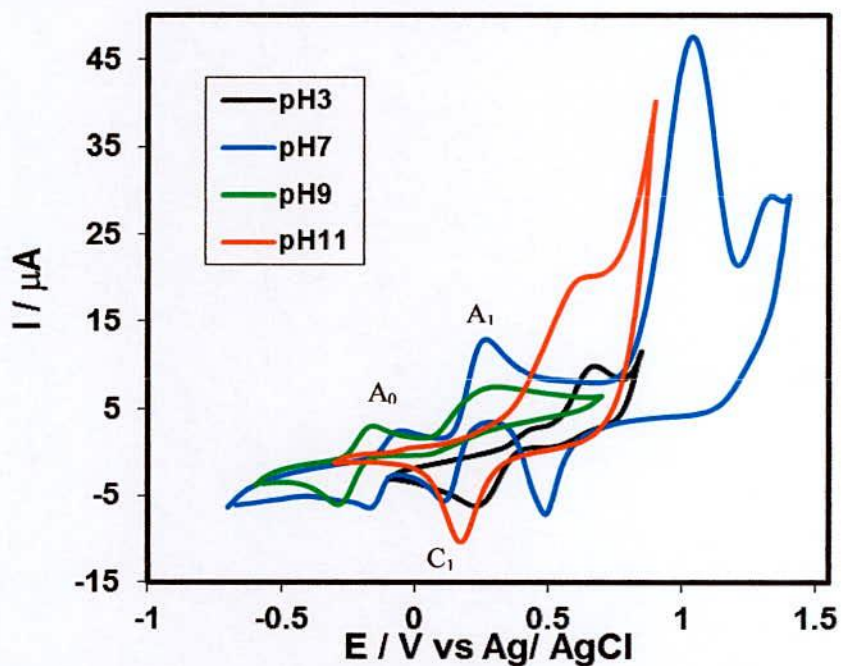


Fig. 4.104: Comparison of cyclic voltammogram of different pH (3, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1 V/s (2<sup>nd</sup> cycle)

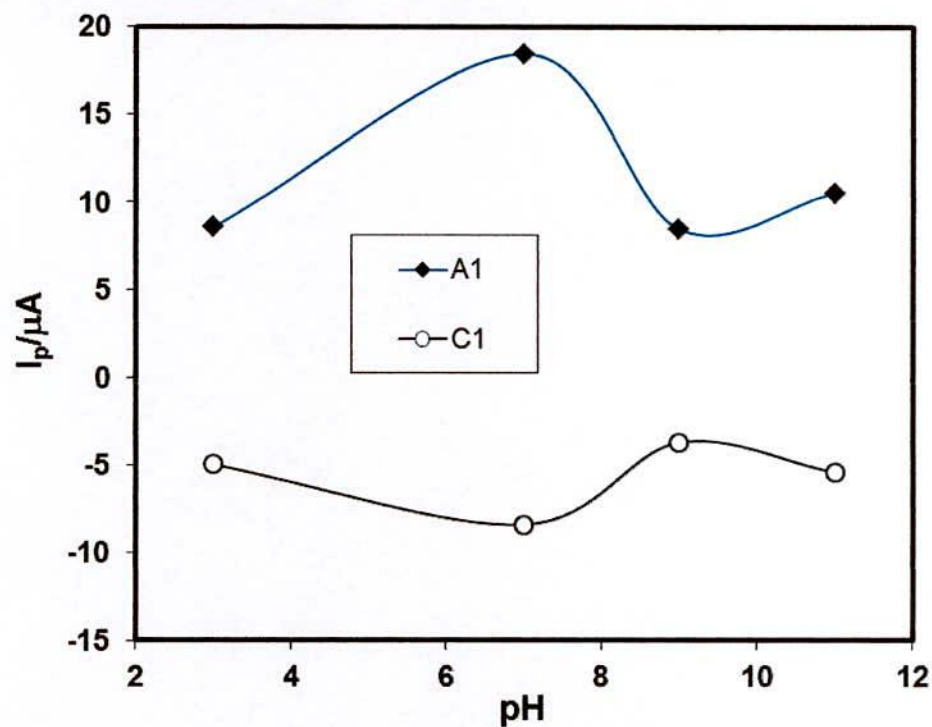


Fig. 4.105: Plots of peak current ( $I_p$ ) versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (1<sup>st</sup> cycle)

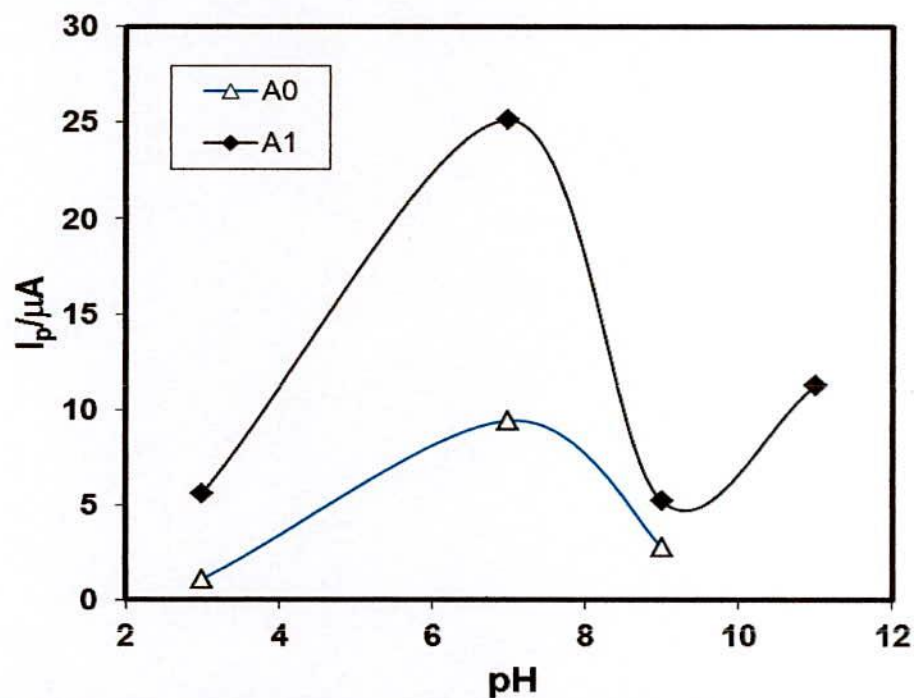


Fig. 4.106: Plots of peak ( $I_p$ ) current versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)



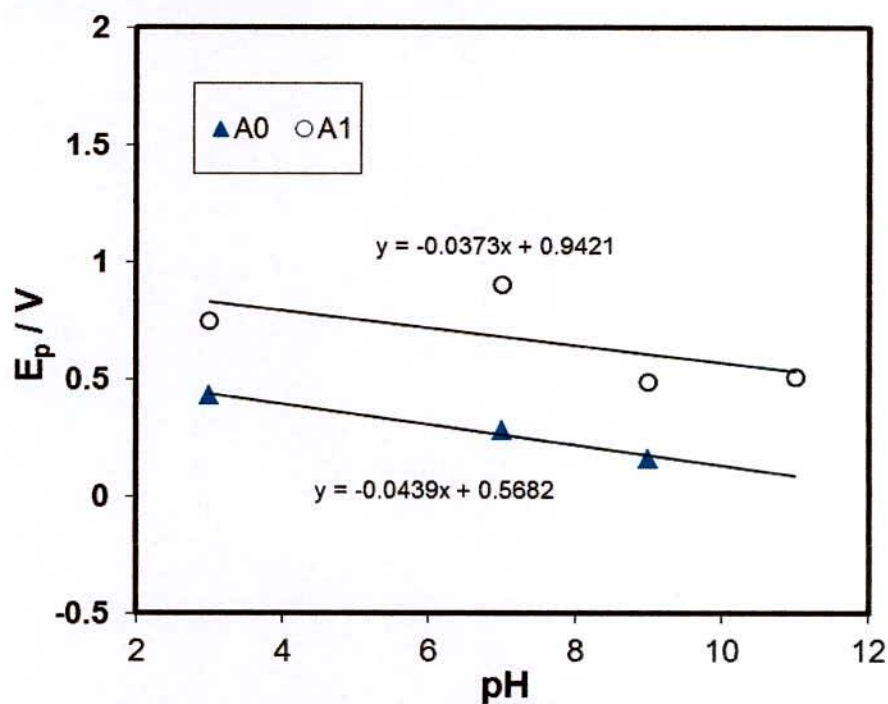


Fig. 4.107: Plots of peak potential ( $E_p$ ) versus pH of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1 V/s (2<sup>nd</sup> cycle)

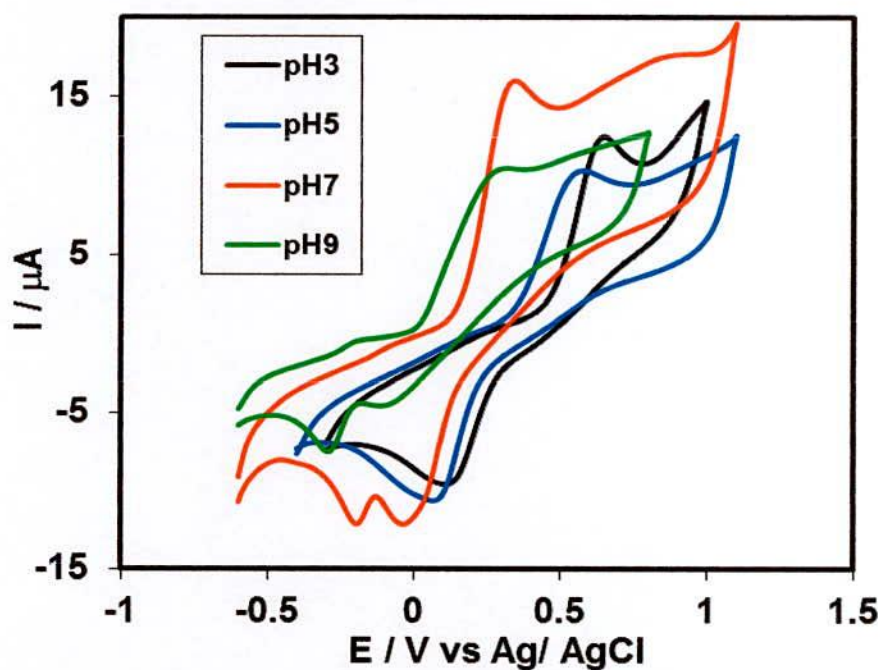


Fig. 4.108: Comparison of cyclic voltammogram of different pH (3, 5, 7 and 9) of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1 V/s (1<sup>st</sup> cycle)

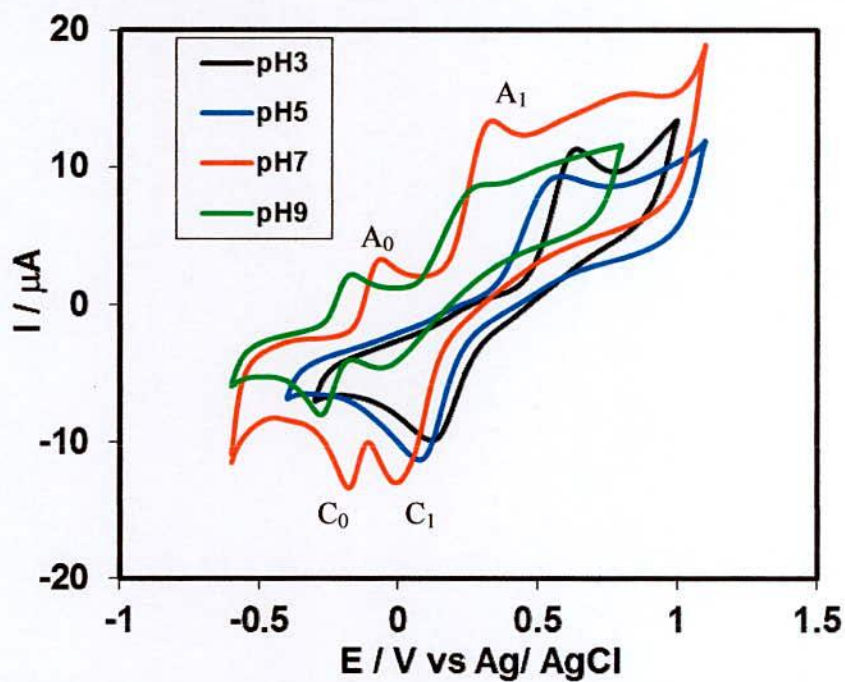


Fig. 4.109: Comparison of cyclic voltammogram of different pH (3, 5, 7 and 9) of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1 V/s (2<sup>nd</sup> cycle)

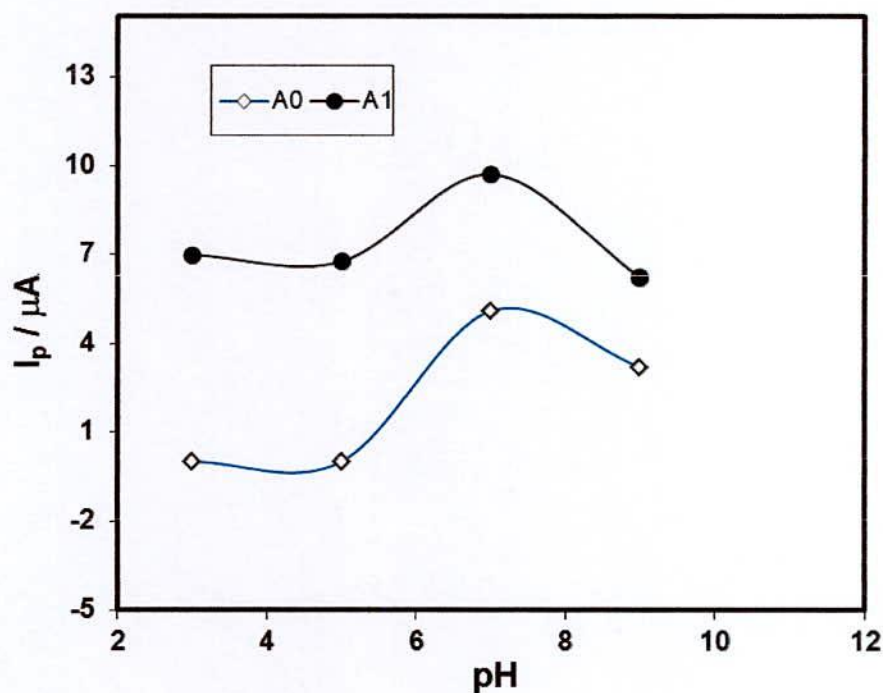


Fig. 4.110: Plots of peak ( $I_p$ ) current versus pH of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1 V/s (2<sup>nd</sup> cycle)



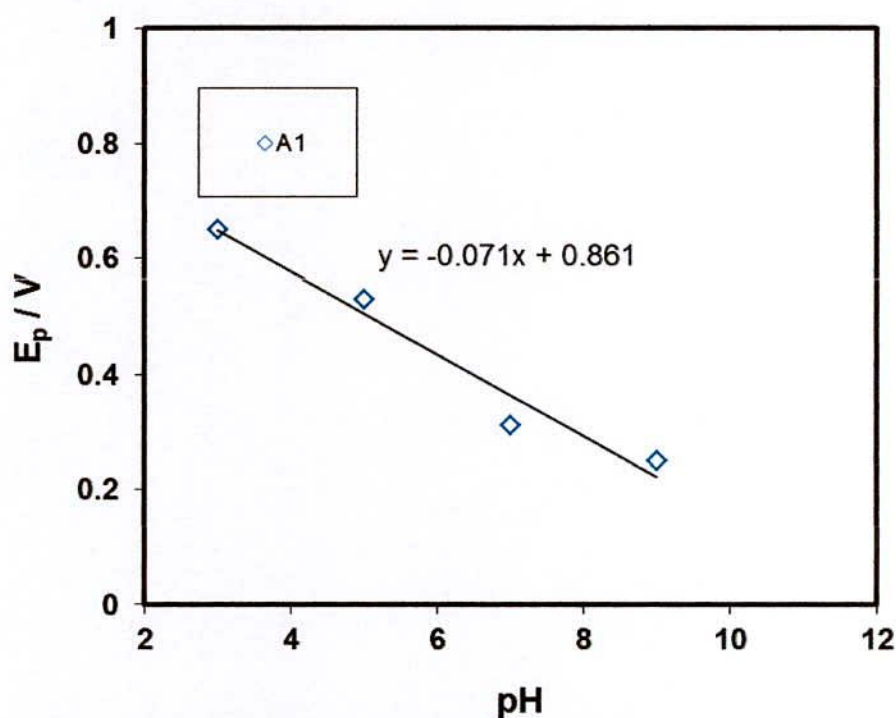


Fig. 4.111: Plots of peak potential ( $E_p$ ) versus pH of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

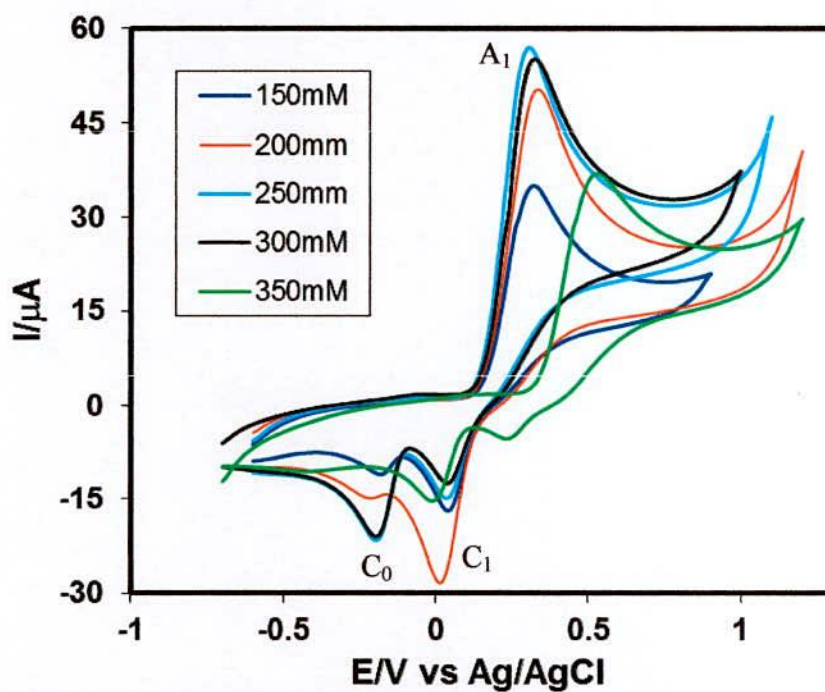


Fig. 4.112: Comparison of cyclic voltammogram of different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle)

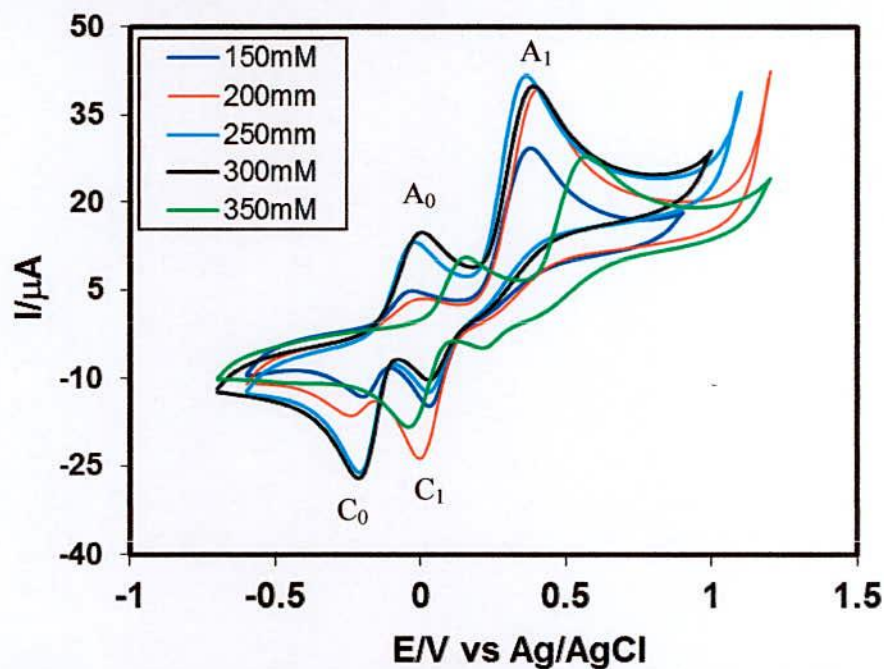


Fig. 4.113: Comparison of cyclic voltammogram of different concentration (100, 150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

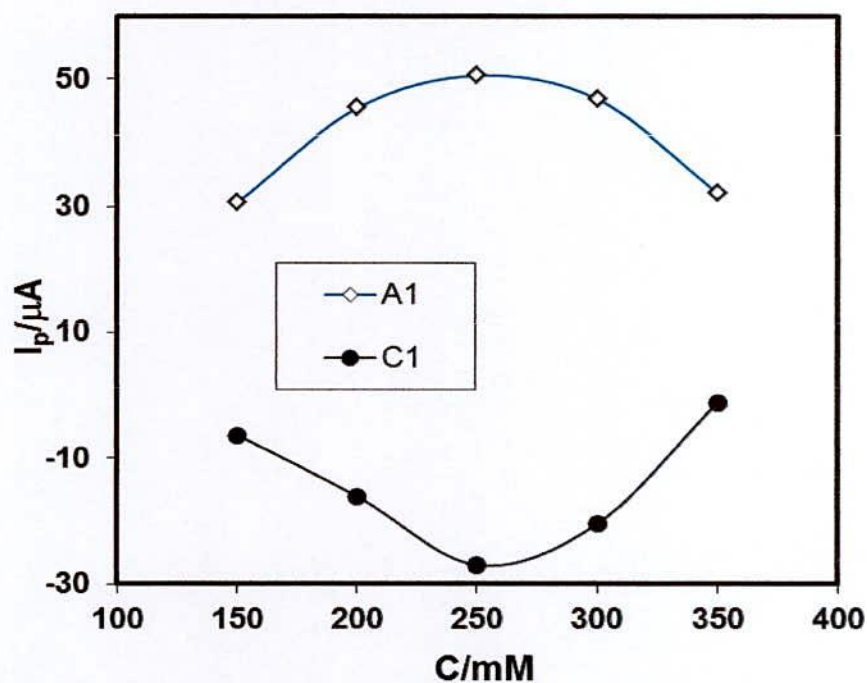


Fig. 4.114: Plots of peak current (I<sub>p</sub>) versus concentration (C) (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle)



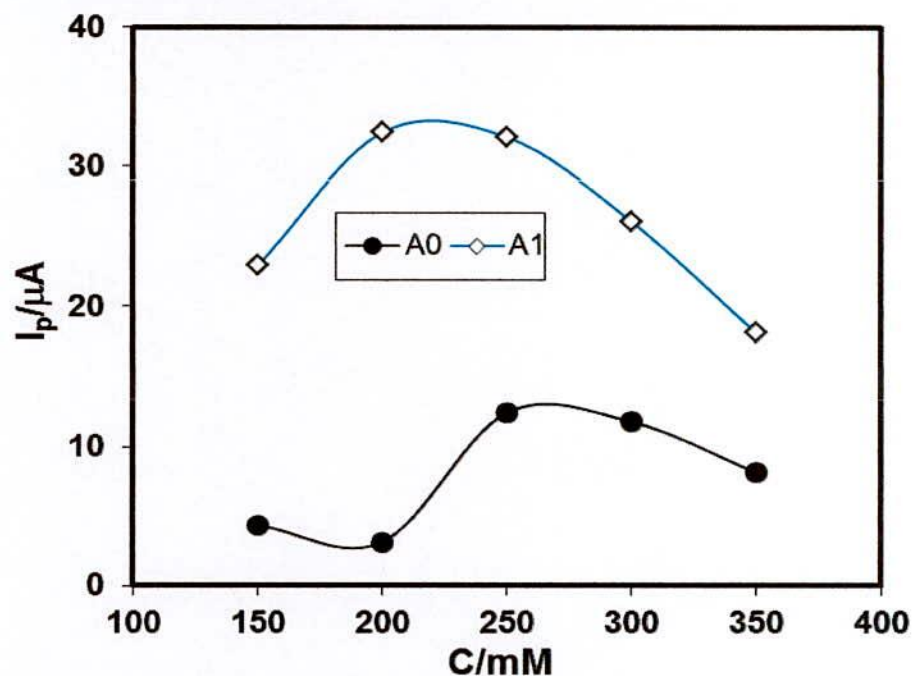


Fig. 4.115: Plots of peak current ( $I_p$ ) versus different concentration ( $C$ ) (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

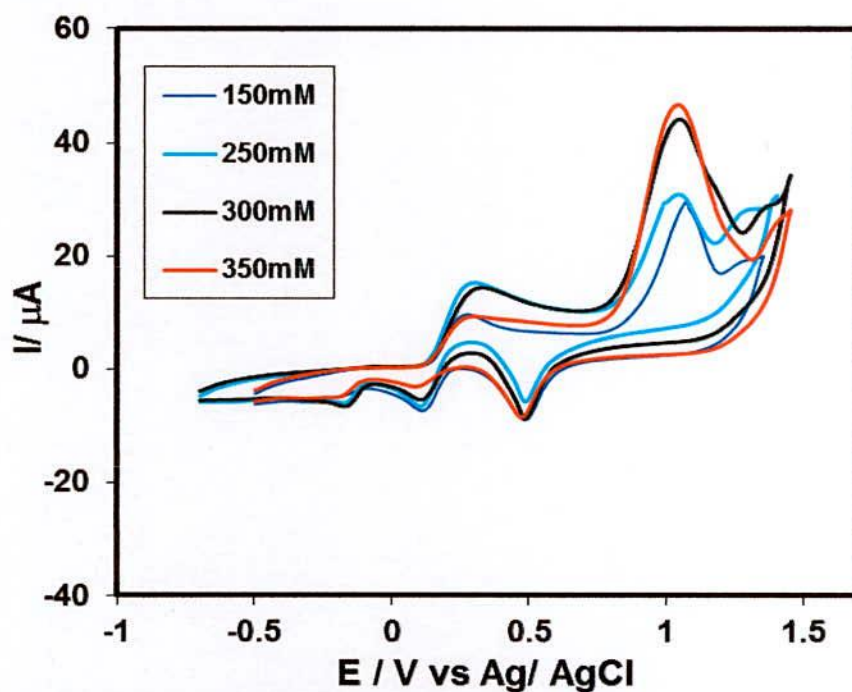


Fig. 4.116: Comparison of CV of different concentration (150, 250, 300 and 350mM) of diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle)

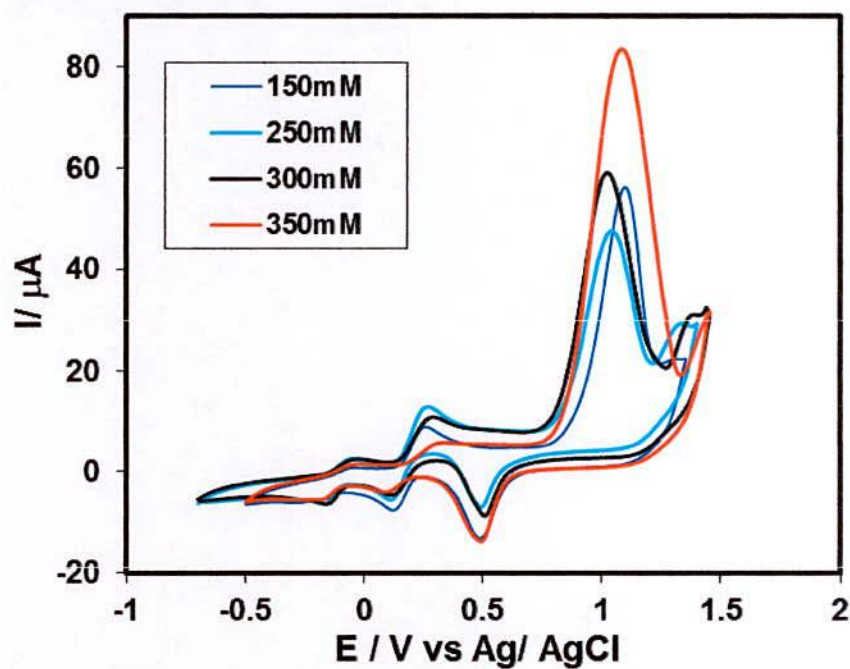


Fig. 4.117: Comparison of CV of different concentration (150, 250, 300 and 350mM) of diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

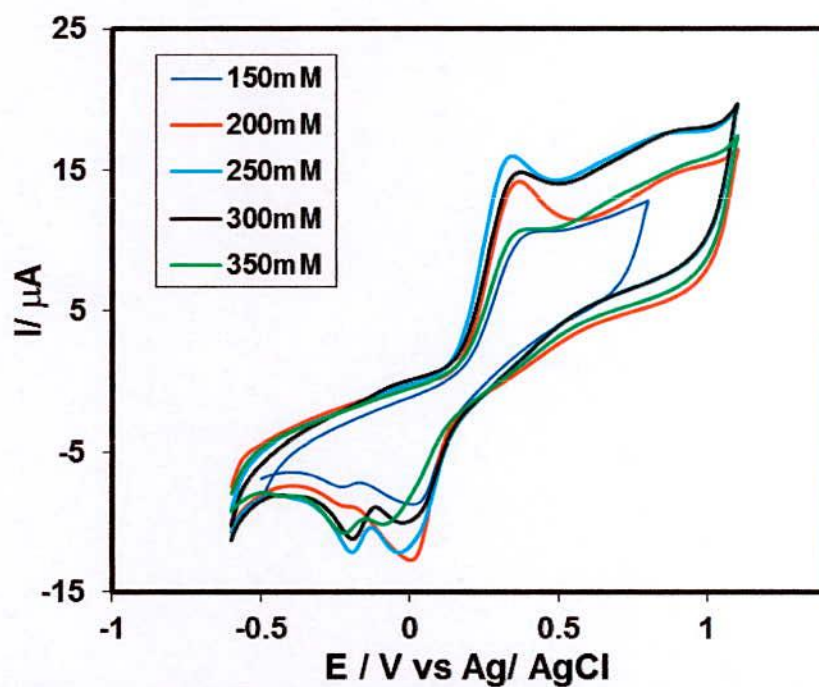


Fig. 4.118: Comparison of CV of different concentration (150, 200, 250, 300 and 350mM) of diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s (1<sup>st</sup> cycle)



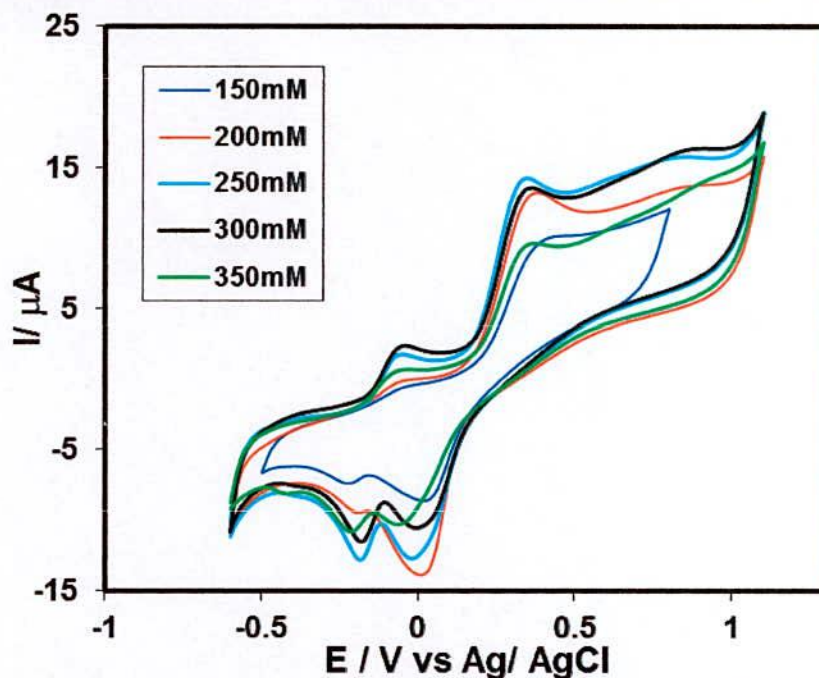


Fig. 4.119: Comparison of CV of different concentration (150, 200, 250, 300 and 350mM) of diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

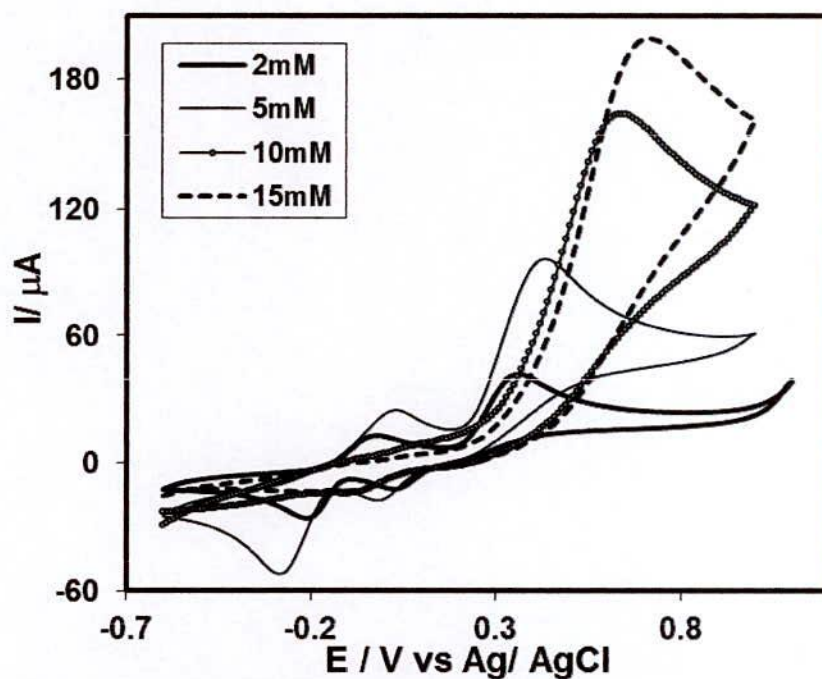


Figure 4.120: CV of composition change of catechol (2, 5, 10 and 15mM) + fixed composition of diethylamine (250mM) of GC electrode in buffer solution (pH 7) at scan rate 0.1Vs<sup>-1</sup> (2<sup>nd</sup> cycle)

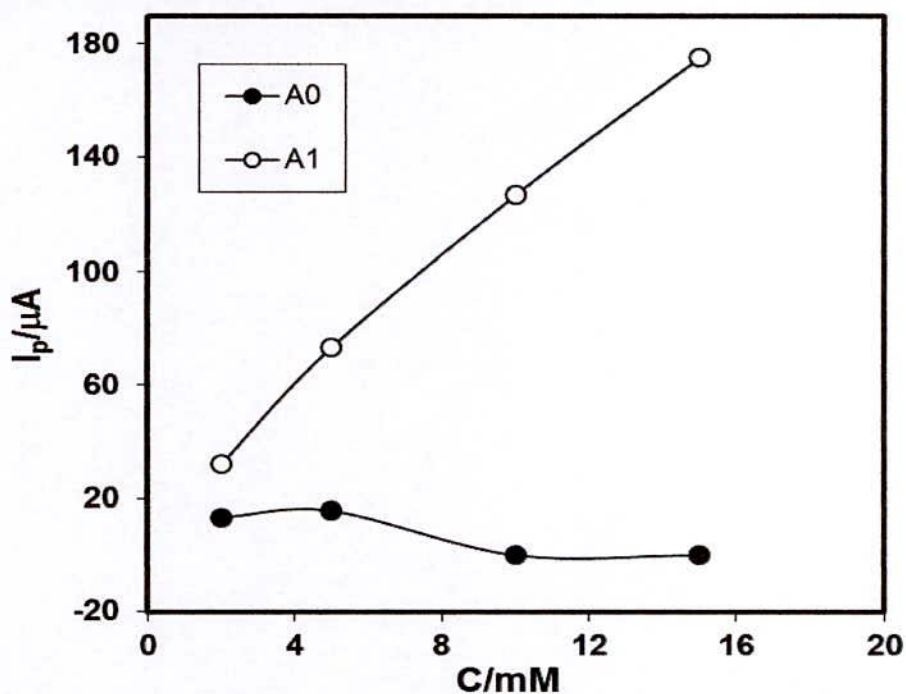


Figure 4.121: Plots of appeared anodic peak ( $A_0$ ) and anodic peak ( $A_1$ ) current ( $I_p$ ) vs different concentration ( $C$ ) of catechol + fixed 250mM diethylamine of GC electrode in buffer solution (pH 7) at scan rate  $0.1 \text{ Vs}^{-1}$  ( $2^{\text{nd}}$  cycle)

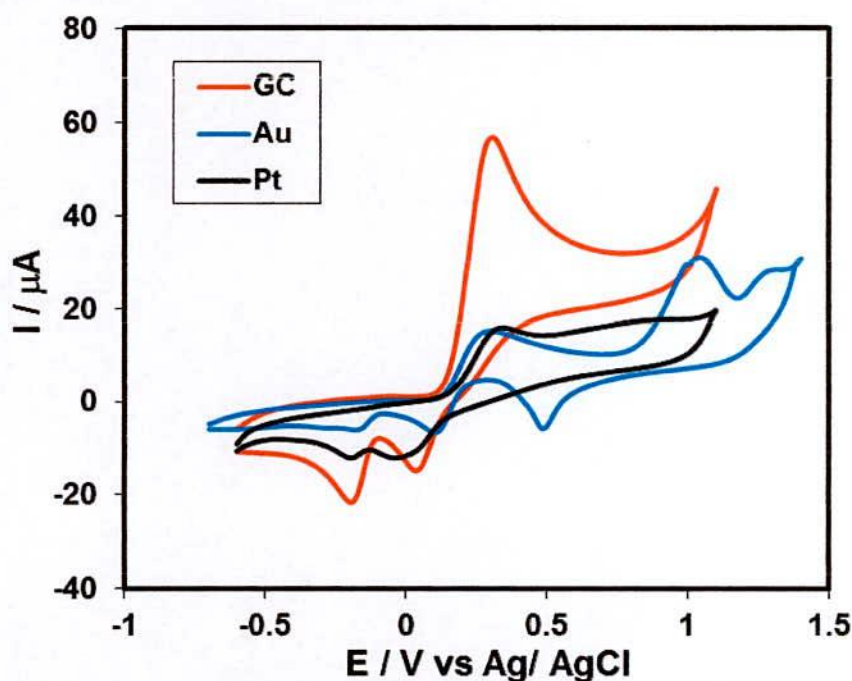


Fig. 4.122: Comparison of CV of 2mM catechol + 250mM diethylamine of GC electrode (3.0mm), Au electrode (1.6mm) and Pt electrode (1.6mm) in buffer solution (pH 7) at scan rate  $0.1 \text{ V/s}$  ( $1^{\text{st}}$  cycle)



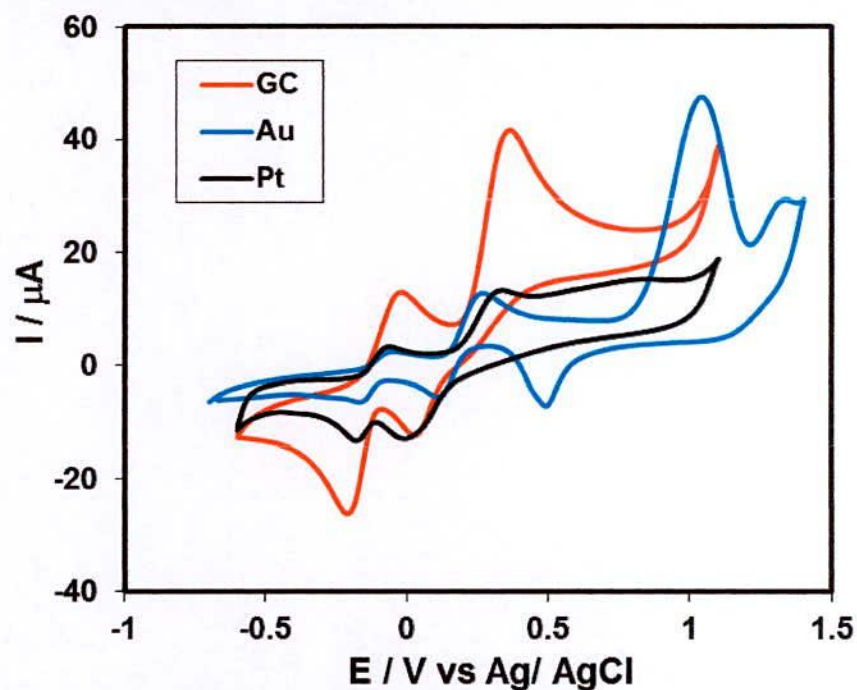


Fig. 4.123: Comparison of CV of 2mM catechol + 250mM diethylamine of GC electrode (3.0mm), Au electrode (1.6mm) and Pt electrode (1.6mm) in buffer solution (pH 7) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

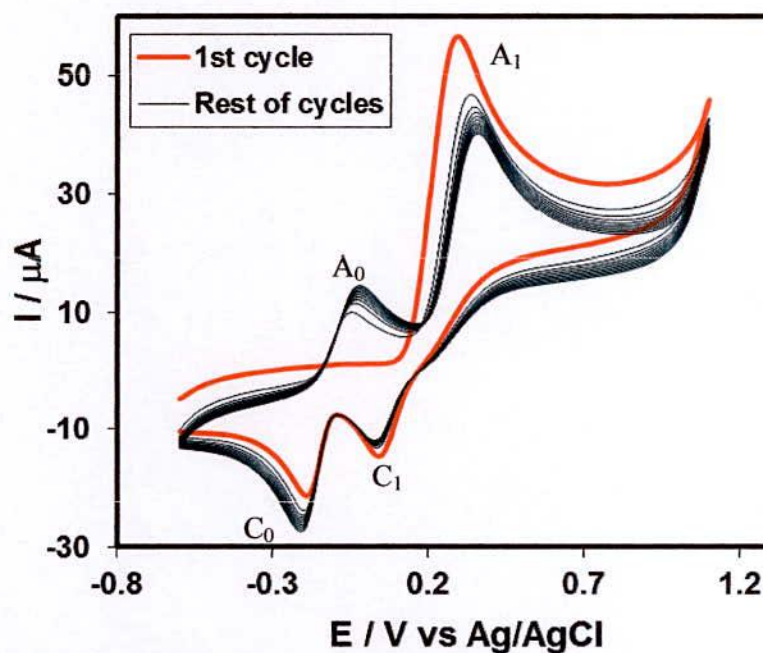


Fig. 4.124: Cyclic voltammogram of 15 cycles of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s

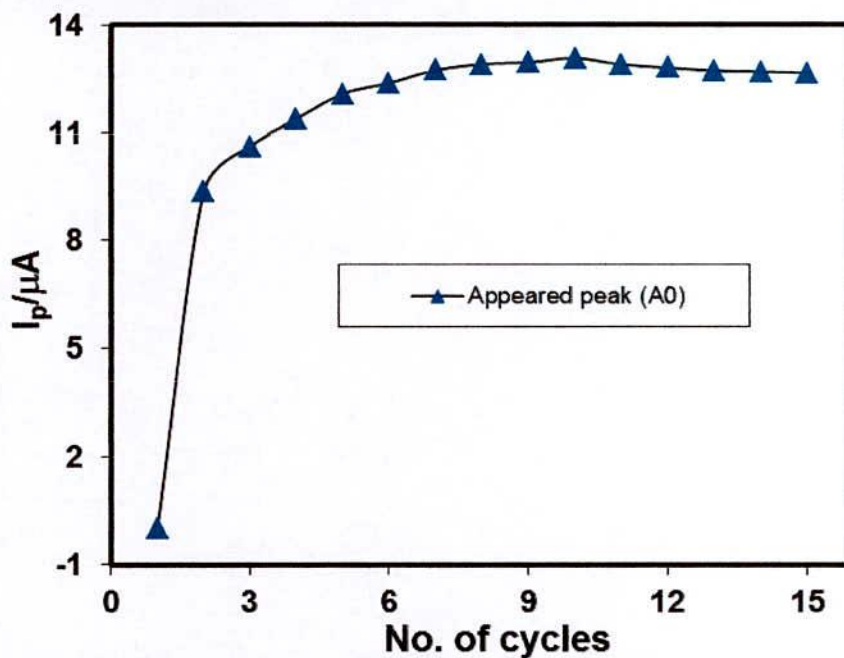


Fig. 4.125: Plots of peak current ( $I_p$ ) versus number of cycles of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at scan rate 0.1V/s

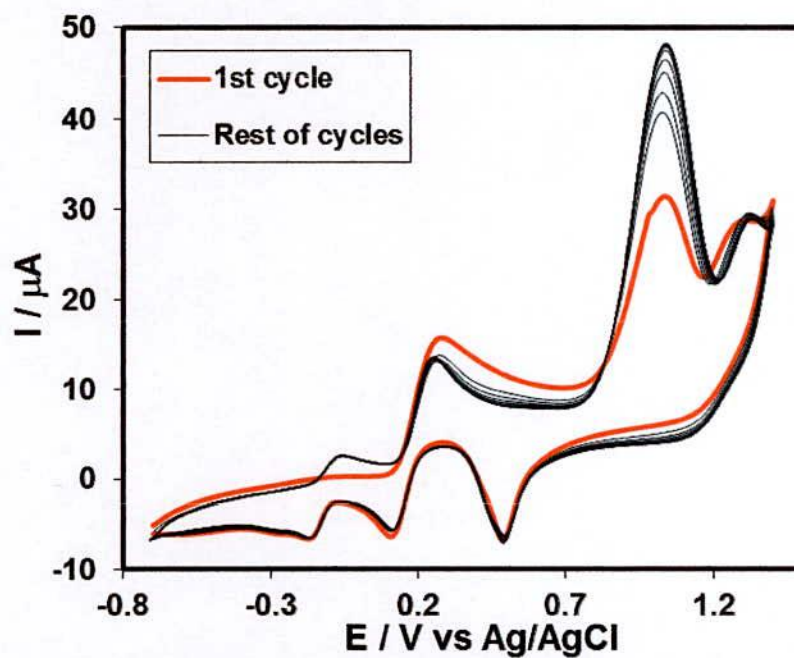


Fig. 4.126: Cyclic voltammogram of 15 cycles of 250mM diethylamine + 2mM catechol of Au electrode in Buffer solution (pH 7) at scan rate 0.1V/s



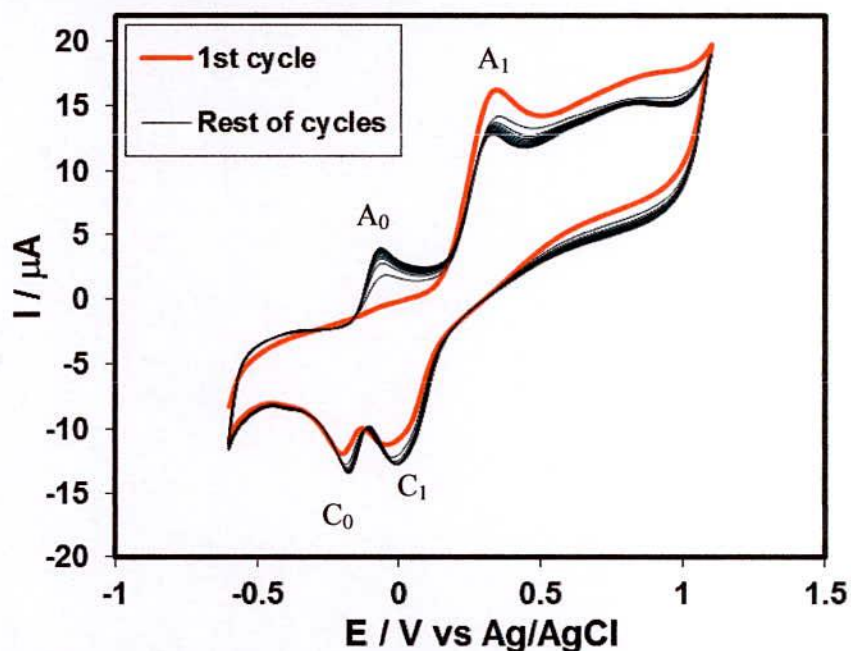


Fig. 4.127: Cyclic voltammogram of 15 cycles of 250mM diethylamine + 2mM catechol of Pt electrode in buffer solution (pH 7) at scan rate 0.1V/s

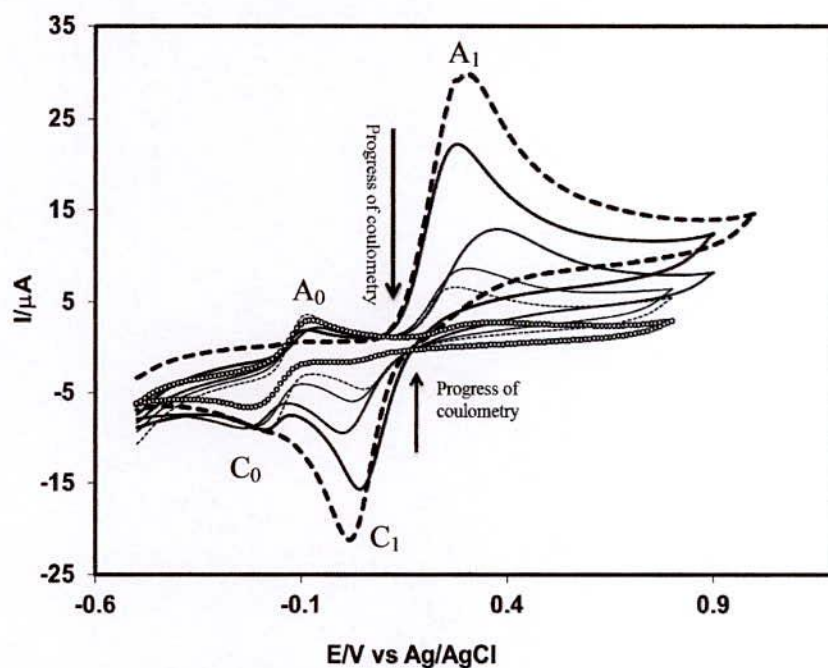


Figure 4.128: Cyclic voltammograms of 0.5mM catechol in presence of 1mM diethylamine of GC electrode during controlled potential coulometry at potential 0.5V in buffer solution (pH 7) at scan rate 0.1V/s

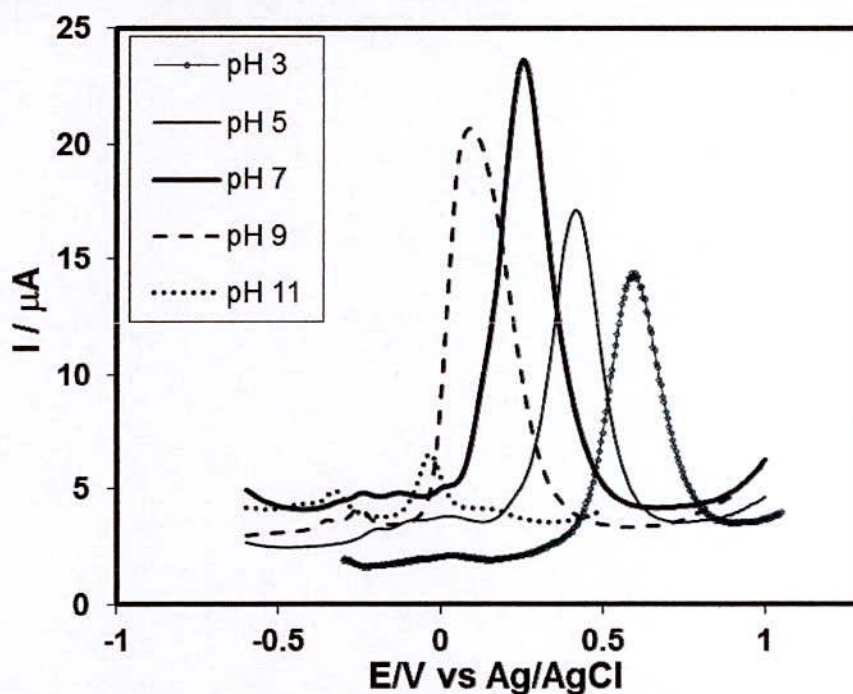


Fig. 4.129: Comparison of differential pulse voltammogram (DPV) of pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (1<sup>st</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

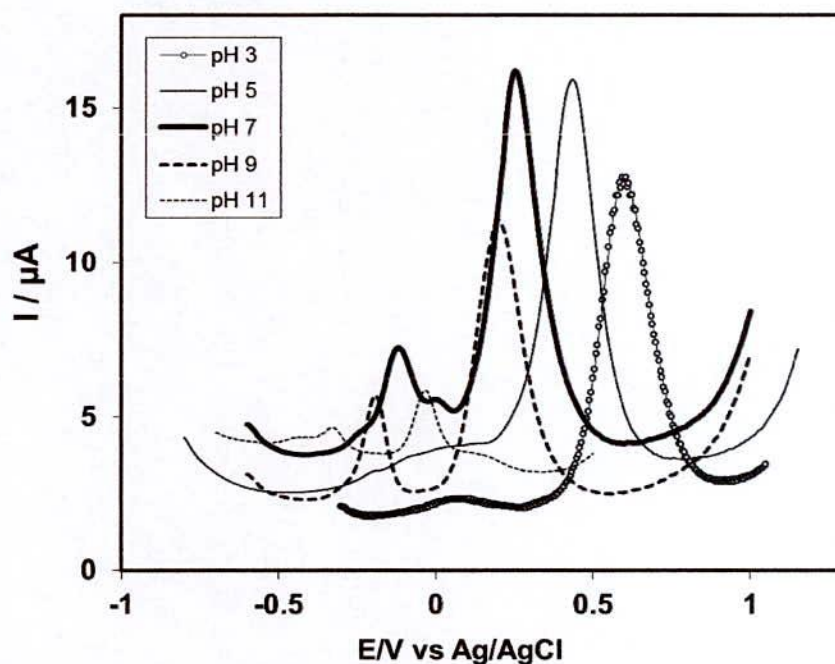


Fig. 4.130: Comparison of differential pulse voltammogram (DPV) of pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)



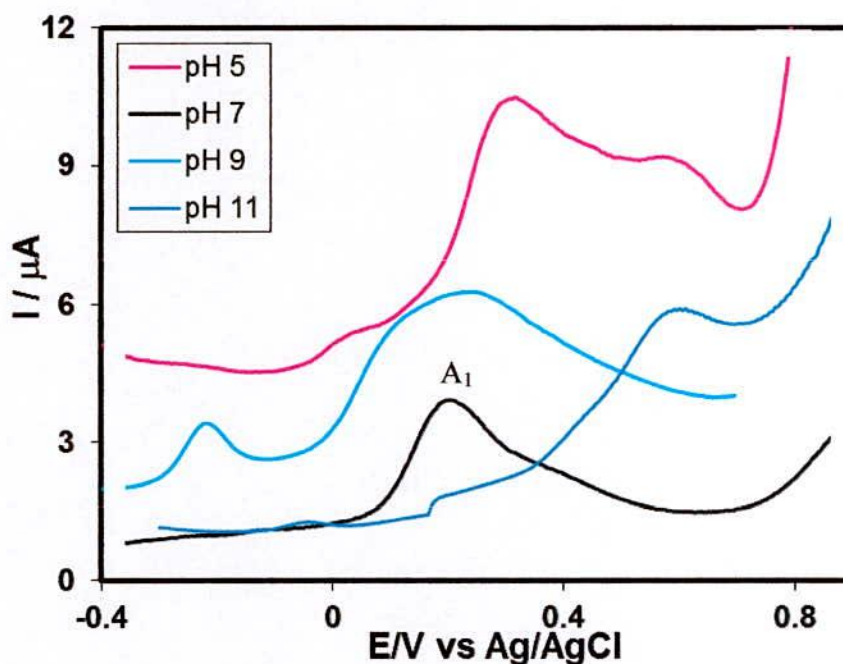


Fig. 4.131: Comparison of differential pulse voltammogram (DPV) of pH (5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (1<sup>st</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

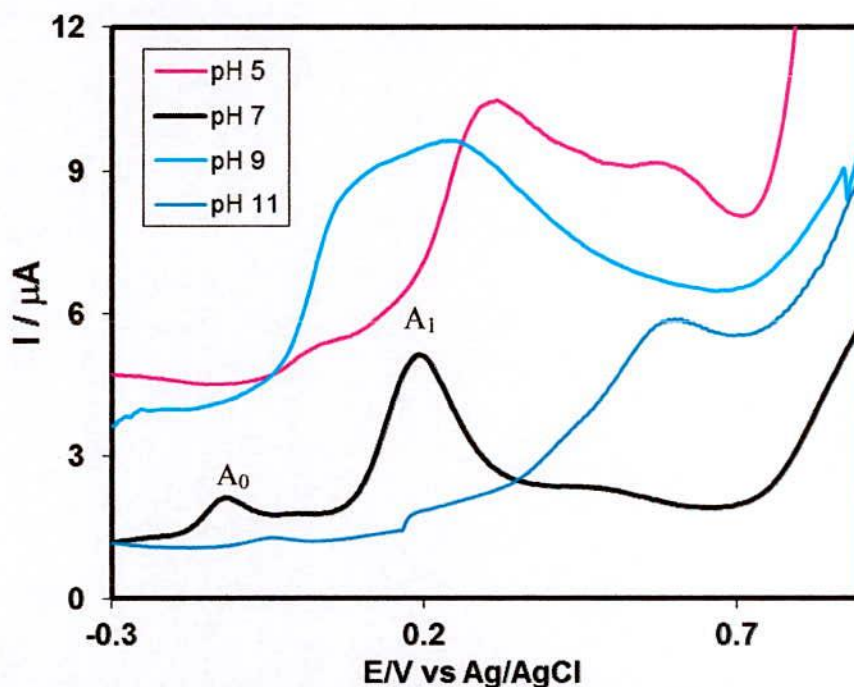


Fig. 4.132: Comparison of differential pulse voltammogram (DPV) of pH (5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

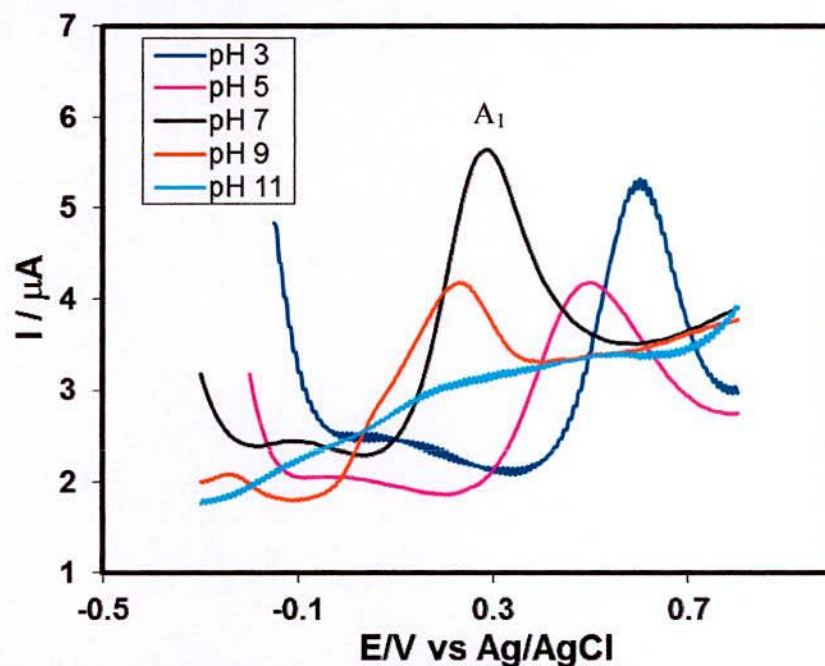


Fig. 4.133: Comparison of differential pulse voltammogram (DPV) of pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1V/s (1<sup>st</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

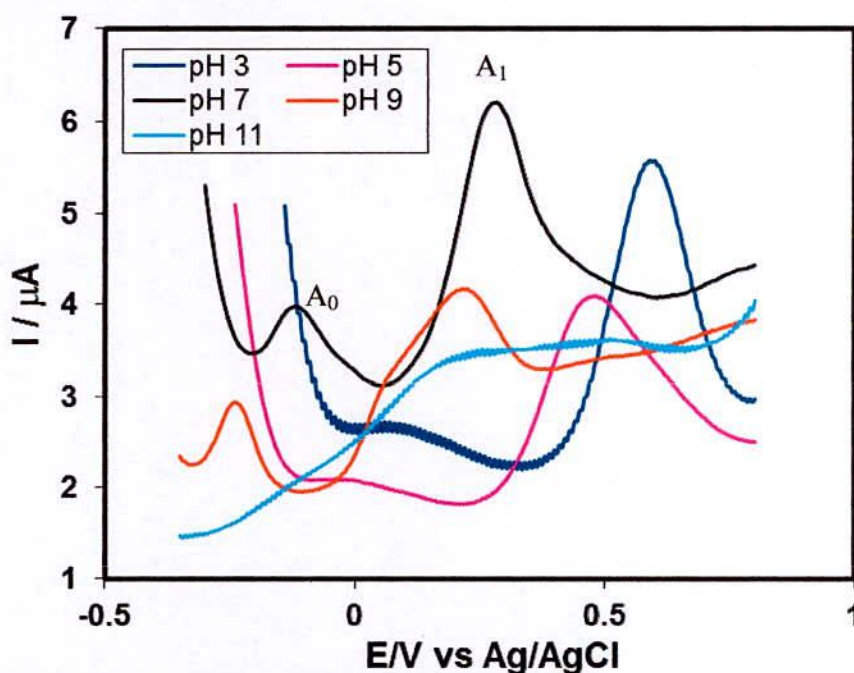


Fig. 4.134: Comparison of differential pulse voltammogram (DPV) of pH (3, 5, 7, 9 and 11) of 250mM diethylamine + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)



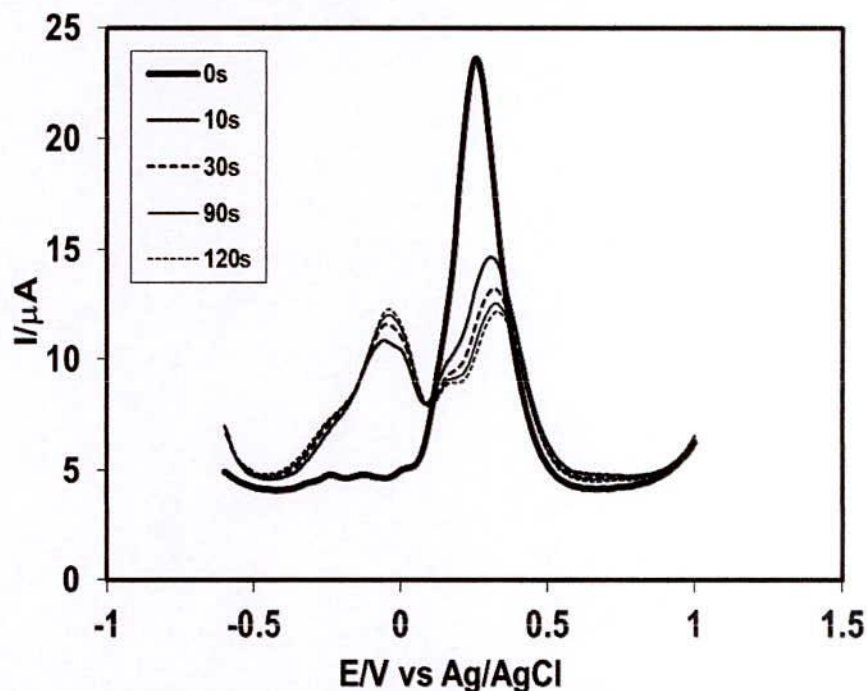


Figure 4.135: Differential pulse voltammogram (DPV) of deposition time change (0, 10, 30, 90 and 120s) of 2mM catechol + 250mM diethylamine in buffer solution (pH 7) at scan rate  $0.1\text{Vs}^{-1}$  ( $E_{\text{pulse}} 0.02\text{V}$ ,  $t_{\text{pulse}} 20\text{ms}$ )

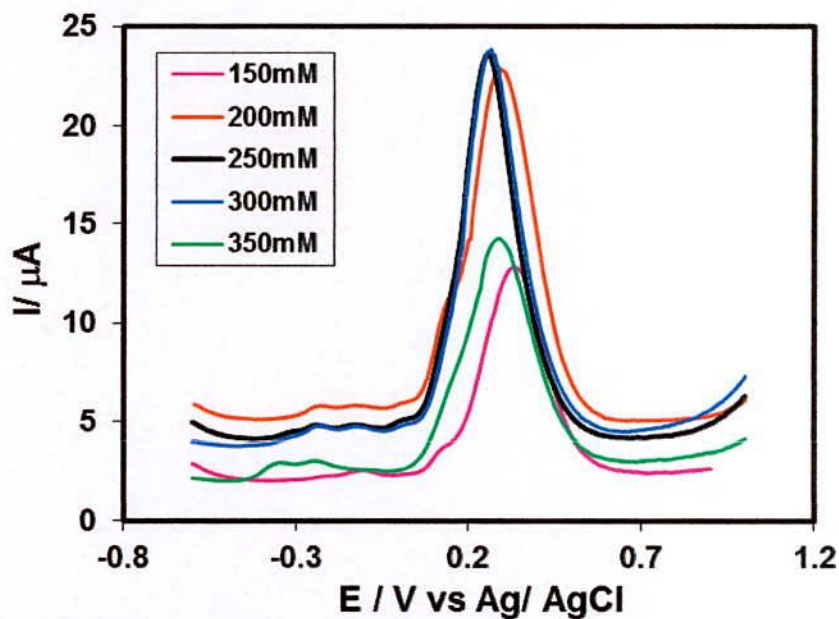


Fig. 4.136: Comparison of DPV of concentration at different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) and scan rate  $0.1\text{V/s}$  (1<sup>st</sup> oxidation) ( $E_{\text{pulse}} 0.02\text{V}$  and  $t_{\text{pulse}} 20\text{ms}$ )

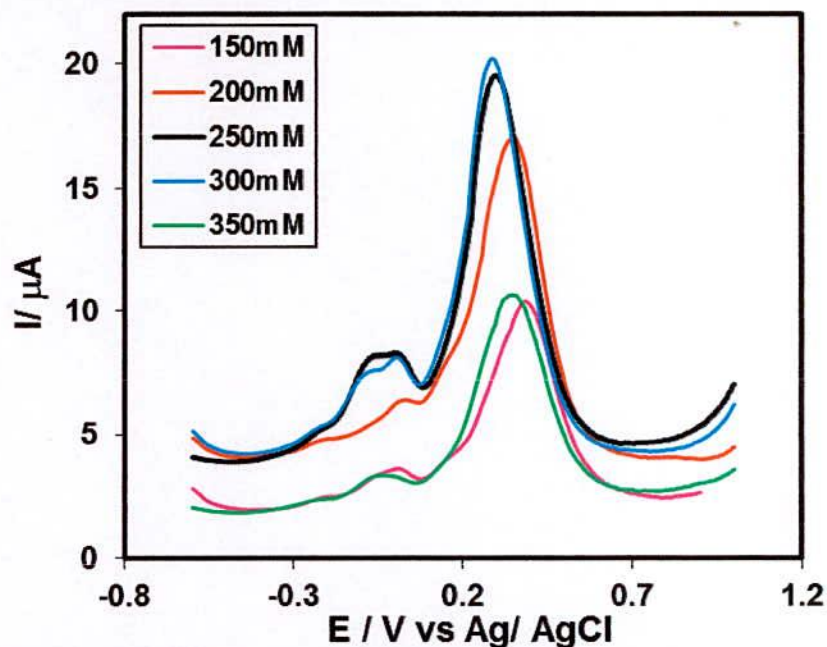


Fig. 4.137: Comparison of DPV of concentration at different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of GC electrode in buffer solution (pH 7) and scan rate 0.1V/s (2<sup>nd</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

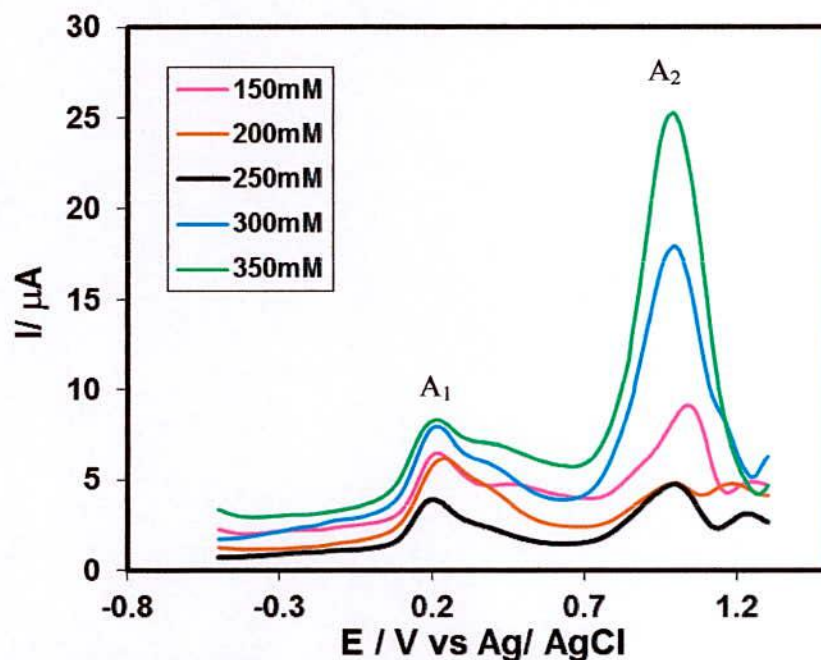


Fig. 4.138: Comparison of DPV of concentration at different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of Au electrode in buffer solution (pH 7) and scan rate 0.1V/s (1<sup>st</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)



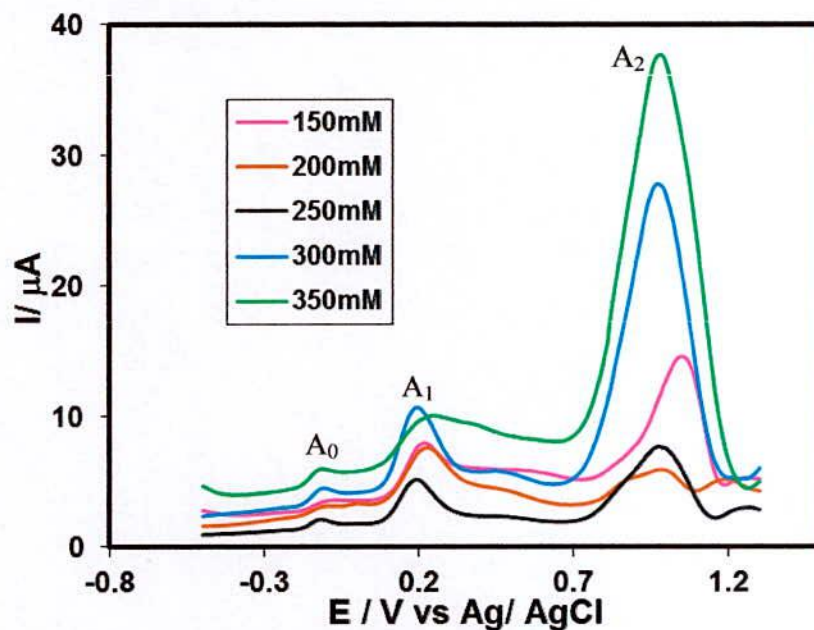


Fig. 4.139: Comparison of DPV of concentration at different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of Au electrode in buffer solution (pH 7) and scan rate 0.1V/s (2<sup>nd</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

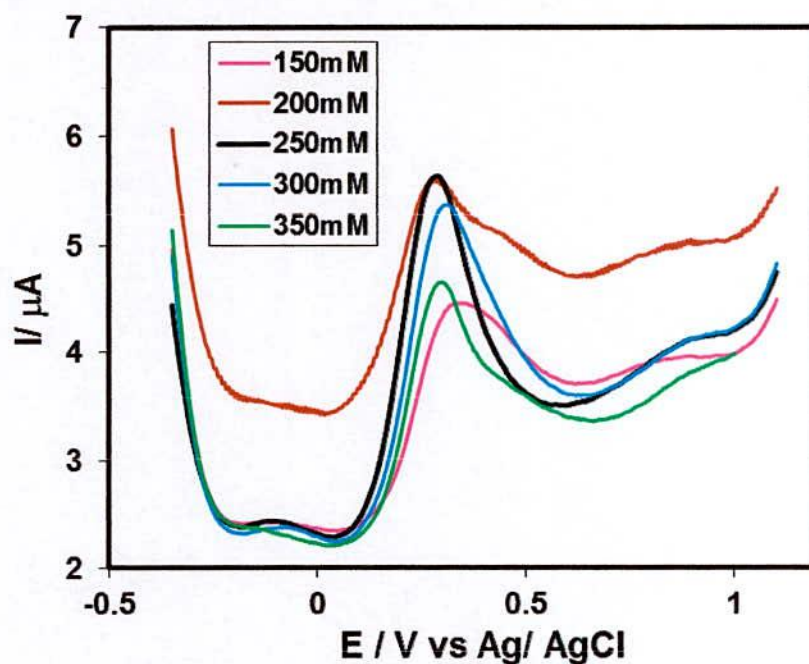


Fig. 4.140: Comparison of DPV of concentration at different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of Pt electrode in buffer solution (pH 7) and scan rate 0.1V/s (1<sup>st</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

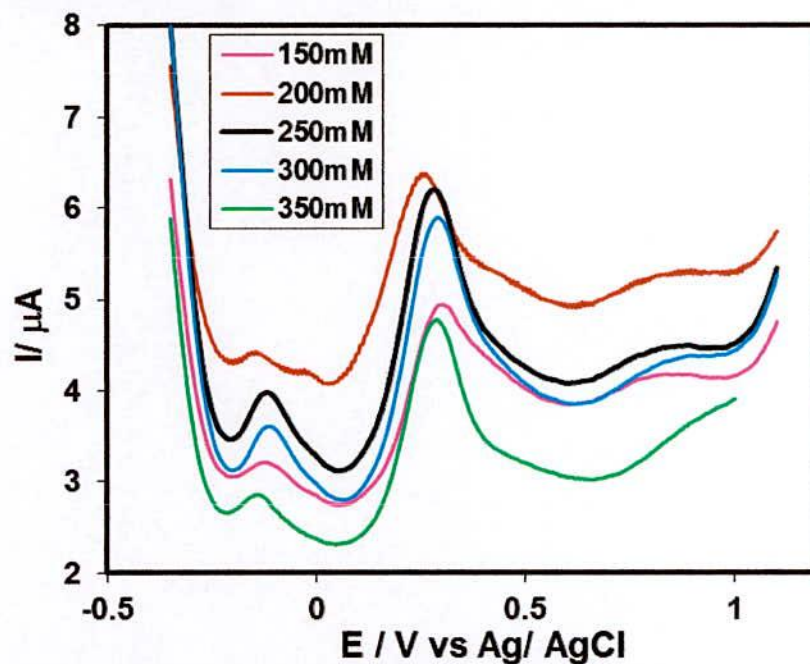


Fig. 4.141: Comparison of DPV of concentration at different concentration (150, 200, 250, 300 and 350mM) of diethylamine + fixed 2mM catechol of Pt electrode in buffer solution (pH 7) and scan rate 0.1V/s (2<sup>nd</sup> oxidation) ( $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms)

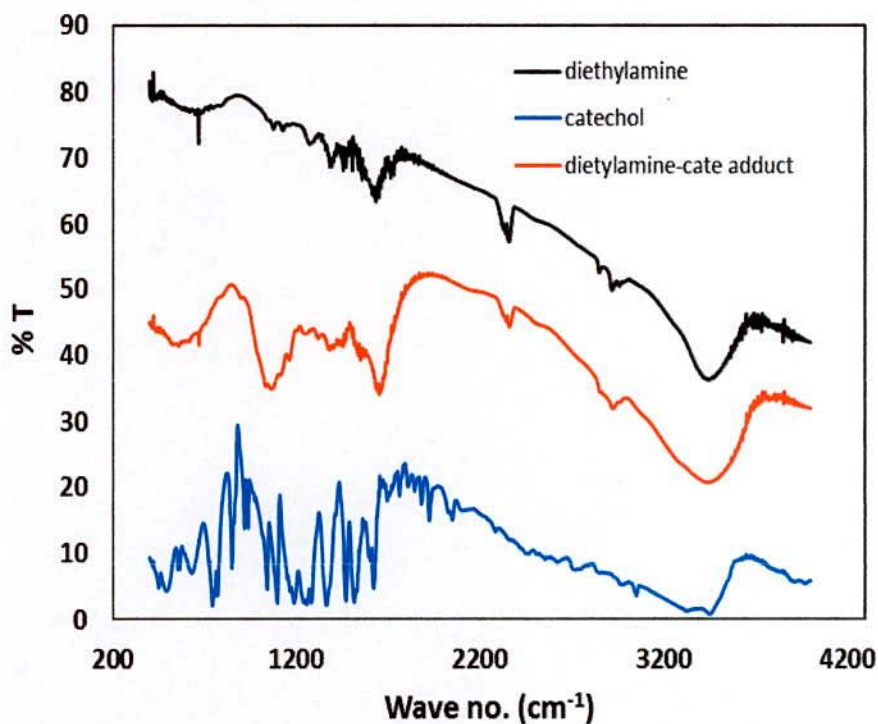


Fig. 4.142: Comparison of FTIR of only catechol, only diethylamine and catechol-diethylamine adduct



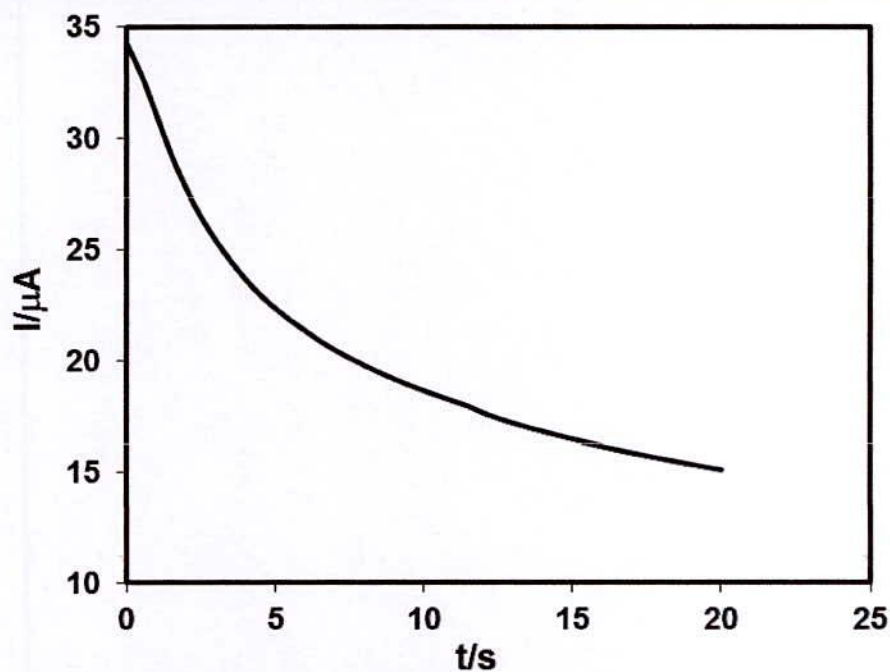


Fig. 4.143: Chronoamperogram of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at potential 0.32V and time 20s

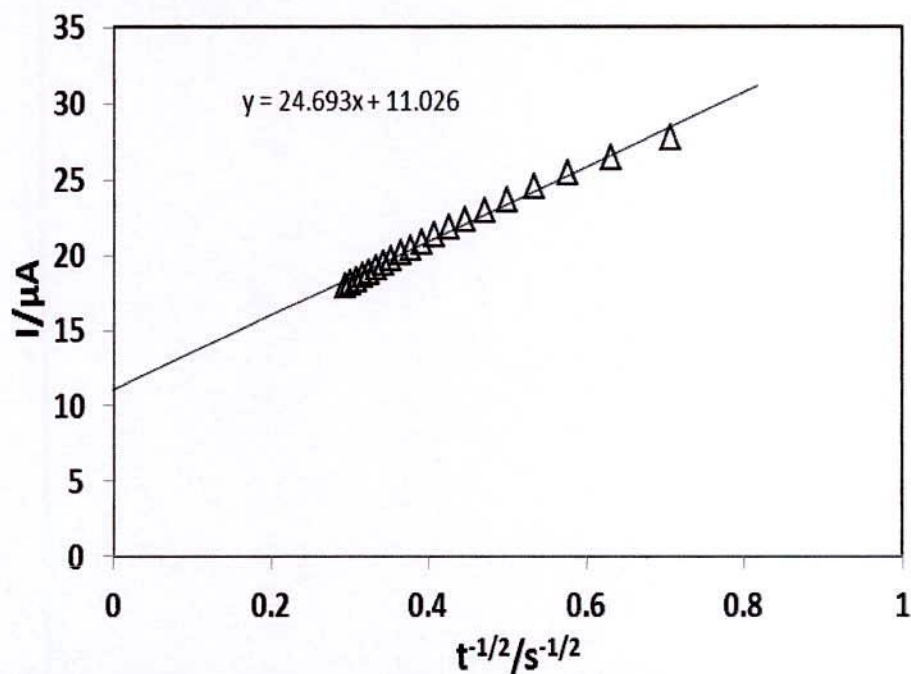


Fig. 4.144: Cottrell plots of 250mM diethylamine + 2mM catechol of GC electrode in buffer solution (pH 7) at potential 0.32V

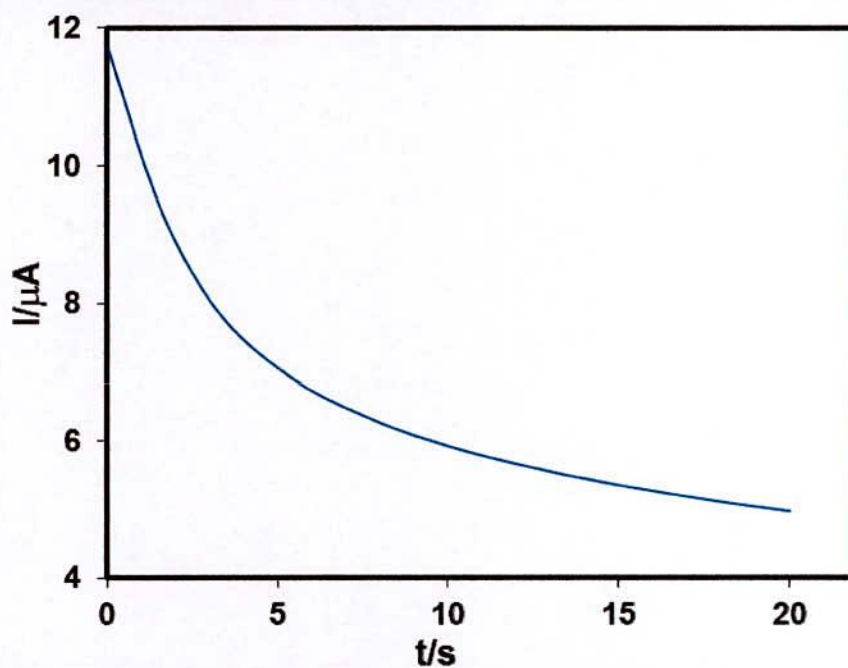


Fig. 4.145: Chronoamperogram of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at potential 0.31V

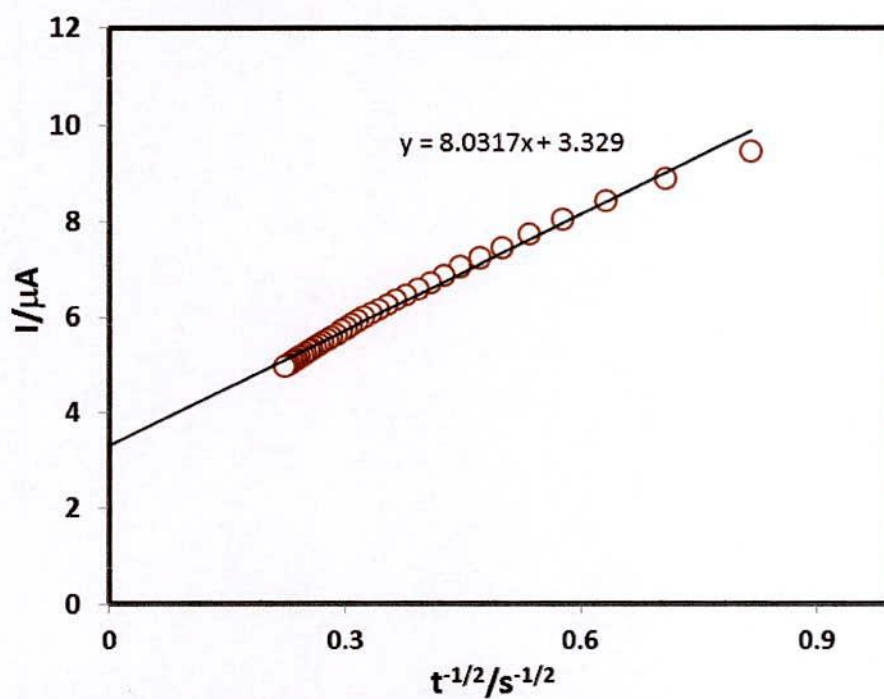


Fig. 4.146: Cottrell plots of 250mM diethylamine + 2mM catechol of Au electrode in buffer solution (pH 7) at potential 0.31V



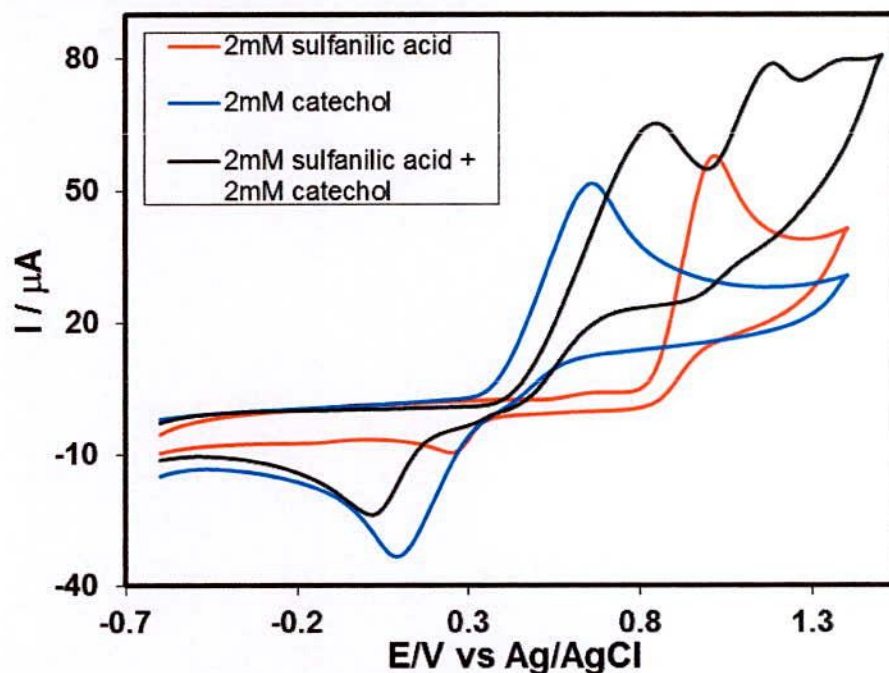


Fig. 4.147: Comparison of cyclic voltammograms of only 2mM sulfanilic acid (red), only 2mM catechol (blue), 2mM catechol + 2mM sulfanilic acid (black) of GC electrode in buffer solution (pH 3) at scan rate 0.1V/s (1<sup>st</sup> cycle)

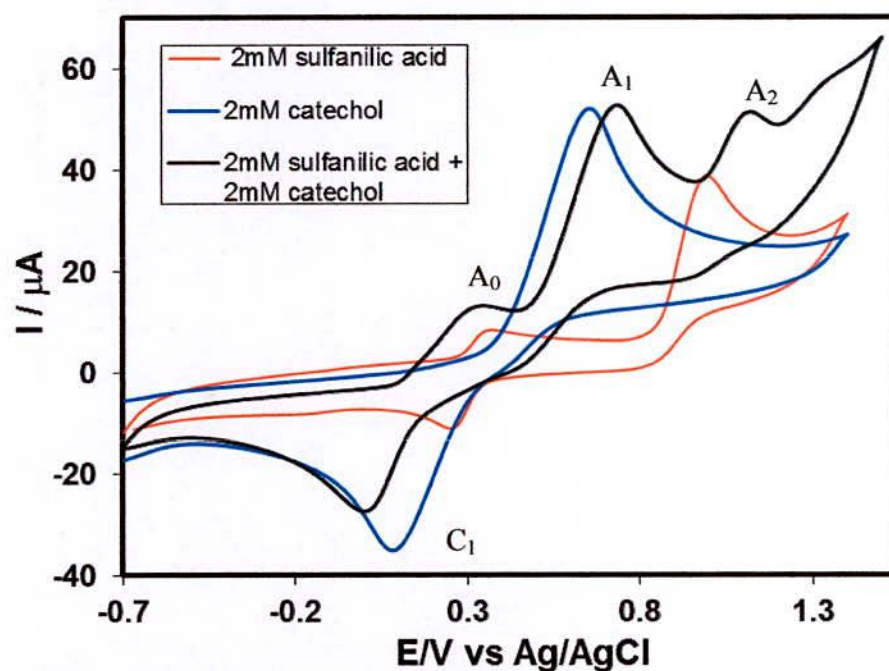


Fig. 4.148: Comparison of cyclic voltammograms of only 2mM sulfanilic acid, only 2mM catechol, 2mM catechol + 2mM sulfanilic acid of GC electrode buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle), where A<sub>0</sub>= Appeared anodic peak, A<sub>1</sub>= 1<sup>st</sup> anodic peak, A<sub>2</sub>= 2<sup>nd</sup> anodic peak and C<sub>1</sub>= 1<sup>st</sup> cathodic peak

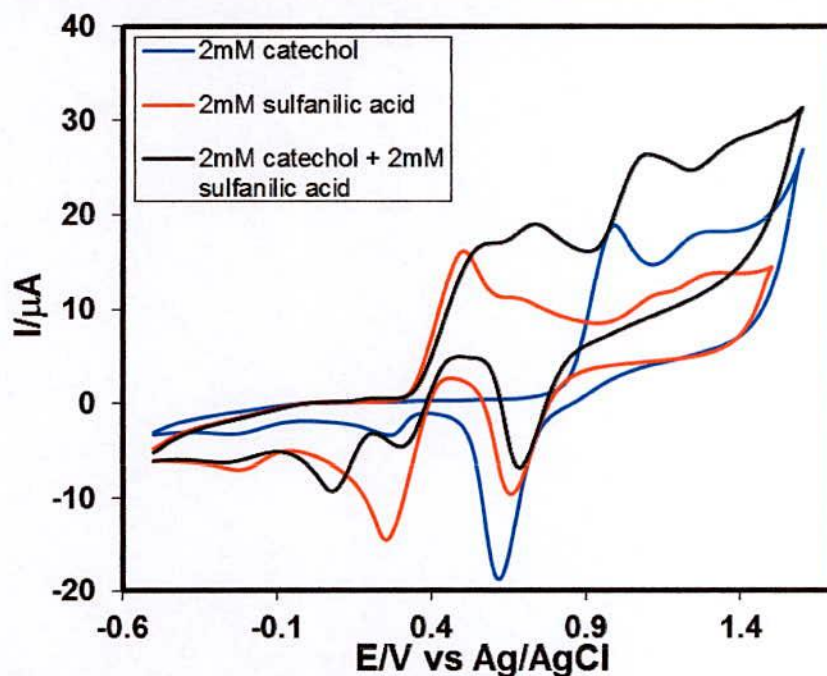


Fig. 4.149: Comparison of cyclic voltammograms of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s (1<sup>st</sup> cycle)

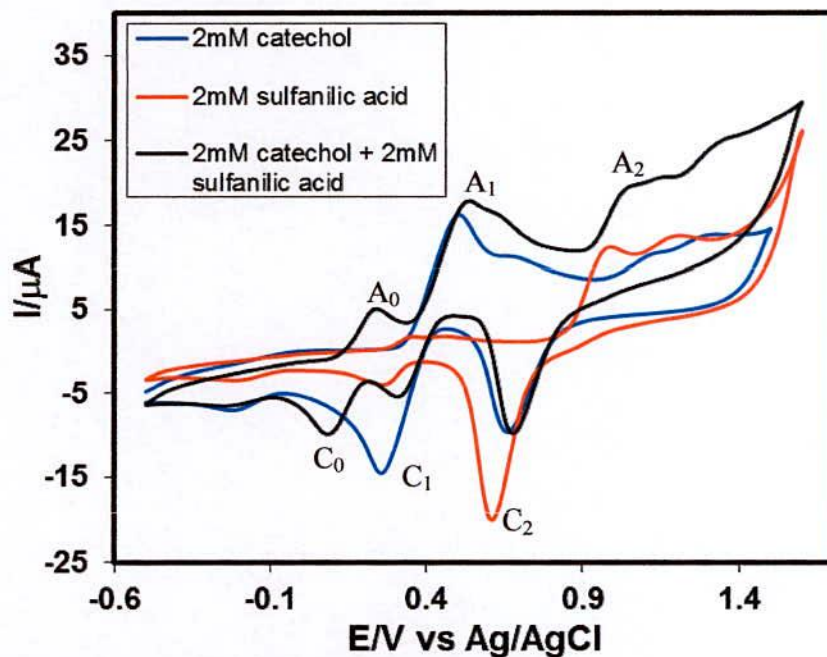


Fig. 4.150: Comparison of cyclic voltammograms of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle), where  $C_0$ = appeared cathodic peak,  $C_2$ = 2<sup>nd</sup> cathodic peak



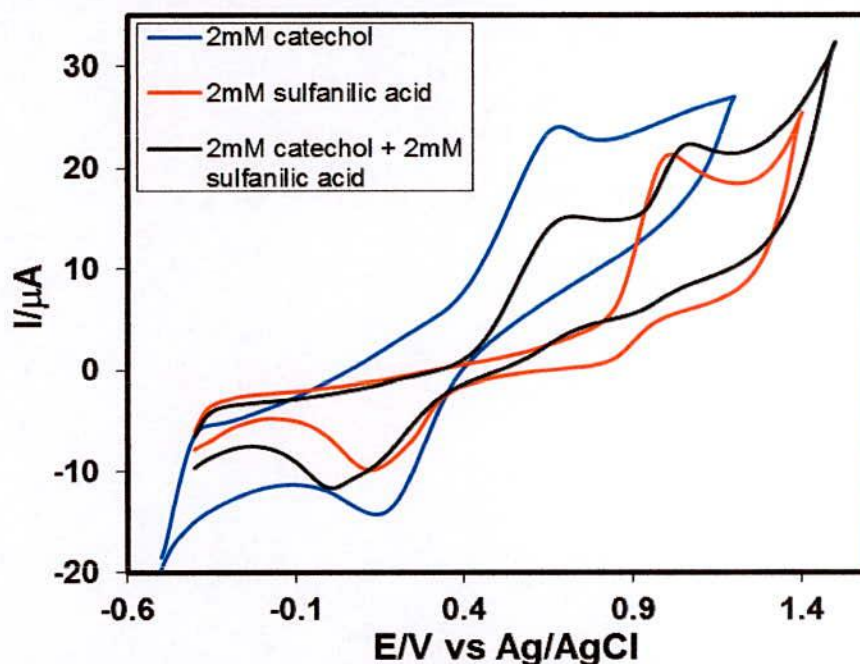


Fig. 4.151: Comparison of cyclic voltammograms of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Pt electrode buffer solution (pH 3) at scan rate 0.1V/s (1<sup>st</sup> cycle)

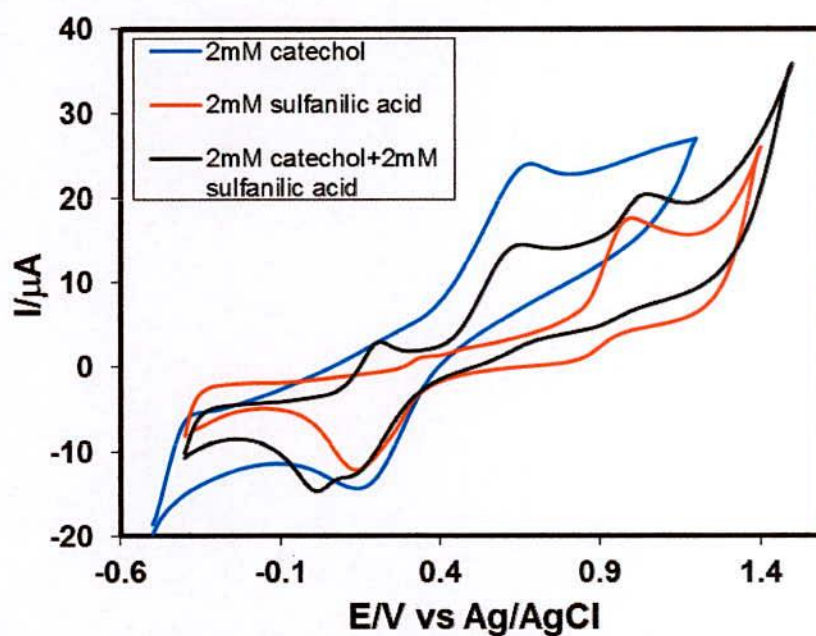


Fig. 4.152: Comparison of cyclic voltammograms of only 2mM catechol, only 2mM sulfanilic acid and 2mM catechol + 2mM sulfanilic acid of Pt electrode buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

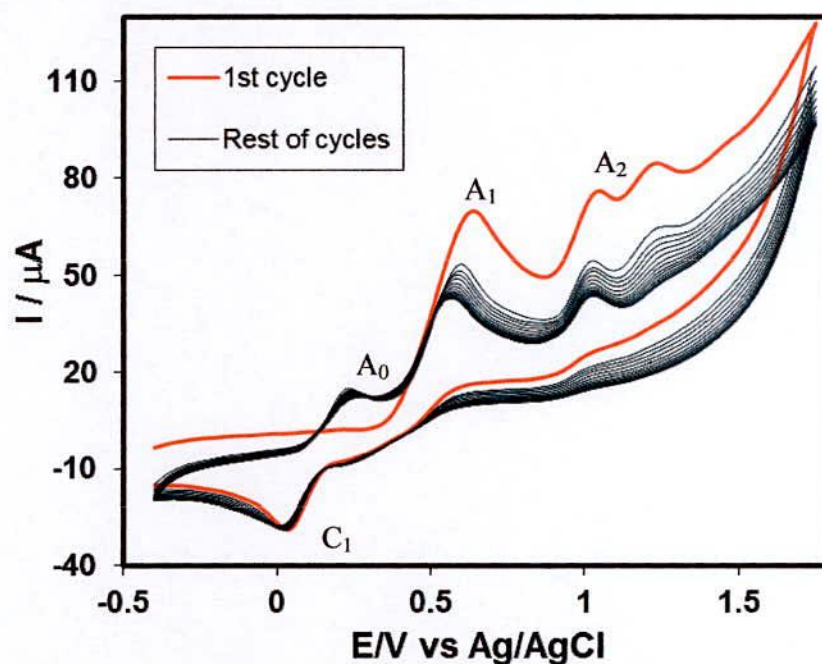


Fig. 4.153: Cyclic voltammogram of 15 cycles of 2mM catechol + 2mM sulfanilic acid of GC electrode in buffer solution (pH 3) at scan rate 0.1V/s

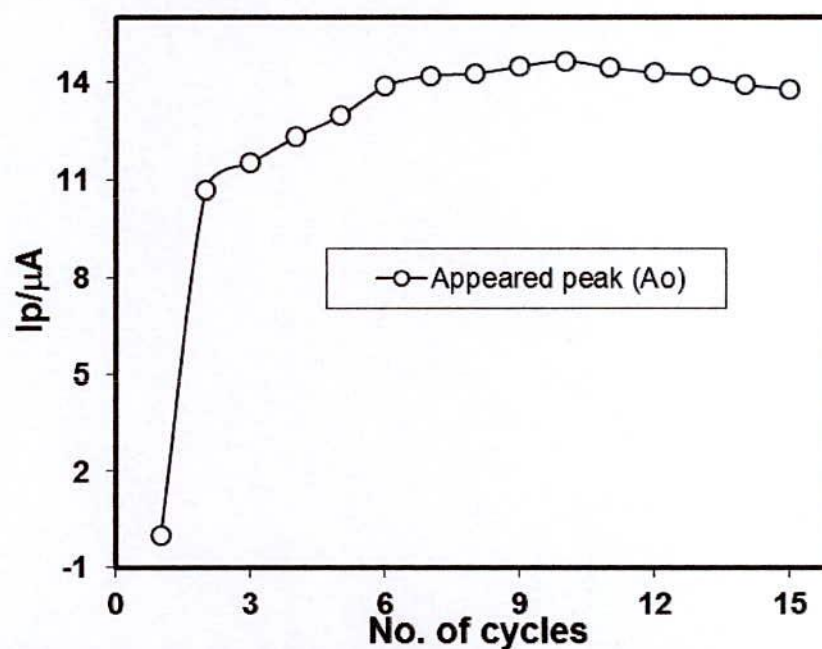


Fig. 4.154: Plots of peak current ( $I_p$ ) versus number of cycles of 2mM sulfanilic acid + 2mM catechol of GC electrode in buffer solution (pH 3) at scan rate 0.1V/s



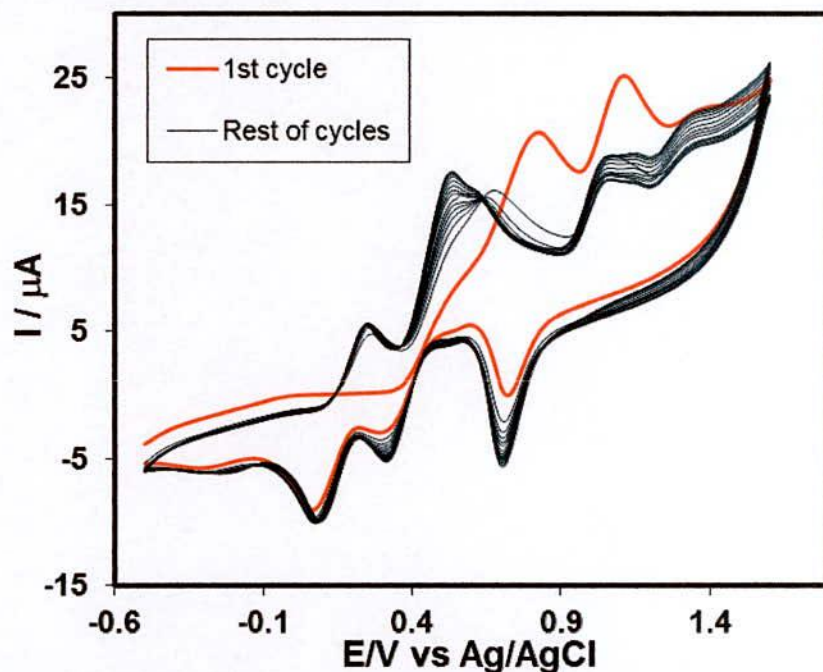


Fig. 4.155: Cyclic voltammogram of 15 cycles of 2mM sulfanilic acid + 2mM catechol of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s

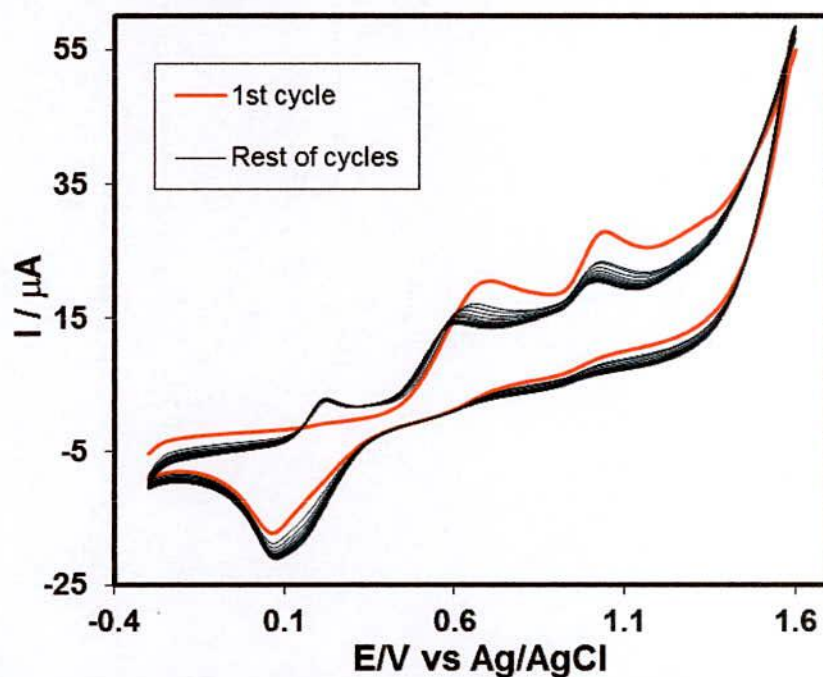


Fig. 4.156: Cyclic voltammogram of 15 cycles of 2mM sulfanilic acid + 2mM catechol of Pt electrode in buffer solution (pH 3) at scan rate 0.1V/s

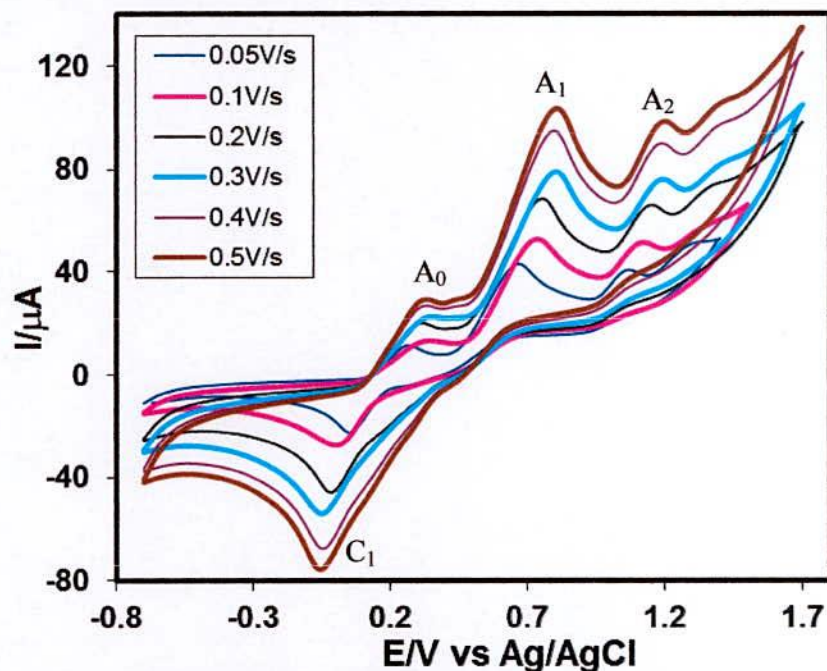


Fig. 4.157: Cyclic voltammogram of 2mM sulfanilic acid + 2mM catechol of GC electrode in buffer solution (pH 3) at different scan rate (2<sup>nd</sup> cycle)

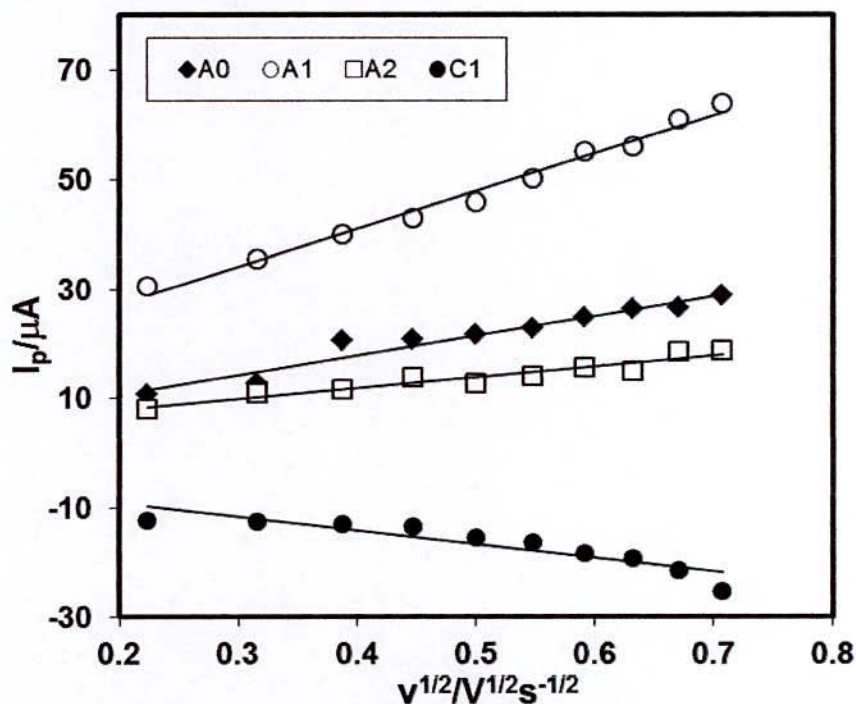


Fig. 4.158: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol at GC electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle



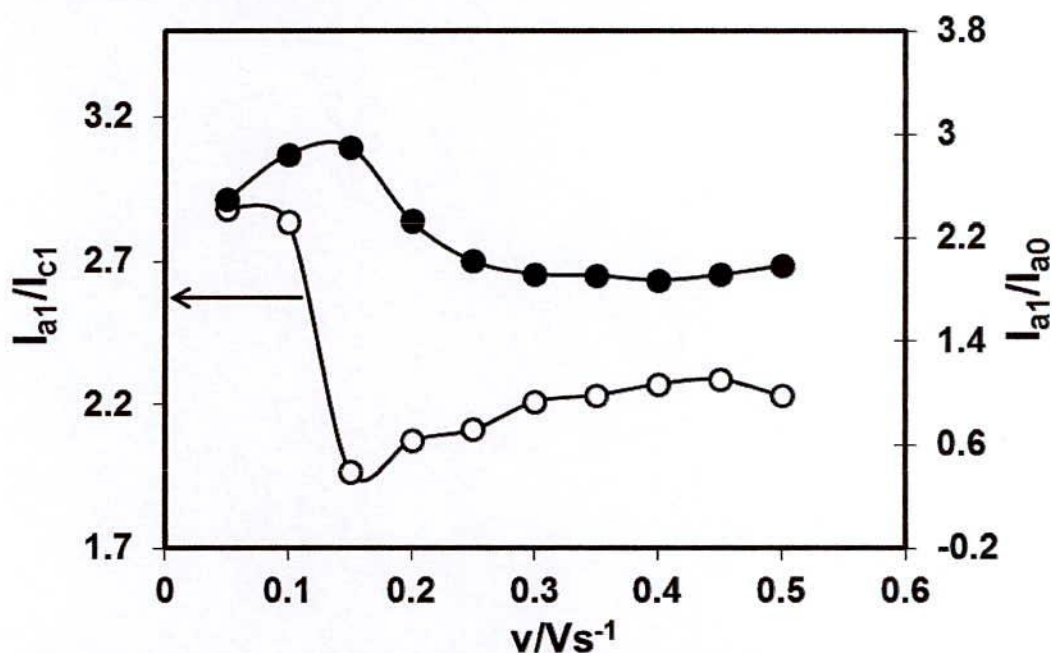


Fig. 4.159: Variation of peak current ratio of corresponding peak ( $I_{pa1}/I_{pc1}$ ) and anodic peak ( $I_{pa1}/I_{pa0}$ ) vs scan rate ( $v$ ) of 2mM catechol + 2mM sulfanilic acid of GC electrode in the second scan of potential in buffer solution (pH 3) at scan rate 0.1V/s

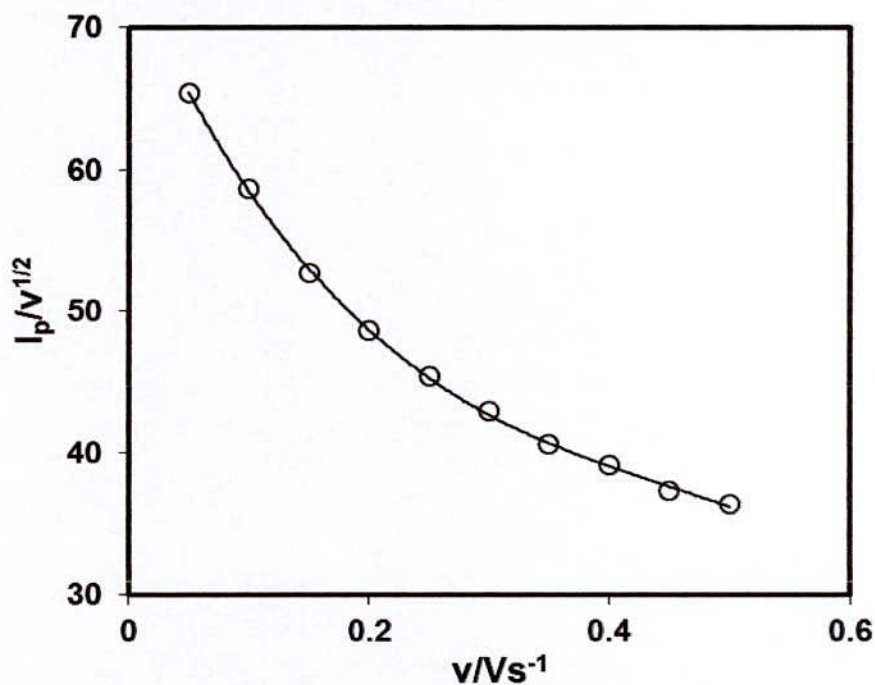


Fig. 4.160: Plots of current function ( $I_p/v^{1/2}$ ) versus scan rate ( $v$ ) of 2mM catechol + 2mM sulfanilic acid of GC electrode in buffer solution (pH 3) in appeared peak of oxidation ( $A_0$ )

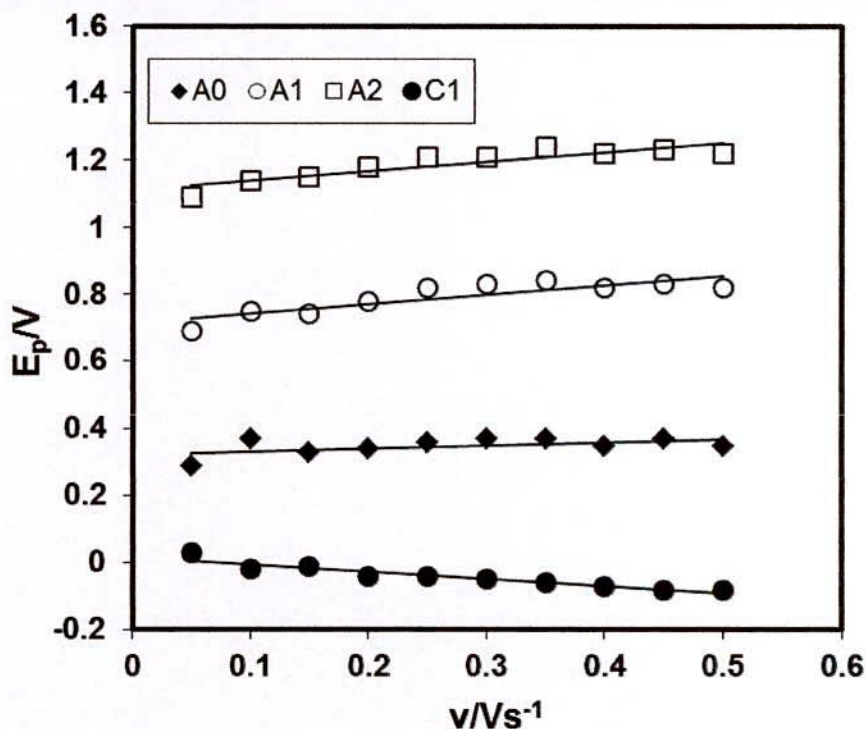


Fig. 4.161: Plots of peak potential ( $E_p$ ) versus scan rate ( $v$ ) of 2mM sulfanilic acid + 2mM catechol of GC electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle

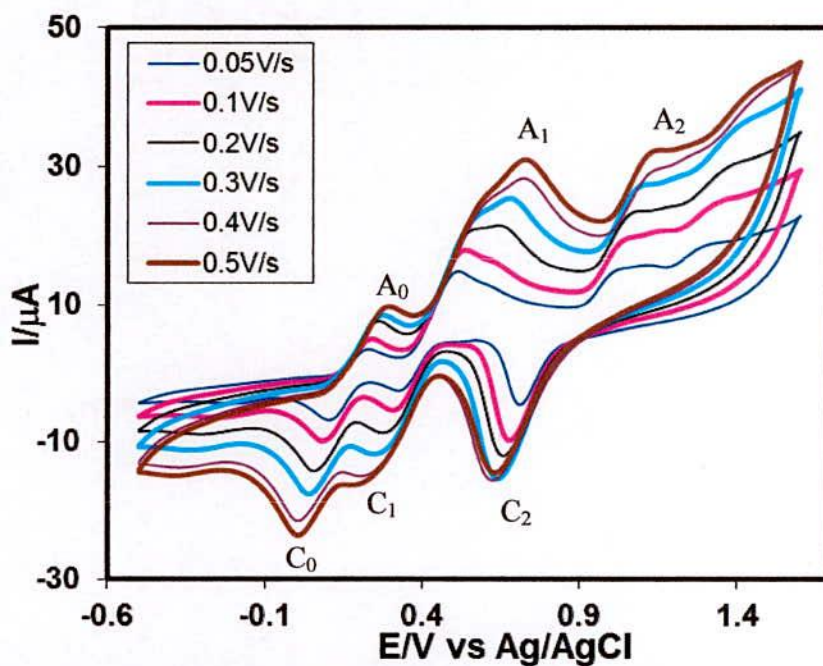


Fig. 4.162: Cyclic voltammogram of 2mM sulfanilic acid + 2mM catechol of Au electrode in buffer solution (pH 3) at different scan rate (2<sup>nd</sup> cycle)



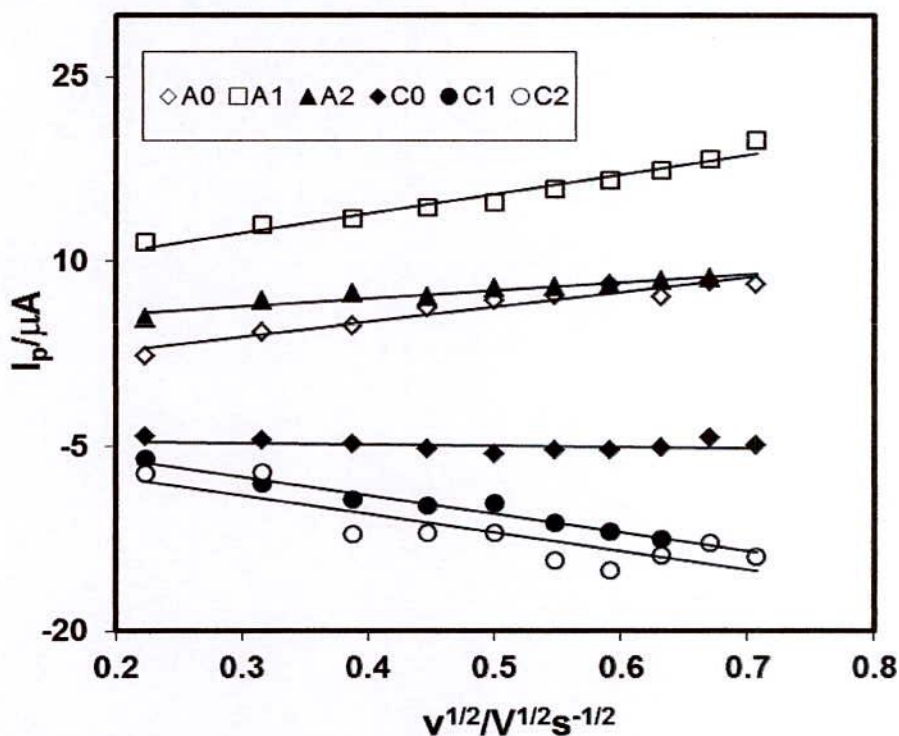


Fig. 4.163: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol of Au electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle

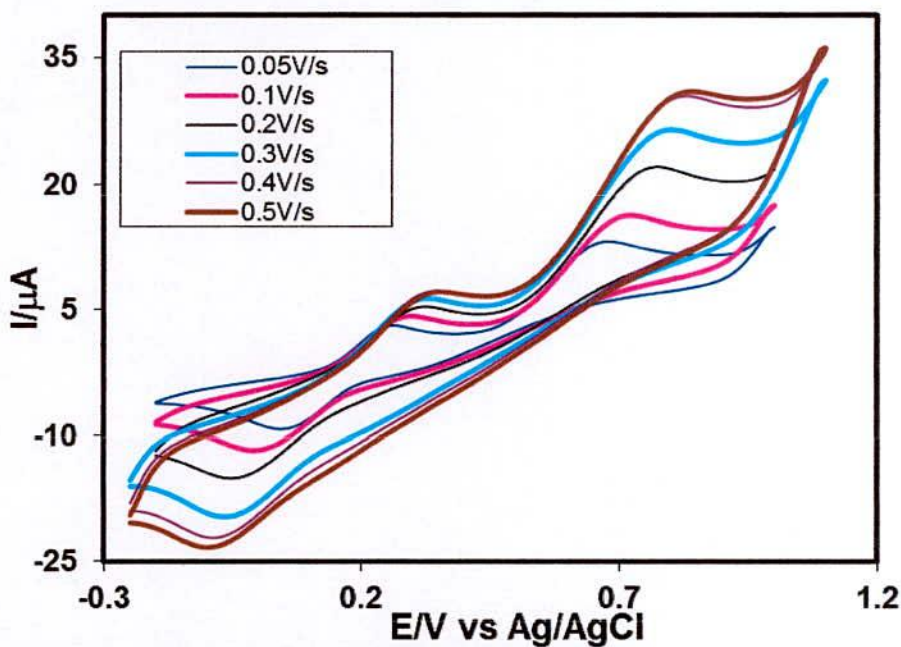


Fig. 4.164: Cyclic voltammogram of 2mM sulfanilic acid + 2mM catechol of Pt electrode in buffer solution (pH 3) at different scan rate (2<sup>nd</sup> cycle)

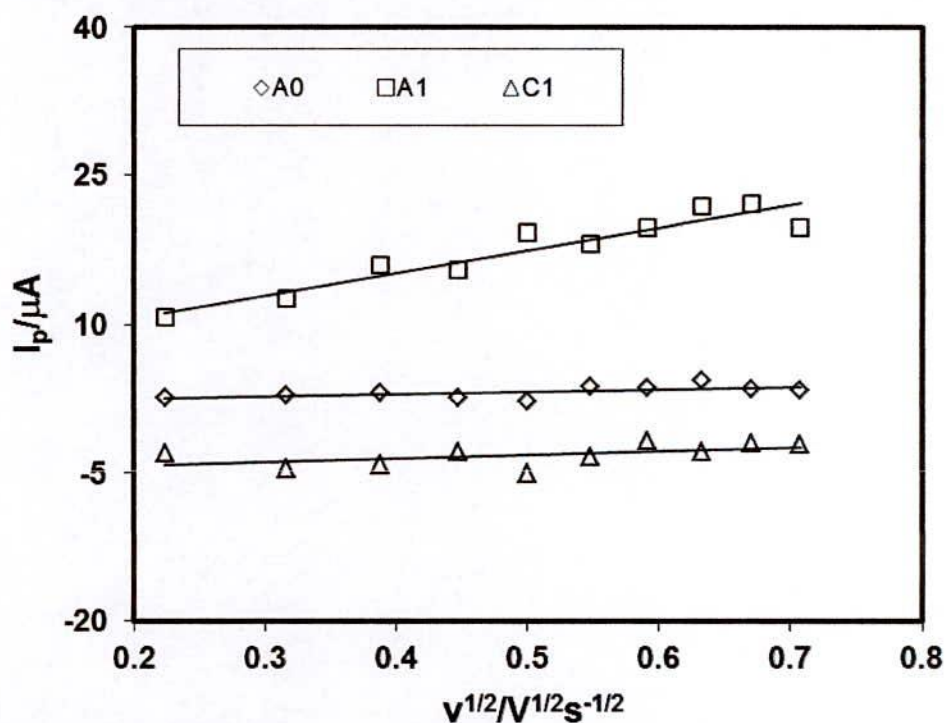


Fig. 4.165: Plots of peak current ( $I_p$ ) versus square root of scan rate ( $v^{1/2}$ ) of 2mM sulfanilic acid + 2mM catechol of Pt electrode in buffer solution (pH 3) at 2<sup>nd</sup> cycle

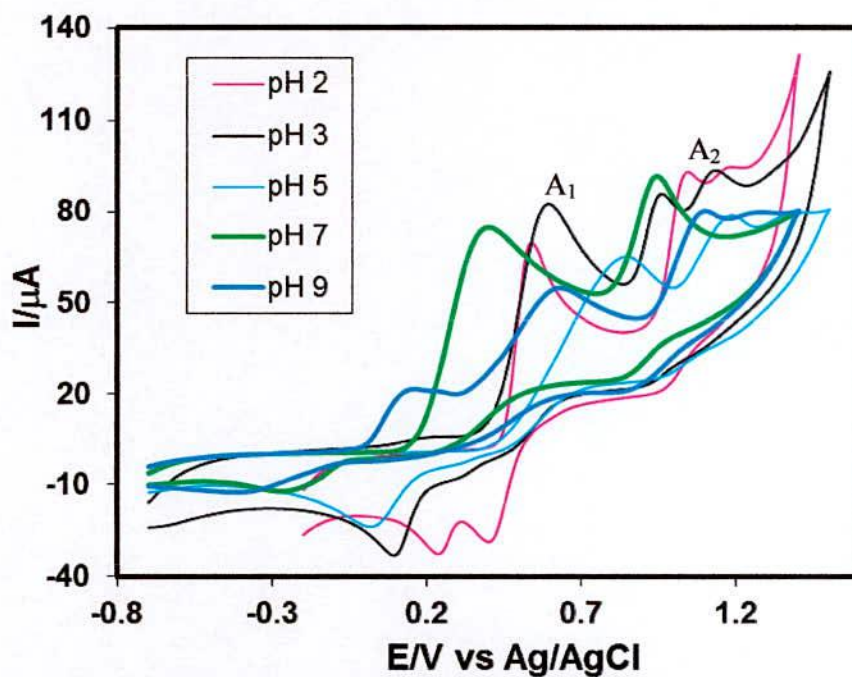


Fig. 4.166: Comparison of cyclic voltammogram of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (1<sup>st</sup> cycle)



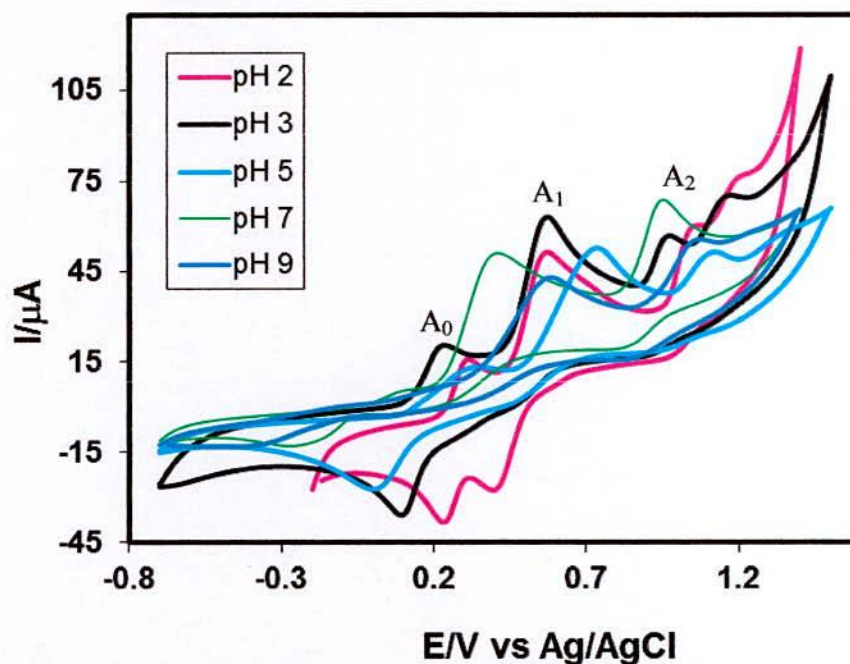


Fig. 4.167: Comparison of cyclic voltammogram of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

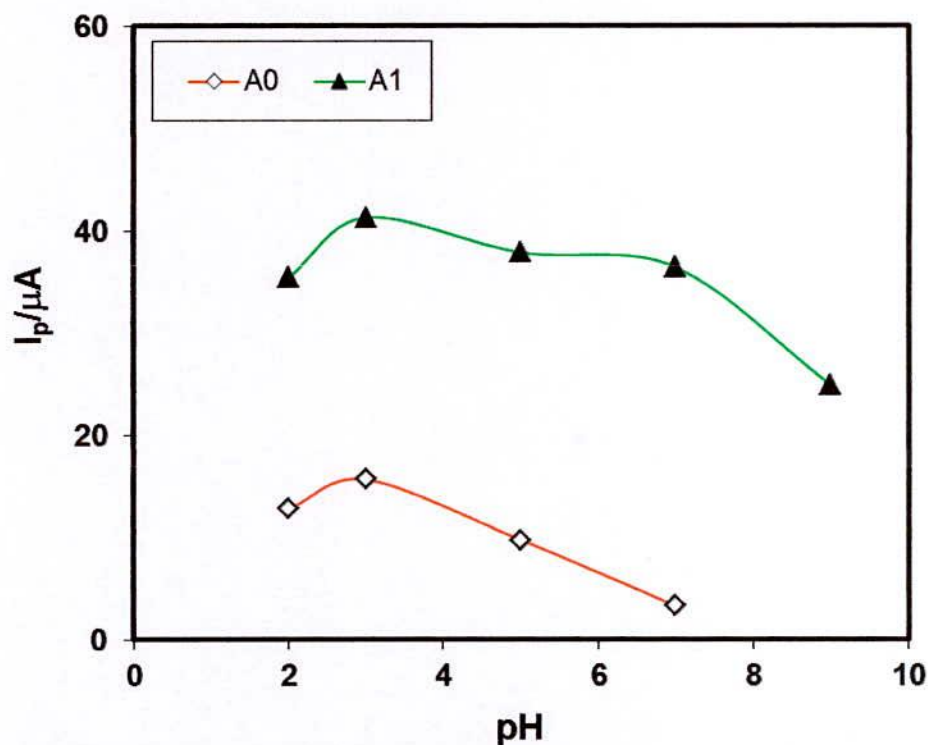


Fig. 4.168: Plots of peak current ( $I_p$ ) versus different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

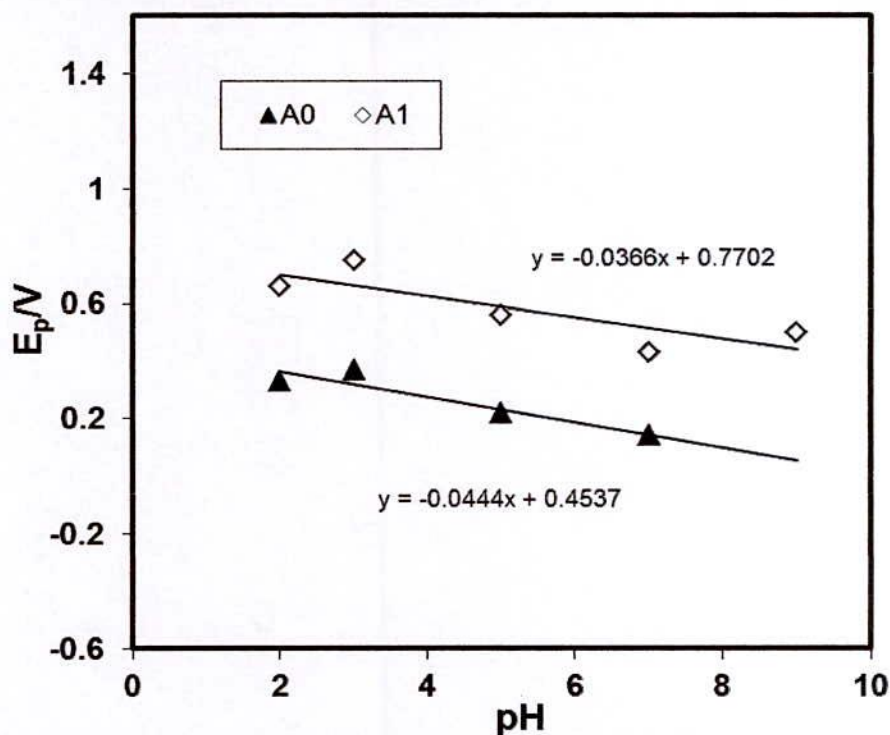


Fig. 4.169: Plots of peak potential ( $E_p$ ) versus different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

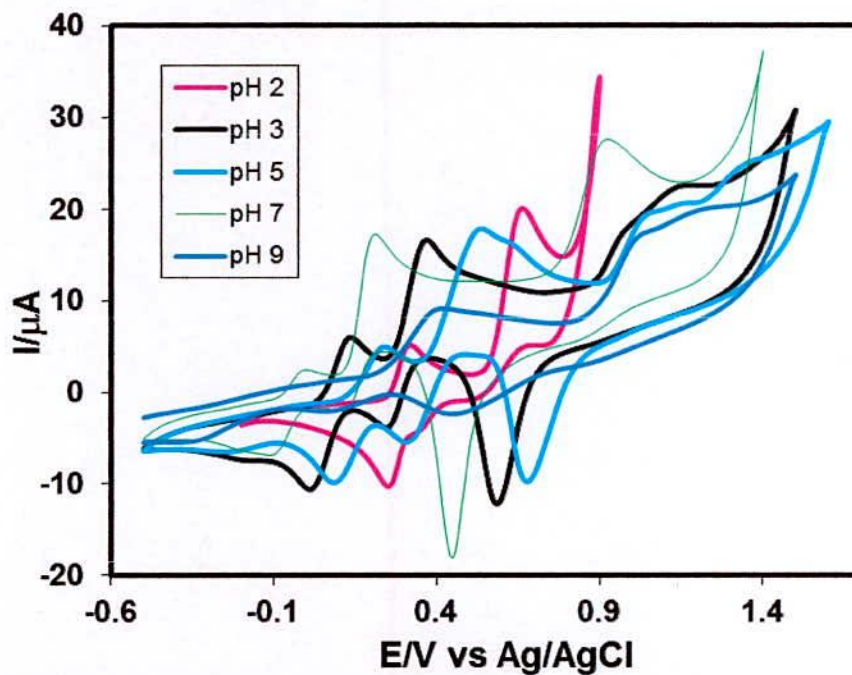


Fig. 4.170: Comparison of cyclic voltammogram of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)



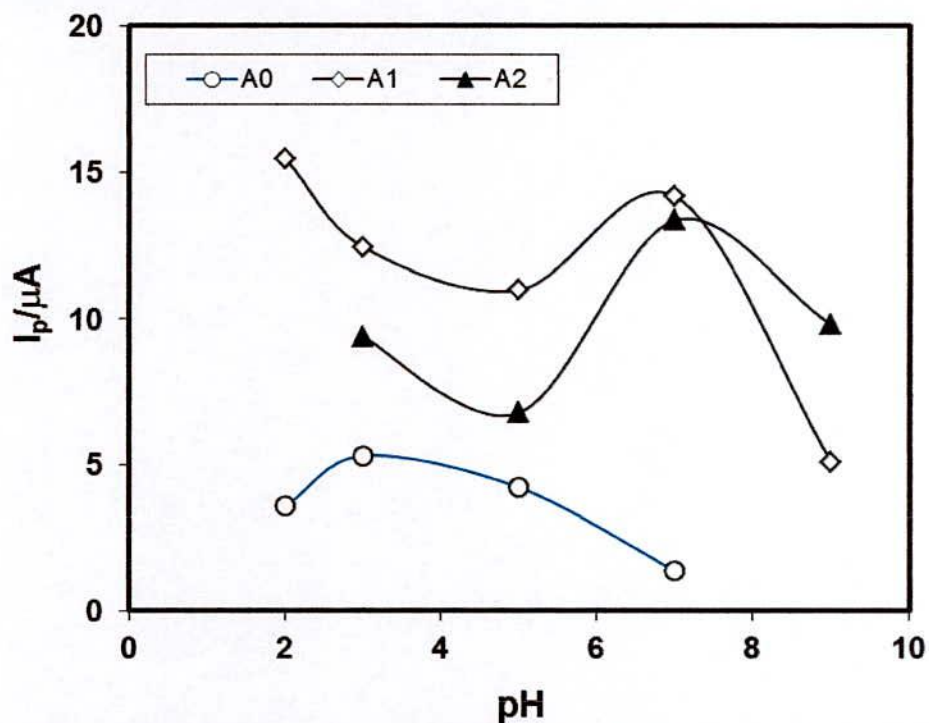


Fig. 4.171: Plots of peak current ( $I_p$ ) versus pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

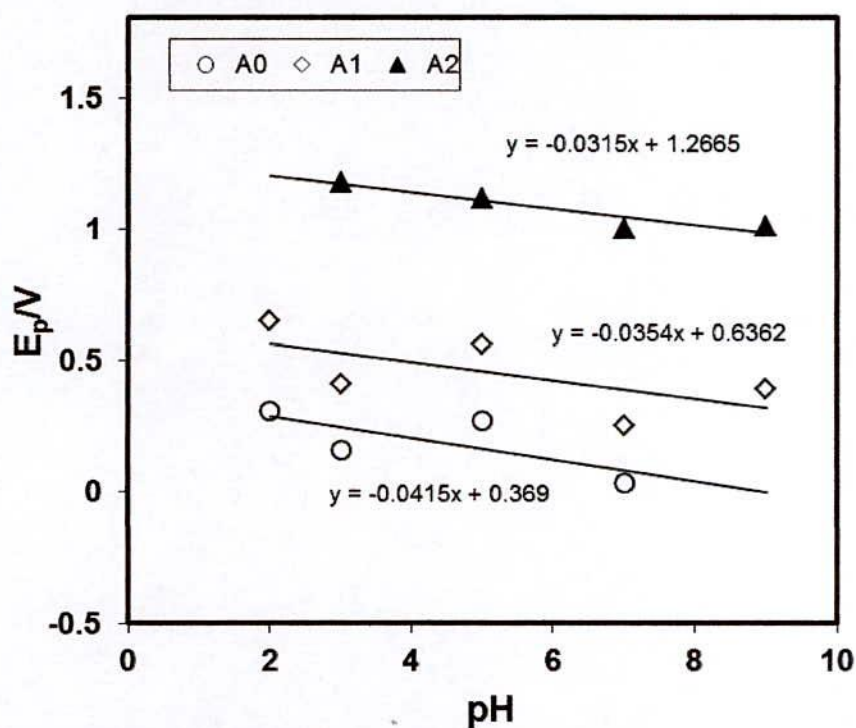


Fig. 4.172: Plots of peak potential ( $E_p$ ) versus pH of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

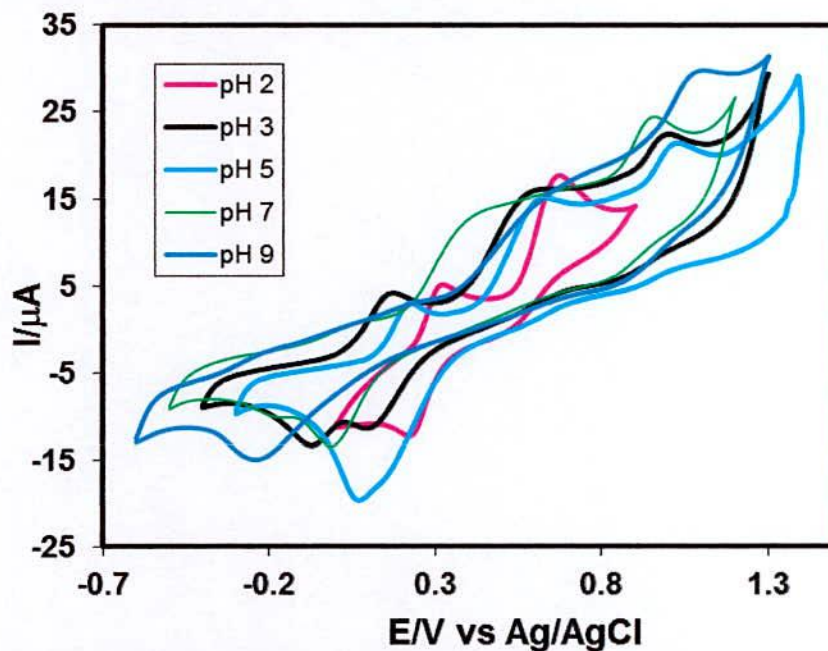


Fig. 4.173: Comparison of cyclic voltammogram of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

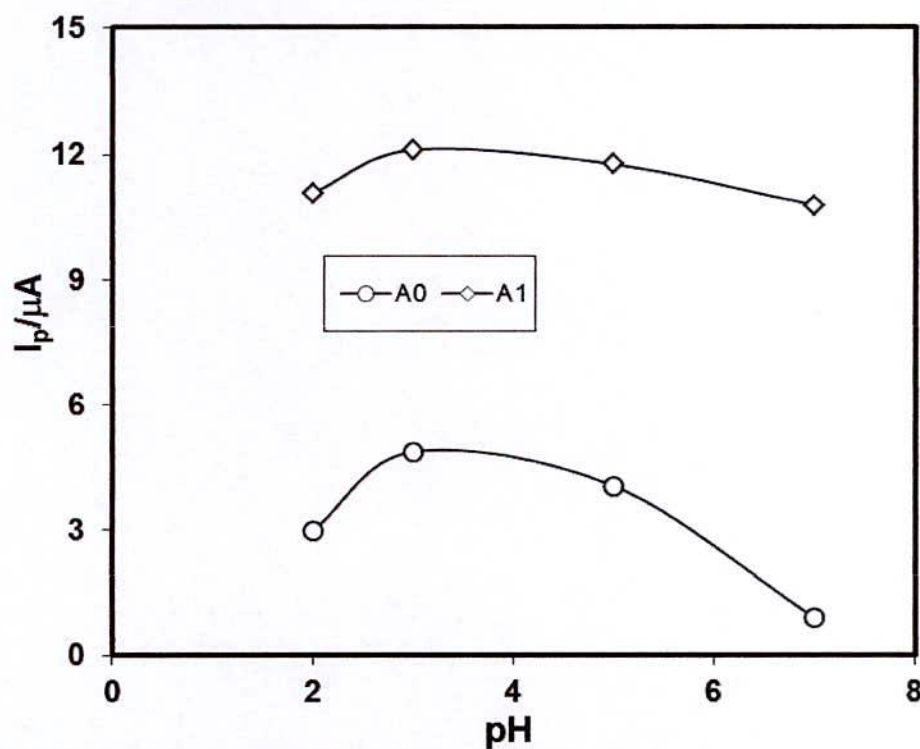


Fig. 4.174: Plots of peak current ( $I_p$ ) versus pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)



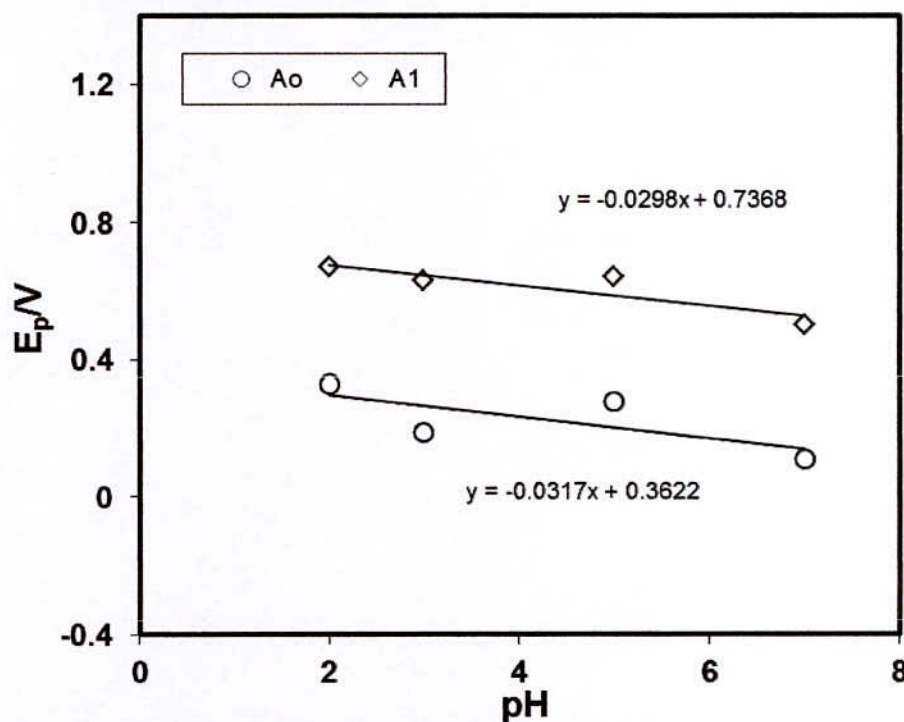


Fig. 4.175: Plots of peak potential ( $E_p$ ) versus pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle)

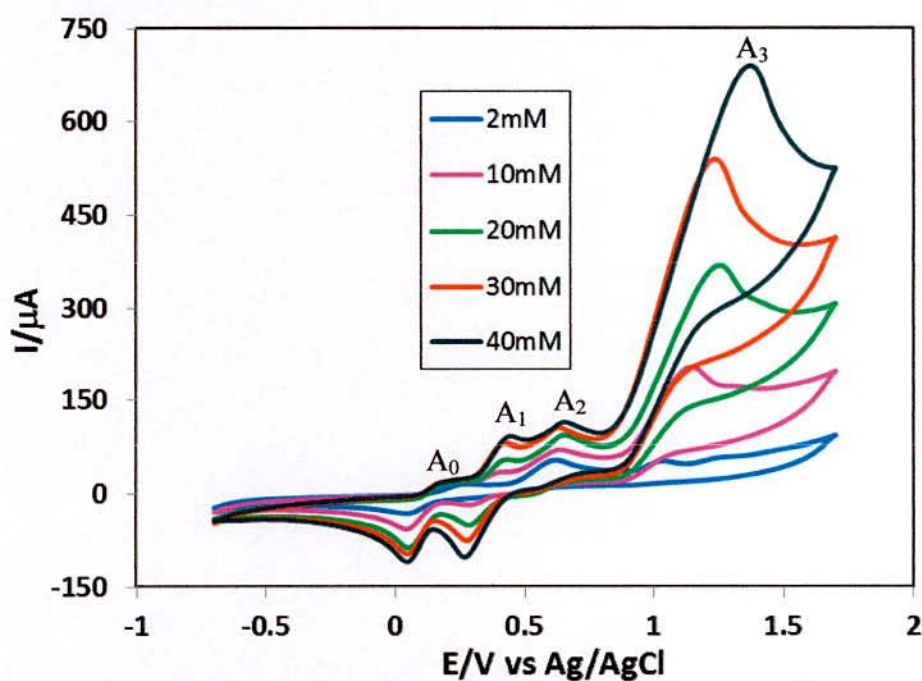


Fig. 4.176: Comparison of cyclic voltammogram of different concentration (2, 10, 20, 30 and 40mM) of sulfanilic acid + fixed 2mM catechol of GC electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle), where  $A_0$ = appeared anodic peak,  $A_1$ = 1<sup>st</sup> anodic peak,  $A_2$ = 2<sup>nd</sup> anodic peak,  $A_3$ = 3<sup>rd</sup> anodic peak

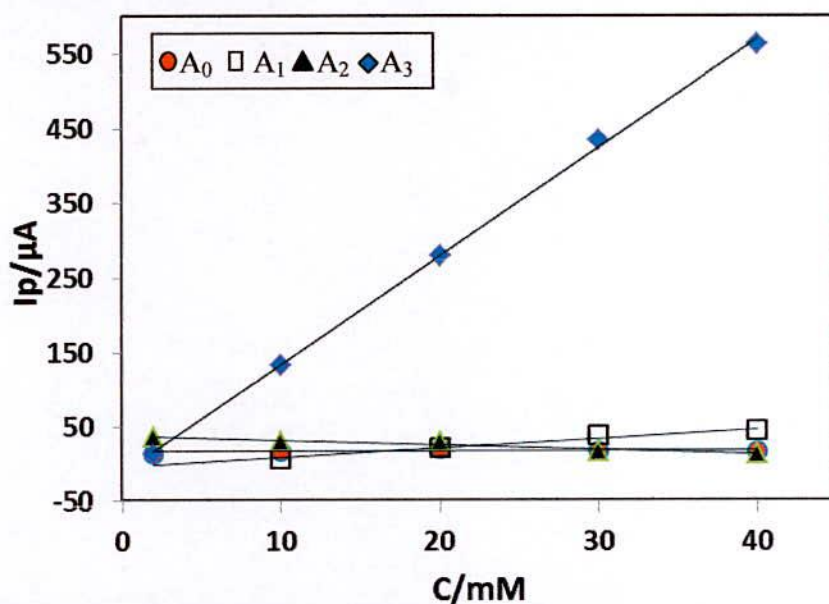


Fig. 4.177: Plots of peak current ( $I_p$ ) versus concentration (C) of sulfanilic acid (2, 10, 20, 30 and 40mM) + fixed 2mM catechol of GC electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

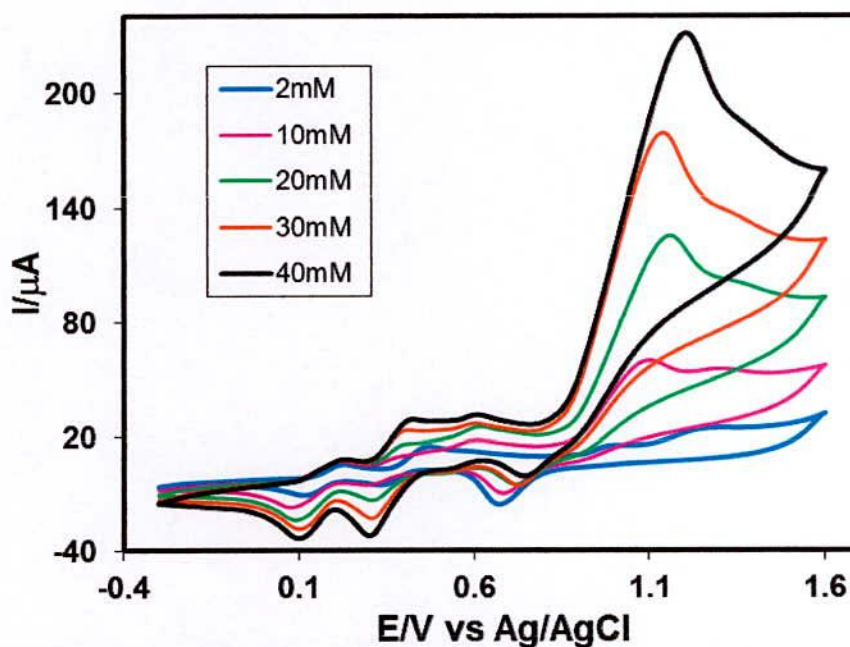


Fig. 4.178: Comparison of cyclic voltammogram of different concentration (2, 10, 20, 30 and 40mM) of sulfanilic acid + fixed 2mM catechol of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle)



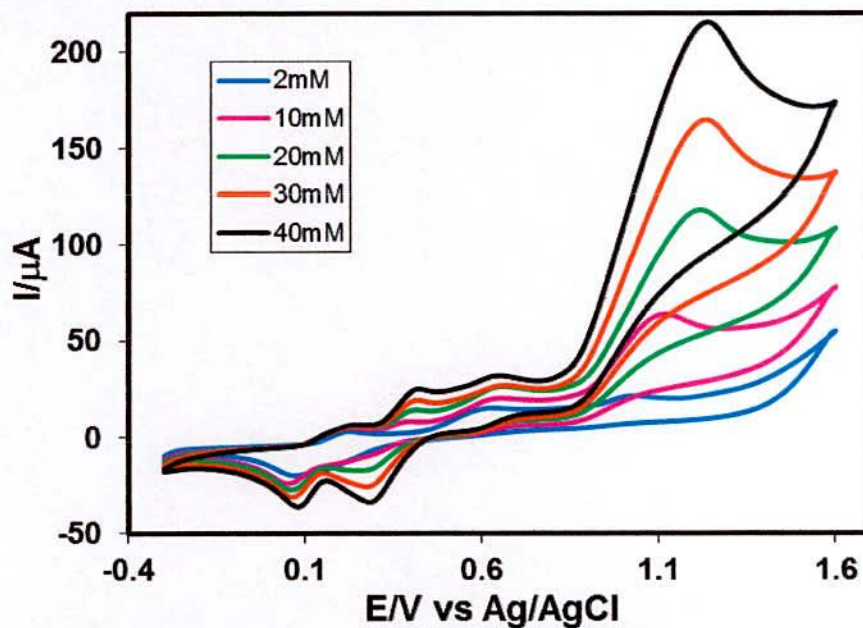


Fig. 4.179: Comparison of cyclic voltammogram of different concentration (2, 10, 20, 30 and 40mM) of sulfanilic acid + fixed 2mM catechol of Pt electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

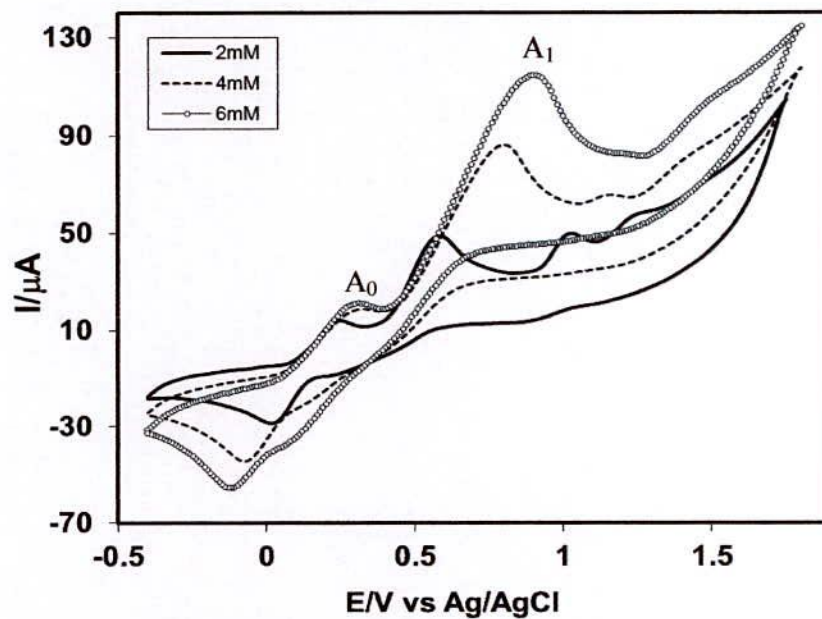


Fig. 4.180: CV of composition change of catechol (2, 4 and 6mM) + fixed composition (2mM) of sulfanilic acid of GC electrode in buffer solution (pH 3) at scan rate 0.1Vs<sup>-1</sup> (2<sup>nd</sup> cycle)

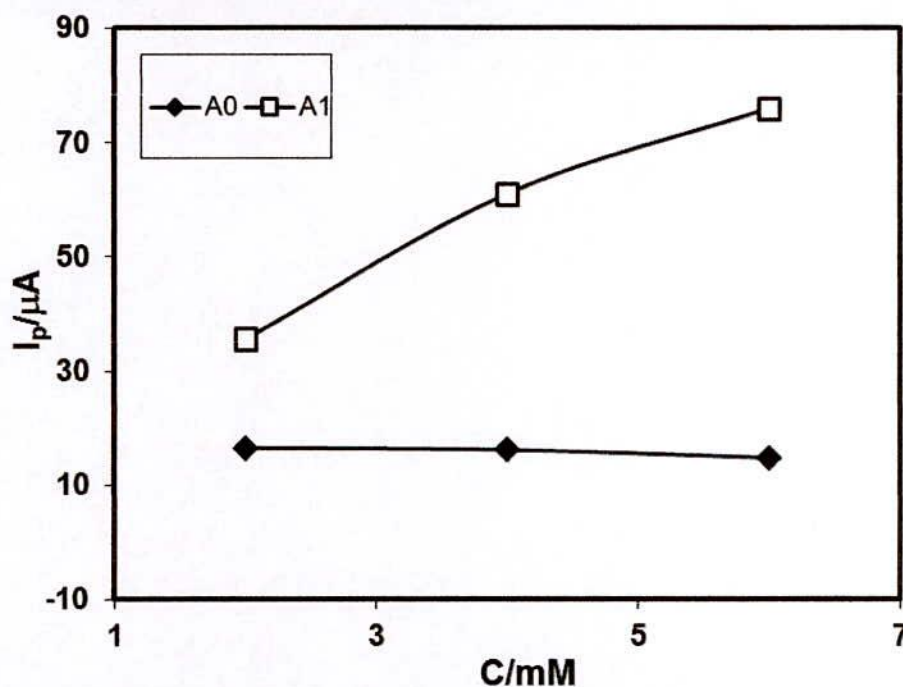


Fig. 4.181: Plots of anodic peak current ( $I_p$ ) vs different concentration (C) of catechol + fixed 2mM sulfanilic acid of GC electrode in buffer solution (pH 3) at scan rate  $0.1 \text{Vs}^{-1}$  ( $2^{\text{nd}}$  cycle)

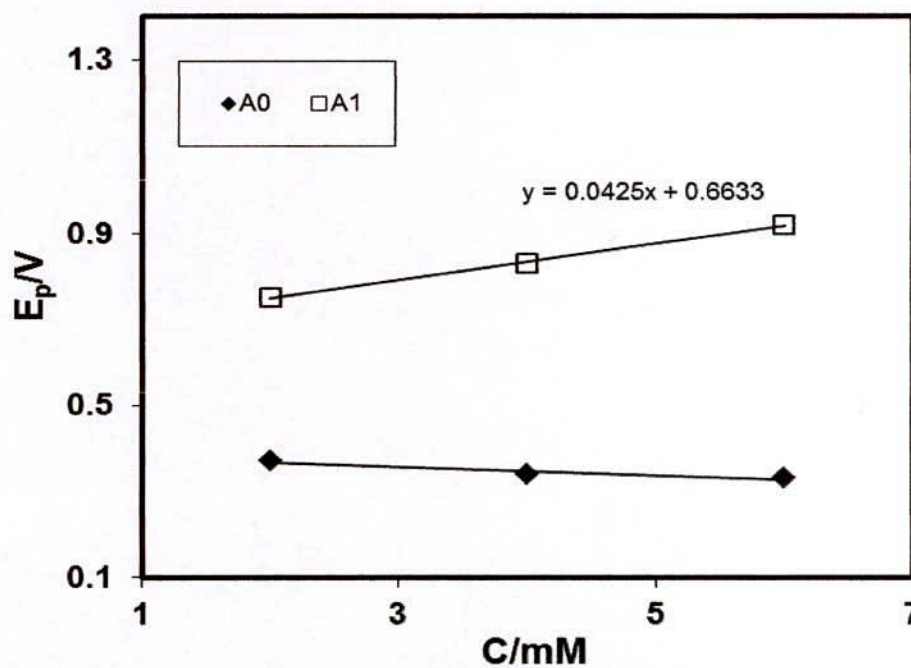


Fig. 4.182: Plots of peak potential ( $E_p$ ) versus different concentration (C) of catechol (2, 4 and 6mM) + fixed 2mM sulfanilic acid of GC electrode in buffer solution (pH 3) at scan rate  $0.1 \text{V/s}$  ( $2^{\text{nd}}$  cycle)



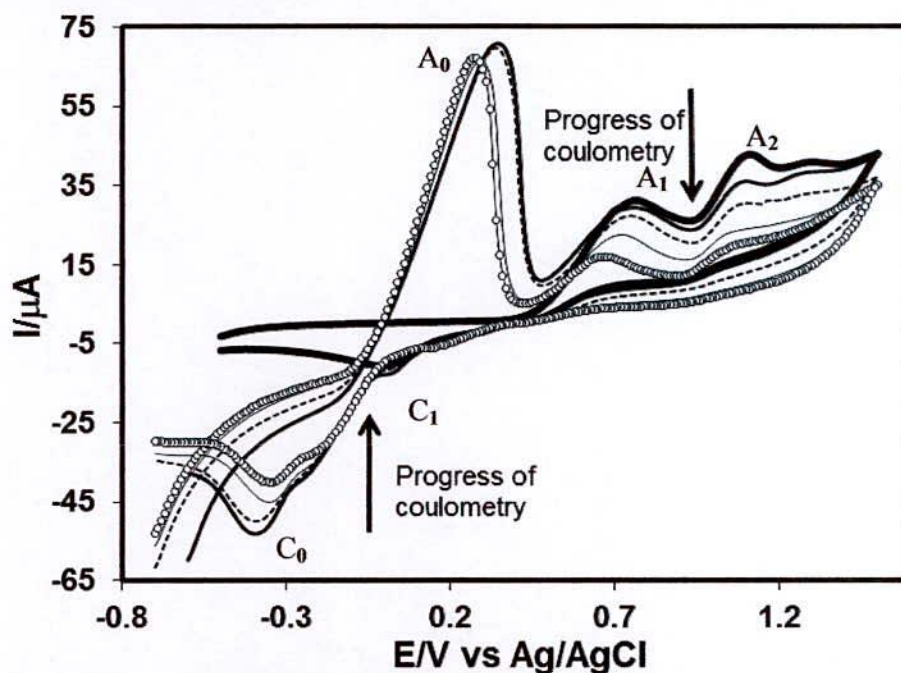


Fig. 4.183: Cyclic voltammogram of 1mM catechol in presence of 1mM sulfanilic acid of GC electrode during controlled potential coulometry at potential 0.5V in buffer solution (pH 3) at scan rate 0.1V/s

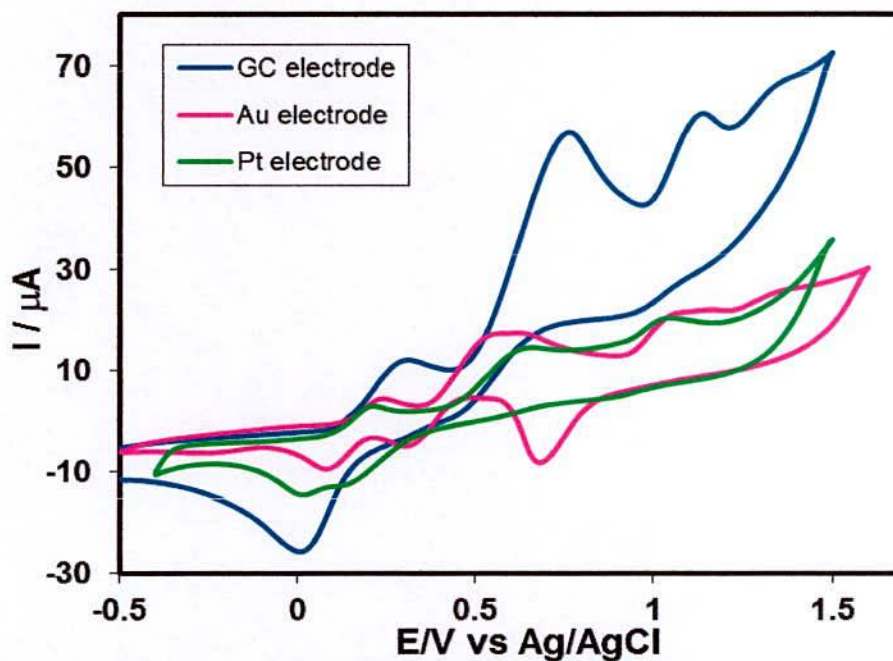


Fig. 4.184: Comparison of cyclic voltammogram of different electrode (GC, Au and Pt) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> cycle)

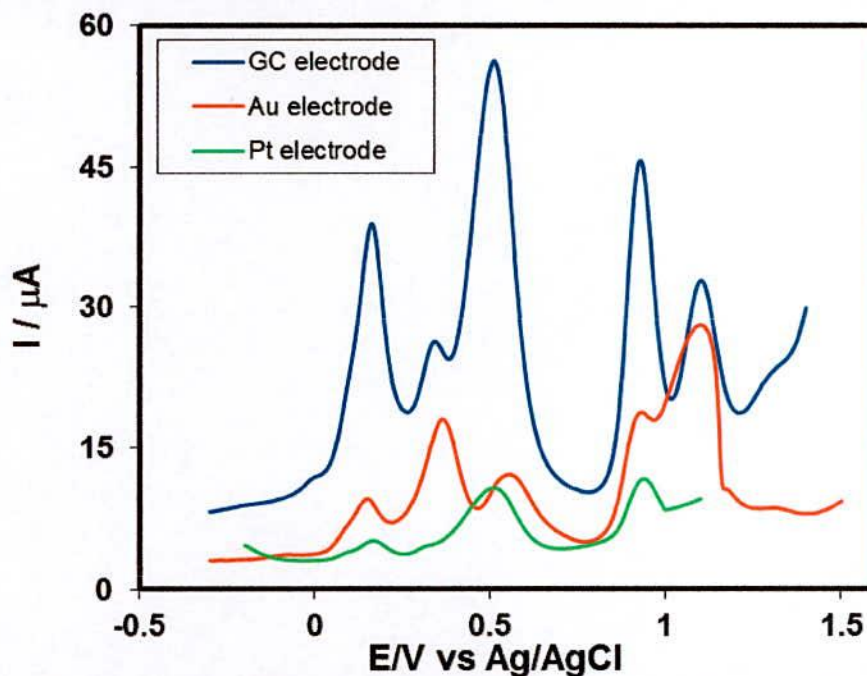


Fig. 4.185: Comparison of differential pulse voltammogram (DPV) of different electrode (GC, Au and Pt) of 2mM sulfanilic acid + 2mM catechol in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> oxidation),  $E_{pulse}$  0.02V and  $t_{pulse}$  20ms

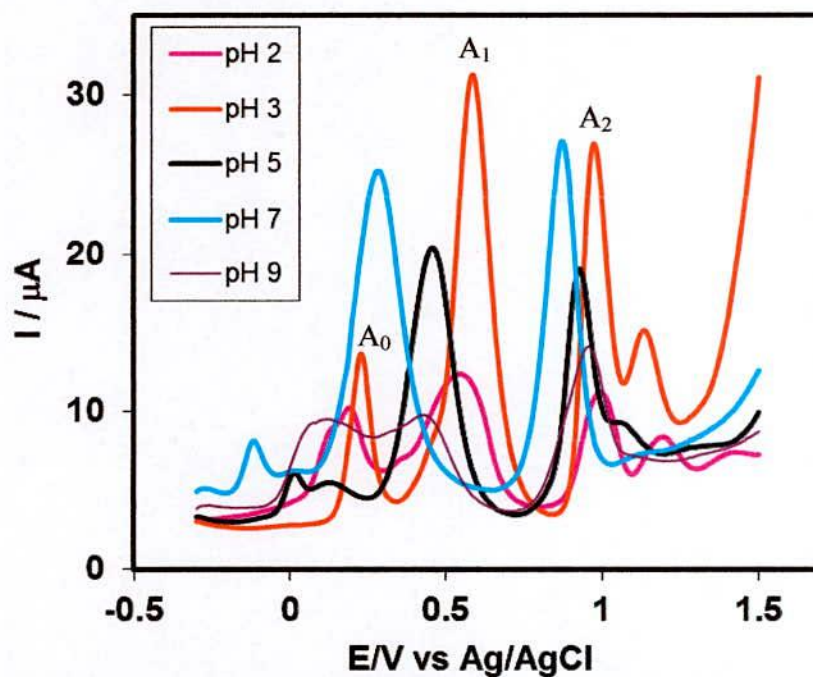


Fig. 4.186: Comparison of DPV of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation),  $E_{pulse}$  0.02V and  $t_{pulse}$  20ms



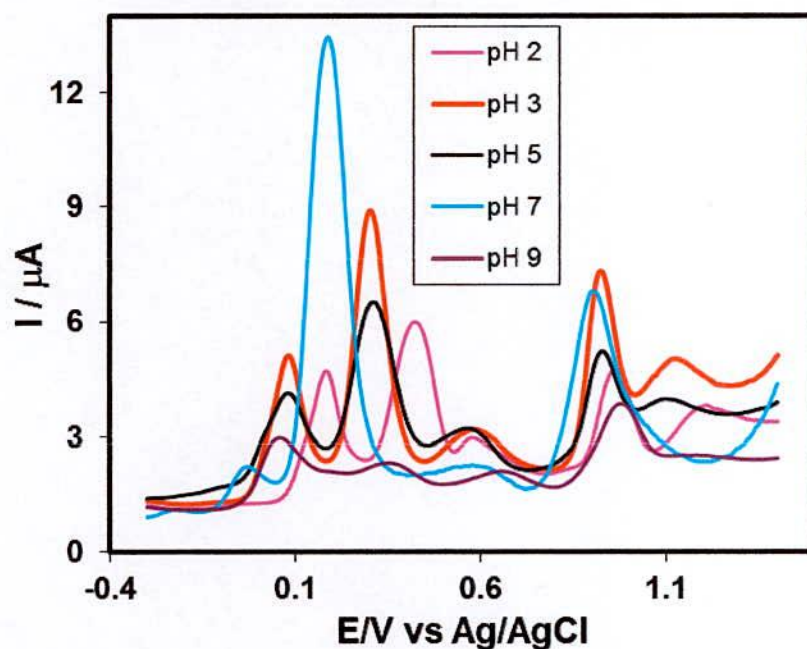


Fig. 4.187: Comparison of DPV of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Au electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation),  $E_{pulse}$  0.02V and  $t_{pulse}$  20ms

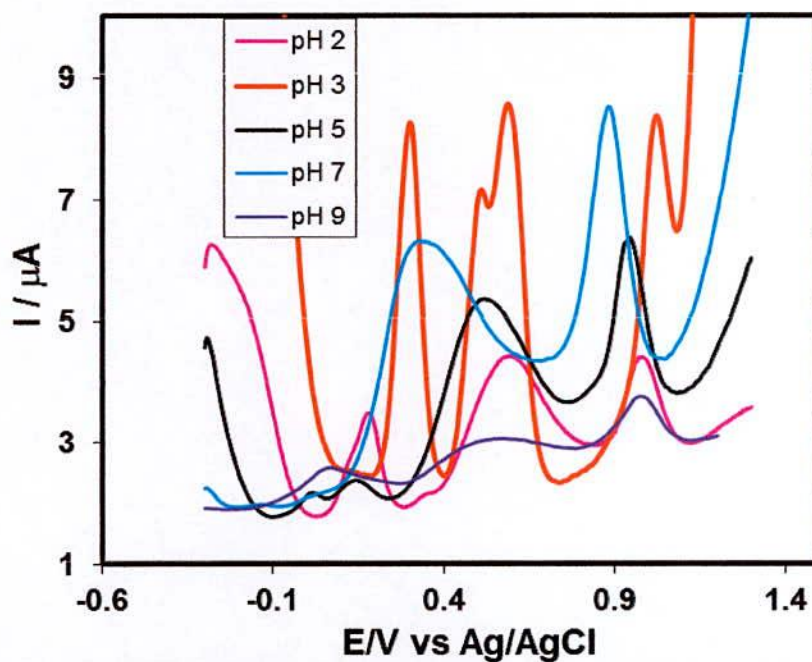


Fig. 4.188: Comparison of DPV of different pH (2, 3, 5, 7 and 9) of 2mM sulfanilic acid + 2mM catechol of Pt electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation),  $E_{pulse}$  0.02V and  $t_{pulse}$  20ms

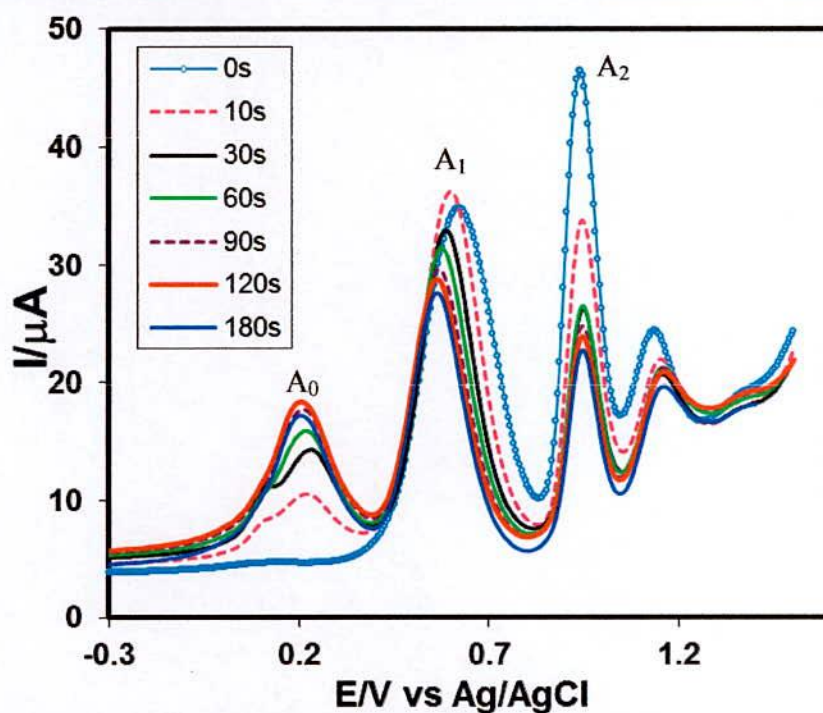


Fig. 4.189: DPV of deposition time change of 2mM sulfanilic acid + 2mM catechol of GC electrode in buffer solution (pH 3) at scan rate 0.1 V/s,  $E_{pulse}$  0.02V and  $t_{pulse}$  20ms

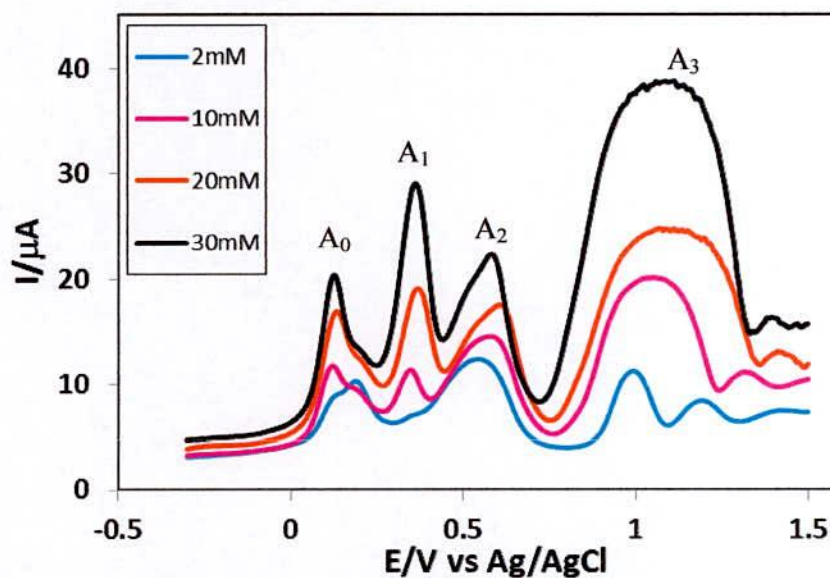


Fig. 4.190: Comparison of DPV of different concentration (2, 10, 20 and 30mM) of sulfanilic acid + fixed 2mM catechol of GC electrode in buffer solution (pH 3) at scan rate 0.1 V/s (2<sup>nd</sup> oxidation),  $E_{pulse}$  0.02V and  $t_{pulse}$  20ms



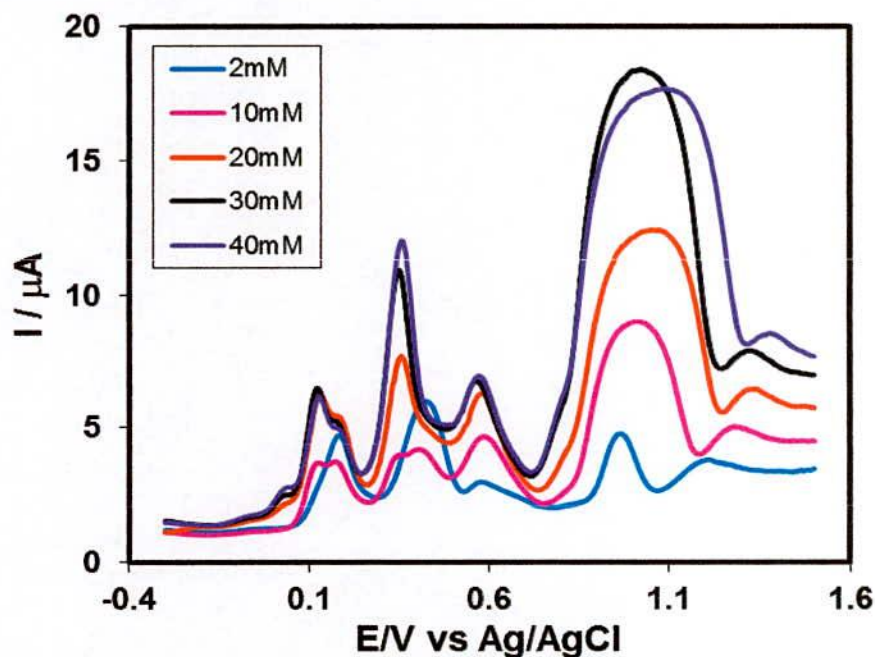


Fig. 4.191: Comparison of DPV of different concentration (2, 10, 20 and 30mM) of sulfanilic acid + fixed 2mM catechol of Au electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> oxidation),  $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms

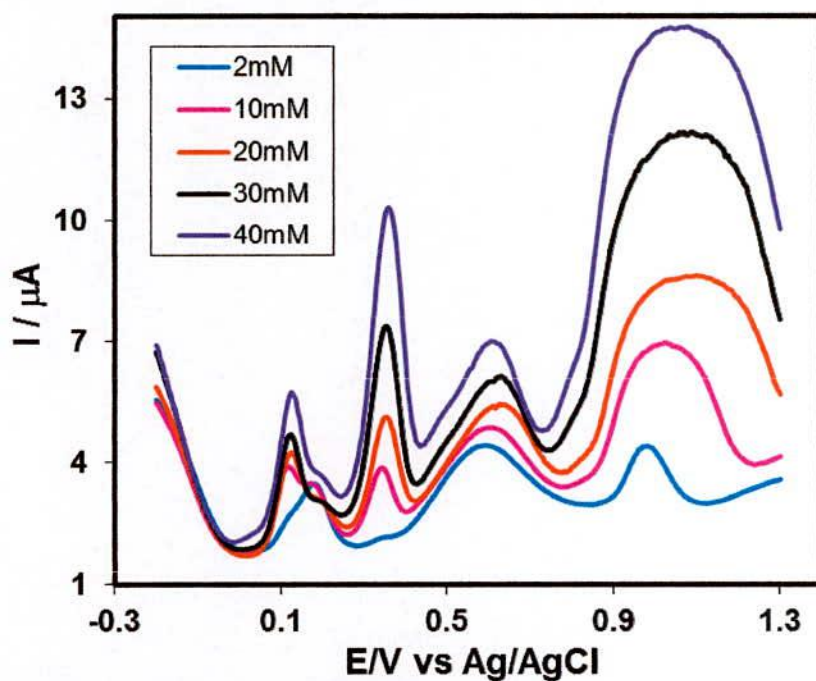


Fig. 4.192: Comparison of DPV of different concentration (2, 10, 20 and 30mM) of sulfanilic acid + fixed 2mM catechol of Pt electrode in buffer solution (pH 3) at scan rate 0.1V/s (2<sup>nd</sup> oxidation),  $E_{\text{pulse}}$  0.02V and  $t_{\text{pulse}}$  20ms

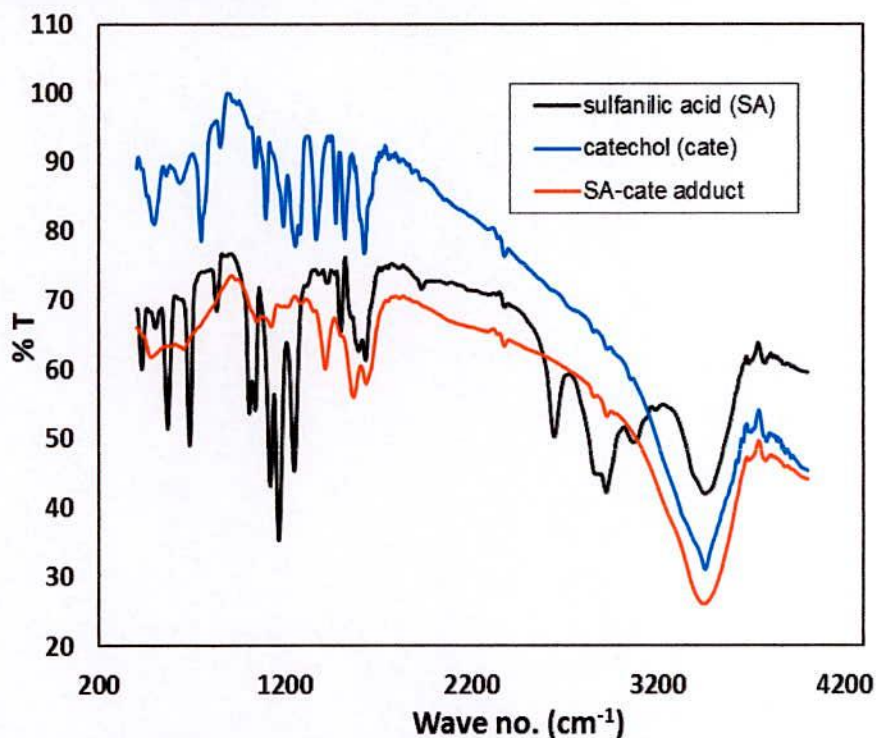


Fig. 4.193: Comparison of FTIR of only catechol, only sulfanilic acid and catechol-sulfanilic acid adduct

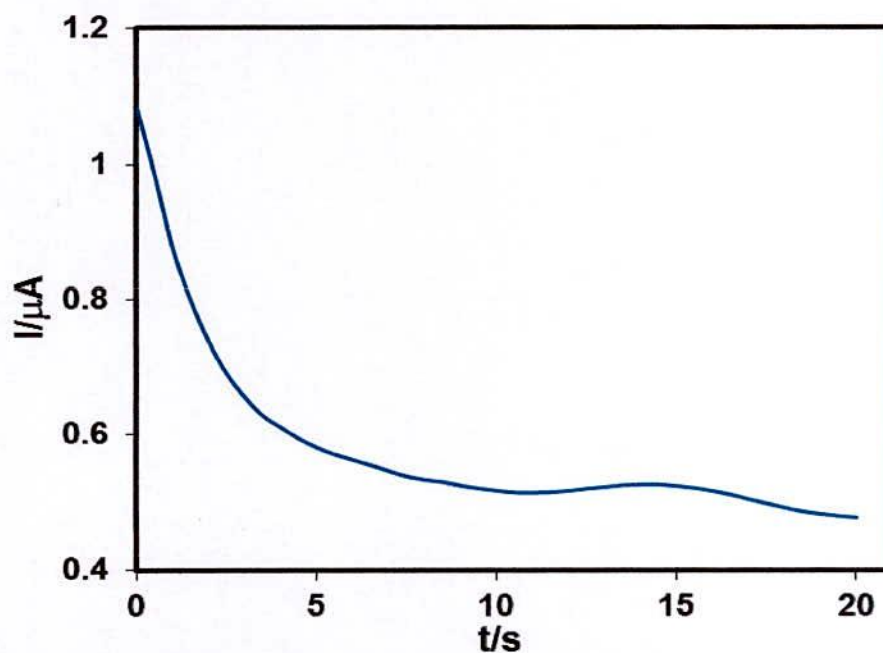


Fig. 4.194: Chronoamperometry curve of 2mM sulfanilic acid + 2mM catechol of GC electrode in buffer solution (pH 3) for forward direction at potential 0.34V



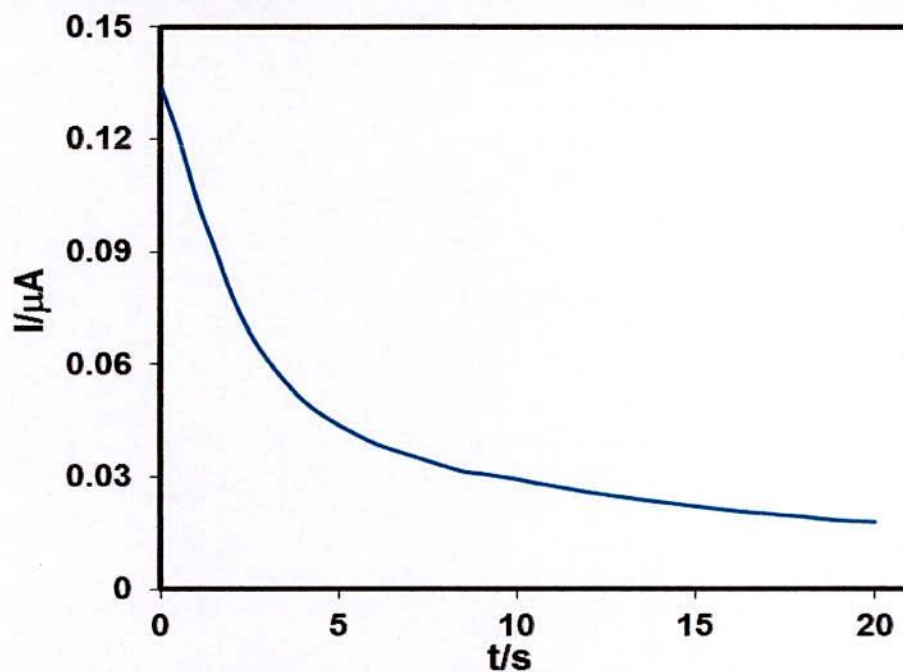


Fig. 4.195: Chronoamperometry curve of 2mM sulfanilic acid + 2mM catechol of Au electrode in buffer solution (pH 3) at potential 0.26V

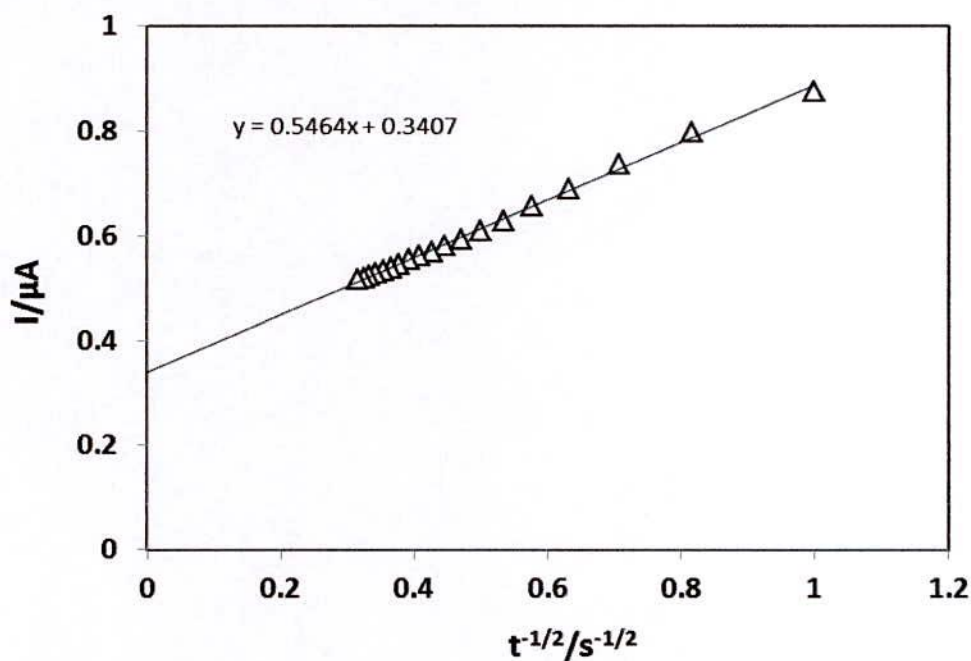


Fig. 4.196: Cottrell plots of the back-ground subtracted currents for 2mM catechol + 2mM sulfanilic acid of GC electrode in buffer solution (pH 3) at potential 0.26V

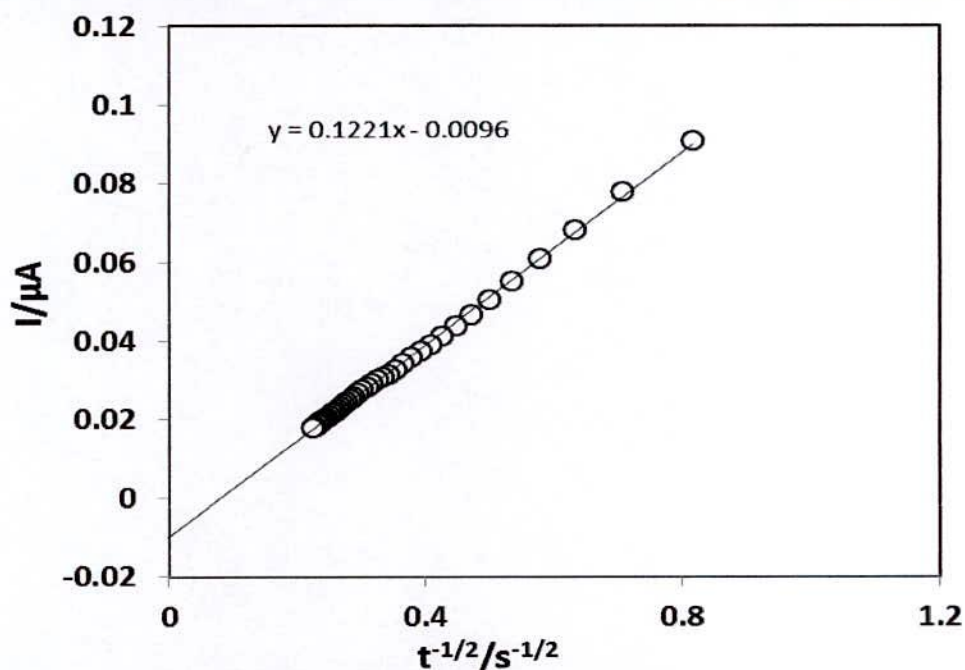


Fig. 4.197: Cottrell plots of the back-ground subtracted currents for 2mM catechol + 2mM sulfanilic acid of Au electrode in buffer solution (pH 3) at potential 0.26V

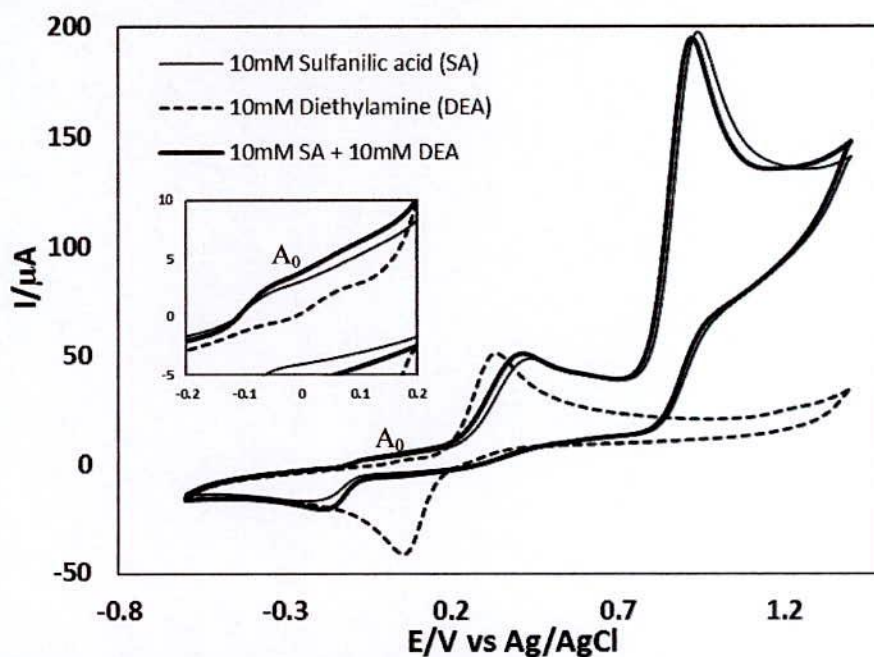


Fig. 4.198: Comparison of CV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 10mM SA + 10mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1 V/s (2<sup>nd</sup> cycle). Inset: appeared anodic peak ( $A_0$ )



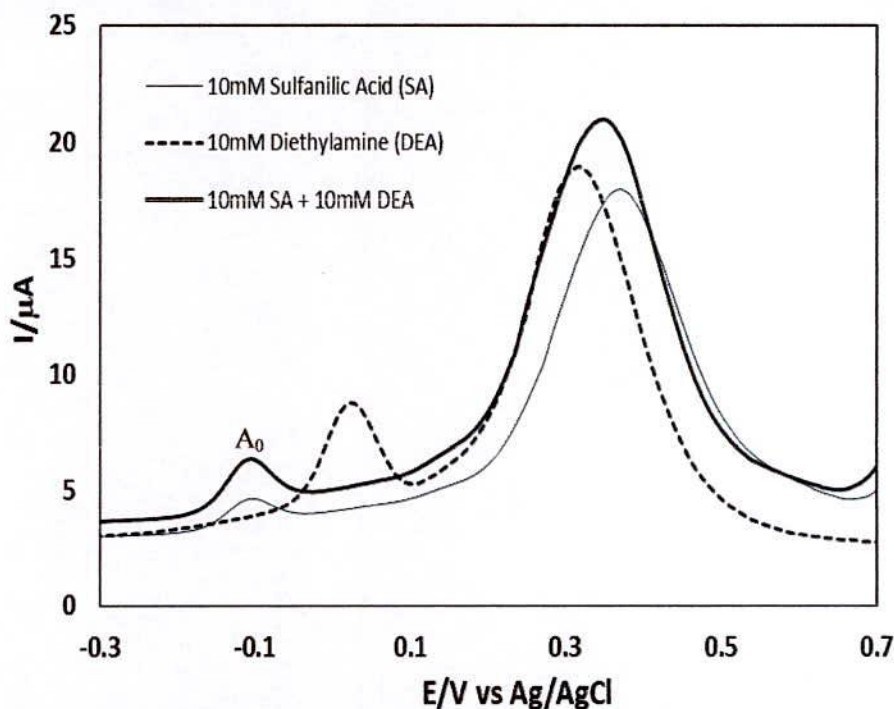


Fig. 4.199: Comparison of DPV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 10mM SA + 10mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation)

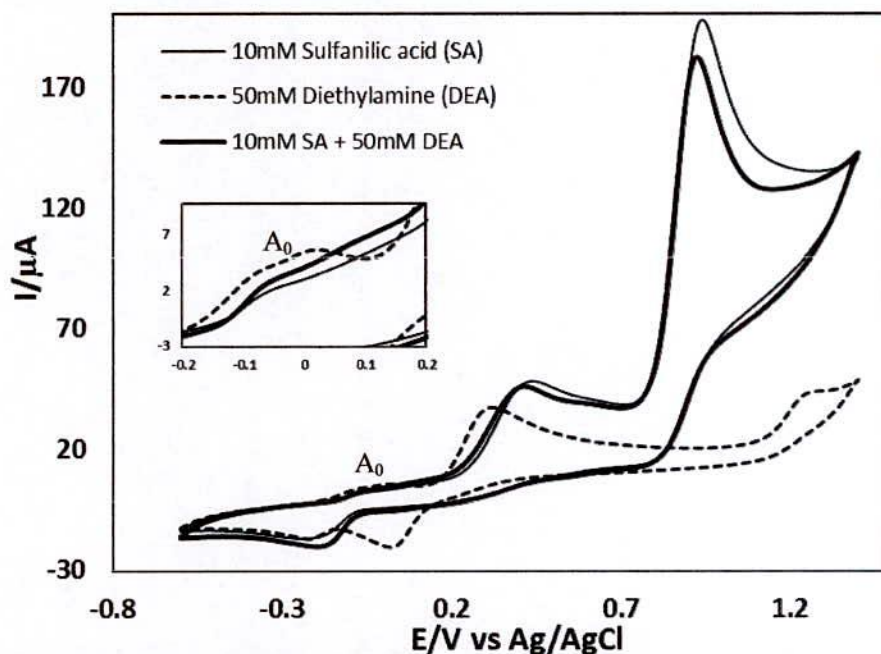


Fig. 4.200: Comparison of CV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 10mM SA + 50mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle). Inset: appeared anodic peak ( $A_0$ )

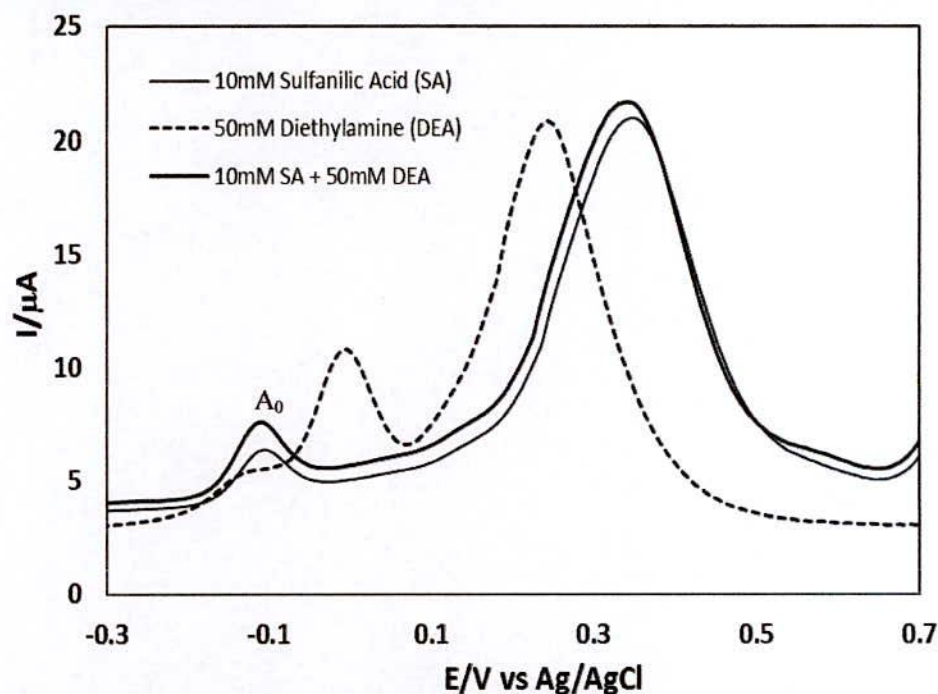


Fig. 4.201: Comparison of DPV of 2mM catechol in presence of 10mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 10mM SA + 50mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1 V/s (2<sup>nd</sup> oxidation)

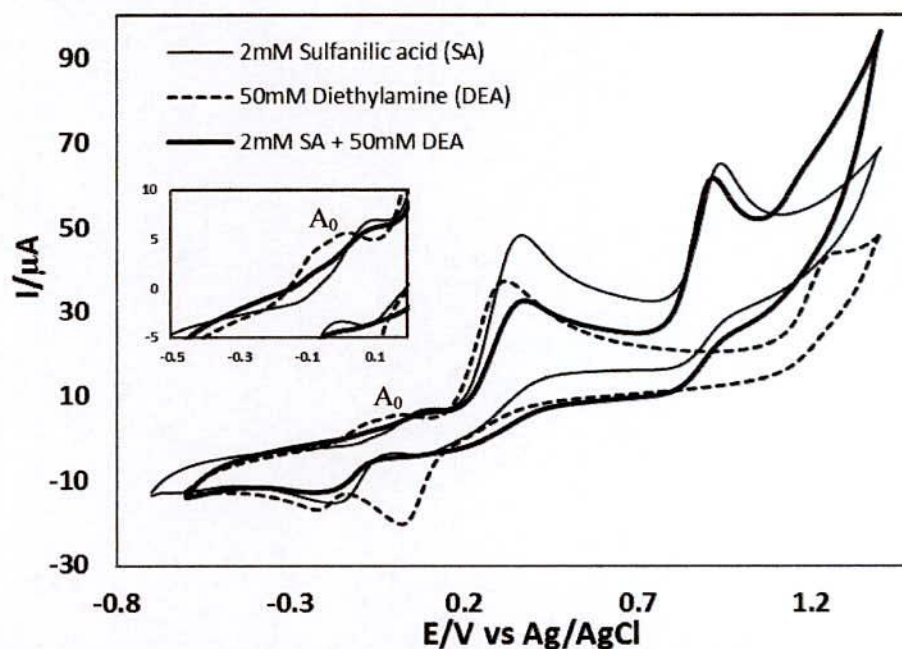


Fig. 4.202: Comparison of CV of 2mM catechol in presence of 2mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 2mM SA + 50mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1 V/s (2<sup>nd</sup> cycle). Inset: appeared anodic peak ( $A_0$ )



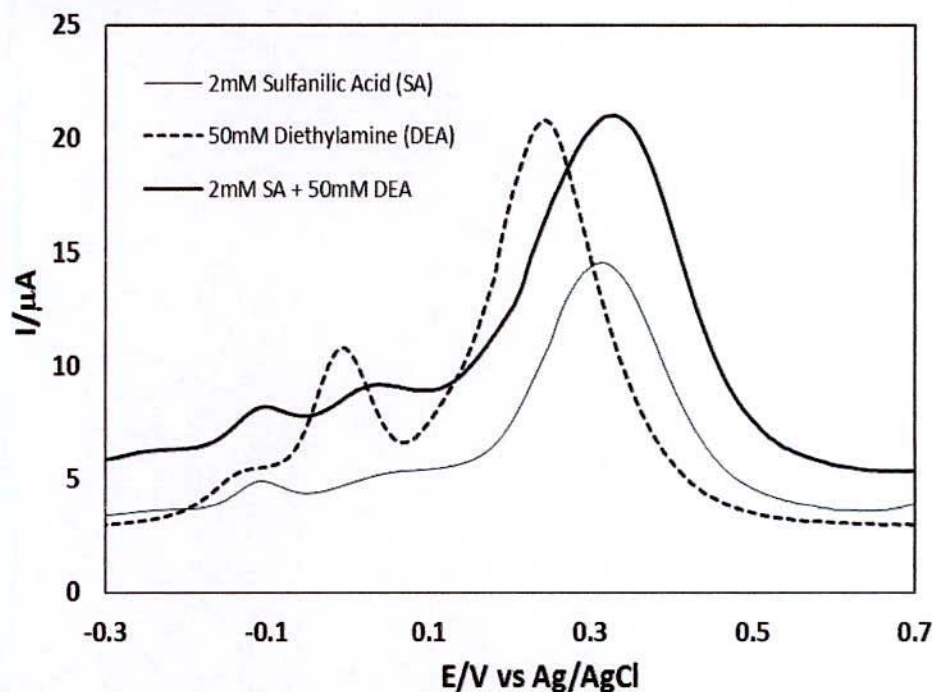


Fig. 4.203: Comparison of DPV of 2mM catechol in presence of 2mM sulfanilic acid (SA), 50mM diethylamine (DEA) and 2mM SA + 50mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> oxidation)

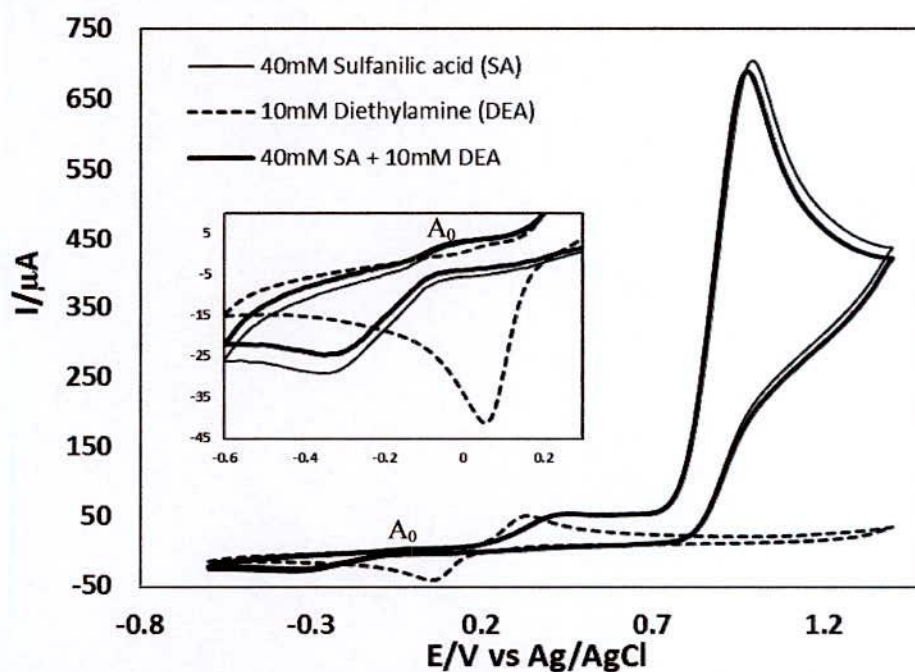


Fig. 4.204: Comparison of CV of 2mM catechol in presence of 40mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 40mM SA + 10mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1V/s (2<sup>nd</sup> cycle). Inset: appeared anodic peak (A<sub>0</sub>)

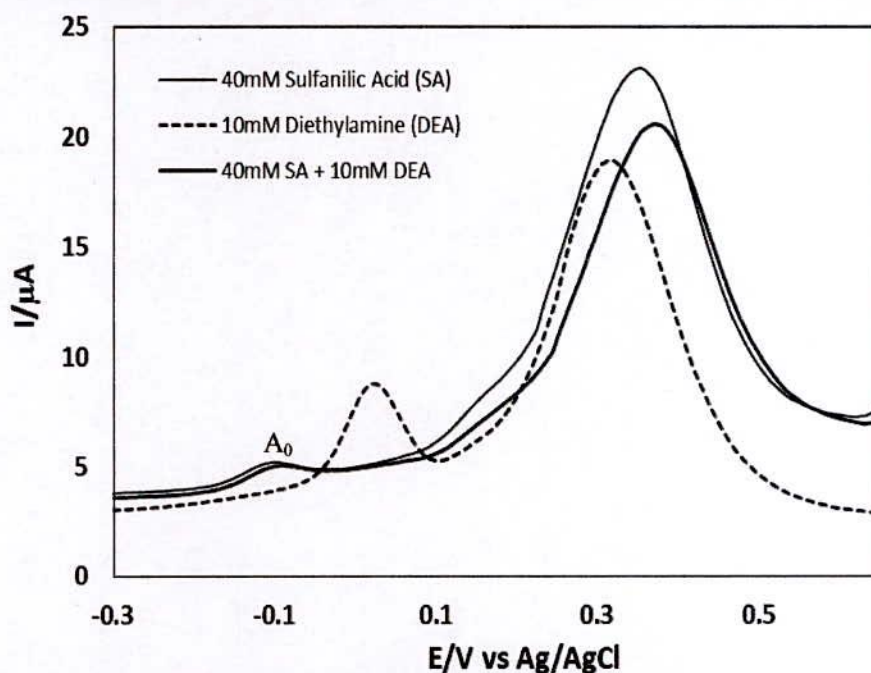


Fig. 4.205: Comparison of DPV of 2mM catechol in presence of 40mM sulfanilic acid (SA), 10mM diethylamine (DEA) and 40mM SA + 10mM DEA in buffer solution (pH 7) of GC electrode at scan rate 0.1 V/s (2<sup>nd</sup> oxidation)



## CHAPTER V

## Conclusions

The reaction of electrochemically generated *o*-benzoquinone from oxidation of catechol as Michael acceptors with diethylamine, sulfanilic acid and sulfanilic acid + diethylamine as nucleophiles has been studied in aqueous solution with various pH, different electrodes and different concentration of nucleophiles using Cyclic voltammetry (CV), Controlled potential coulometry (CPC), Differential pulse voltammetry (DPV) and Chronoamperometry (CA) techniques. The participation of reaction of *o*-benzoquinone with nucleophiles in the second scan of potential was observed.

Pure diethylamine are electro-inactive whereas pure catechol and sulfanilic acid are electro-active. The redox reactions of catechol are quasi-reversible. The products generated from the reaction that undergo electron transfer at more negative potentials than the catechol. Electrode effects on CV and DPV of catechol in presence of diethylamine and sulfanilic acid was investigated. The nature of voltammograms, peak position and current intensity for the studied systems are different for different electrodes. The voltammetric response of GC electrode is better than Au and Pt electrodes.

The nucleophilic substitution reactions are pH dependent. For diethylamine the maximum peak current is obtained at pH 7 whereas the maximum peak current of sulfanilic acid is obtained at pH 3. The electro-oxidation of catechol-diethylamine adduct is facilitated in neutral media whereas catechol-sulfanilic acid in acid media. The oxidation reaction of catechol-diethylamine adduct preceded via the  $1e^-/1H^+$  process whereas catechol-sulfanilic acid adduct proceeded via the  $2e^-/2H^+$  process. This also suggests that during the reaction not only electron but also proton are released from the catechol-amine adduct. The reactions are also concentration dependent. The reaction was mostly favorable in 250 mM of diethylamine

with fixed 2 mM of catechol. The reaction of catechol in presence of sulfanilic acid was favorable in 2 mM sulfanilic acid with 2 mM catechol.

All the studied system shows that peak current of both the anodic and the corresponding cathodic peaks increases with the increasing of scan rate. The nearly proportionality of the anodic and corresponding cathodic peak suggest that the peak current of the reactant at each redox reaction is controlled by diffusion process. The current function decreased with the increasing of scan rate is ascribed that the nucleophilic addition of diethylamine occurs through an ECE mechanism but of sulfanilic acid occurs through an ECECE mechanism. It is seen that the diethylamine is less reactive than the sulfanilic acid toward the catechol.

Controlled-potential coulometry was studied of catechol in presence of diethylamine and sulfanilic acid. During the course of coulometry the appeared anodic and cathodic peak height was increase to the advancement of coulometry, parallel to the decrease in height of existing anodic and cathodic peaks. The electro-synthesized products originated from catechol with diethylamine and sulfanilic acid was isolated. The formations of products were also confirmed by FTIR spectra.



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