

Voltammetric Studies of Catechol Behavior in Presence of 4,4'-bipyridine via Convulsive Voltammetry, Chronoamperometry and Digital Simulation

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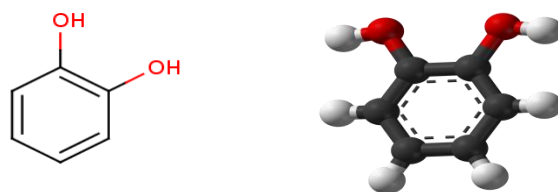
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Voltammetric studies of catechol behavior with and without 4,4'-bipyridine was performed via cyclic, convulsive voltammetry, chronoamperometric and digital simulation at gold electrode in 0.5 M KNO₃ aqueous solution as background electrolyte. This study aim o to explain the catechol behavior in case of existence of 4,4'-bipyridine in 0.5 M KNO₃ aqueous solution. Voltammetric studies revealed that the electrooxidative process of catechol yield active, o-benzoquinone as intermediate, which reacts with 4, 4'-bipyridine to produce the derivative of catechol substance. The electrochemical parameters were determined experimentally and confirmed via generation of theoretical voltammograms. Based on the voltammetric behavior of the investigated compound, the electrode mechanism was proposed.

Keywords: Convulsive voltammetry, EC process, Chronoamperometry, 4, 4-bipyridine

1. INTRODUCTION

Electrochemistry afford very important and flexible tools for an explanation of the electrochemical electrode processes. Catechol (CC) and 4,4'- bipyridine redox systems have been amply studied because of their biological influence, as well as the fundamental significance of their redox chemistry [1]. CC and HQ isomers usually coexisting in environmental and biological cases and the coincidental measurement of their amount is an interesting subject in electroanalytical chemistry. Some of organic electrode reactions are represented by producing an intermediate which is reacting at the surface of the electrode by EC reaction for species. The major purpose of the voltammetric examinations is the explanation of the type of electrode process of the present system. Amidst the organic substances, catechol can be calmly loss electron and converting to the analogous reactive o-benzoquinone principally due to its small oxidation potential [2]. The structure of catechol is shown below in scheme 1 and its molecular formula is C₆H₆O₂.



Scheme 1. Skelton of catechol

Catechol represent a good example of the biological processes which behave as a reactive place of charge transfer in the framework of several natural and biological reactive compounds able to display both anti- and pro-oxidant nature [3]. Catechol has extreme value, importance in biological analysis because of its good electrochemical activity and it can be useful for characterization of various analytical methods. It is applied in dyeing, photography, agrochemicals, plastic fabrication, rubber, antiseptic, dye stuffs, electroplating and light moderator, in organic combination and preparation, industrial pharmacy [2, 3 - 7].

The aim of this study was to perform a deep illustration analysis of the electrochemical nature of catechol in absence and in the presence of 4, 4'- bipyridine in aqueous solution via convolutive cyclic voltammetry, chronoamperometry and digital simulation due to the lack of the study of these compounds using convolutive voltammetry.

2. EXPERIMENTAL

2.1. Chemicals

From Aldrich Chemical Co. 4,4'-bipyridine, catechol and KNO_3 were purchased and they were used as bought. All chemicals used were of spectral pure grade.

2.2. Instrumentation

Cyclic voltammetry, convolution-deconvolution transforms and chronoamperometry experiments were carried out using Computer-controlled Potentiostat Model 283 and PAR Model 175 Universal Programmer (from EG and G). The experiments were made using a conventional three electrode electrochemical cell arrangement. The gold electrode with area $6.75 \times 10^{-3} \text{ cm}^2$ was used as active electrode, helicoid platinum wire as a counter electrode and saturated Ag/AgCl as a standard electrode. The voltage was measured versus the Ag/AgCl electrode at 25°C and 0.5 mol/L KNO_3 as background electrolyte. Cyclic voltammetric data were carried out at scan rate between 0.01 to 5 V/s at $(25 \pm 2)^\circ\text{C}$.

2.3. Digital simulation

Generation of theoretical cyclic voltammograms is a good way for elucidation of the complicated electrode pathway, confirm and verify the nature of electrochemical reactions and also conducted to inspect the i - E curves for many types of electrode reactions with different rate of electron transfer [8 – 10]. EG & G condosim software package was used for generation of the theoretical cyclic voltammograms via digital simulation on PC computer. The simulation process was performed using finite difference techniques.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry study

The redox nature of catechol in the absence and existence of 4,4'-bipyridine, was achieved experimentally using voltammetric methods e.g., CV, Conv. and chronoamperometry measurements in 0.5 M KNO₃ aqueous solution as background electrolyte at room temperature.

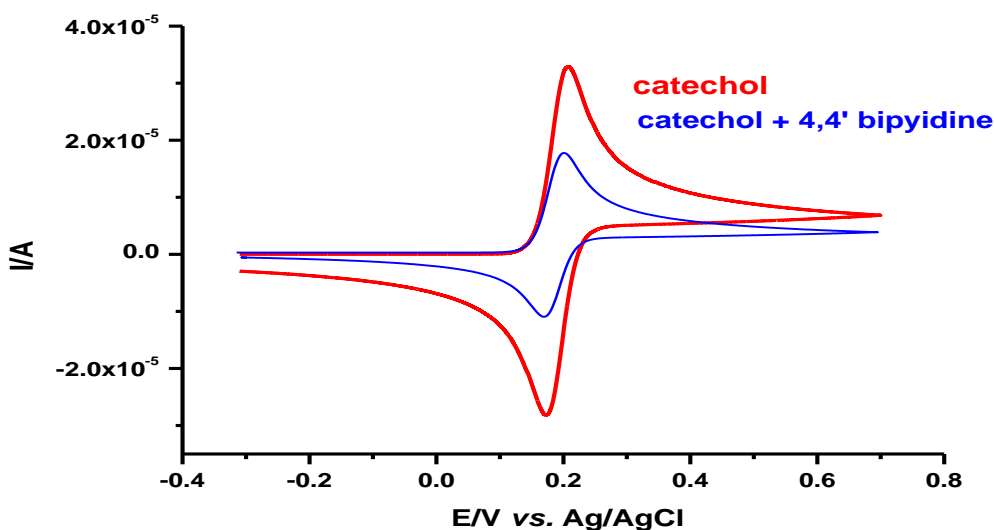


Figure 1. Cyclic voltammograms of 2.5 mM catechol with 2.5 mM of 4, 4'-bipyridine at gold electrode in 0.5 M KNO₃ at scan rate of 0.1 V s⁻¹, T = 25 °C.

As indicated in Figure 1 the cyclic voltammogram of catechol in the absence of 4,4'-bipyridine revealed a single oxidative peak ($E_{pa} = 0.210$ V) coupled with reductive peak ($E_{pc} = 0.183$ V) at 25 °C. The coupled peaks demonstrate a fast, simple electron transfer at all scan rates. While in the presence of 4,4'-bipyridine the oxidative and reductive peaks located at 0.20 V and 0.176 V respectively.

Table 1. Values of the parameters for catechol without 4,4'-bipyridine at a gold electrode using various voltammetric tools and digital simulation (Sim) technique.

Technique	$k_s \times 10^2$ cm.s^{-1}	E^0 /V	$D \times 10^5$ $\text{cm}^2.\text{s}^{-1}$
Sim	4.95	0.195	5.18
CV	4.90	0.197	5.12
Conv.	----	0.192	5.25
			5.31*
Decon.		0.193	5.27
CA	4.65	----	5.65

* Value of D calculated via Eq. (3)

The coupled peaks clarify a sluggish chemical process following a fast electron transfer at all scan rates (EC scheme) [11]. In the proper range of scan rates ($0.01 - 5 \text{ Vs}^{-1}$), the peak separation potentials ($\Delta E_p = E_{pc} - E_{pa}$) exhibits variation between $29 - 31 \pm 2 \text{ mV}$ which similar to the established value (29 mV) for one step $2e^-$ Nernstian process [12]. The estimation of the formal potential (E^0) was executed from the half values of the forward and backward peak potentials point of the voltammograms and cited in Table 1. The heterogeneous rate constant of electron transfer (k_s) was determined from $i - E$ curve via peak separation using ΔE_p values *versus* rate constants [13]. After subtraction of background and uncompensated resistance correction, the diffusion coefficient D was calculated from relationship (1) [12],

$$i_p = (2.99 \times 10^5) n^{3/2} S C^{\text{bulk}} D^{1/2} \nu^{1/2} \quad (1)$$

given that i_p is the maximum amplitude of the peak current, n is the total of electrons involved in reaction, S is the surface electrode area, C^{bulk} is the total concentration of the species and the remaining symbols have the usual definition. The value of calculated D was found to be $5.27 \pm 0.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

3.2. Convolution-deconvolution voltammetry

Convulsive voltammetry has been profitably useful to the scrutiny of the strategy of various electrochemical processes [14 – 20]. The D value of the studied compound was driven from relationship (2), [15]

$$I_{\text{lim}} = n F S D^{1/2} C^{\text{bulk}} \quad (2)$$

Where I_{lim} is the limiting current value accomplished for I_1 when the potential is forced to adequately value past the peak, and the other symbols have their normal meanings. Also, D value was also calculated via the equation (3),

$$I_{\text{lim}} = (i_p)_{\text{rev}} / 2.788 (\nu)^{1/2} \quad (3)$$

where $(i_p)_{\text{rev}}$ was described in equation 1. The I_1 convulsive curve of the examined catechol in case of nonexistence of 4,4'-bipyridine was pictorial in Figure 2 which shows a complete overlay when the potential is driven toward forward direction and when it driven to reverse direction and clearly express the rapidity of electrode reaction [20]

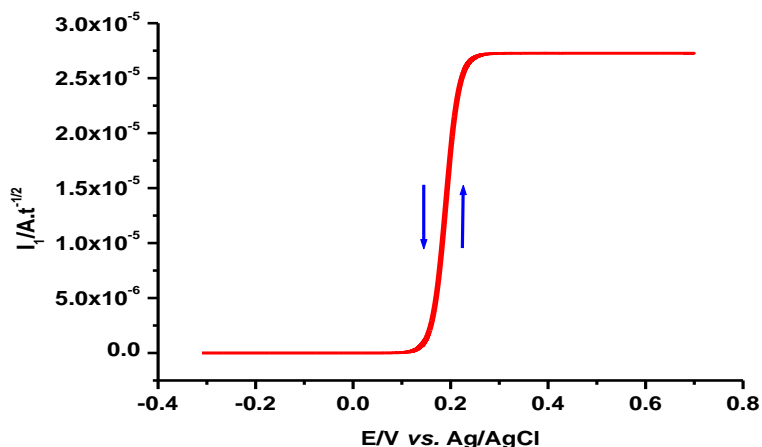


Figure 2. I_1 convolution of catechol in nonexistence of 4,4'-bipyridine in 0.5 M KNO_3 at gold electrode, sweep rate $0.1 \text{ V}\cdot\text{s}^{-1}$, $T = 25 \text{ }^\circ\text{C}$.

Values of D extracted from equations 1,2 and 3 are shown in Table 1.

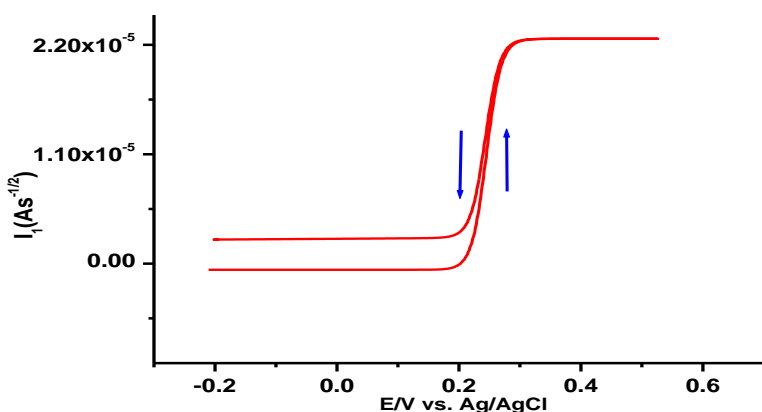


Figure 3. I_1 convolution current of catechol in the presence of 4,4'-bipyridine in 0.5 M KNO_3 at gold electrode, sweep rate 0.1 V s^{-1} , $T = 25 \text{ }^\circ\text{C}$.

As shown in Figure 3 the end of the reverse sweep of I_1 curve of catechol in existence of 4,4'-bipyridine does not come again to the initial value approve the existence of chemical reaction after the electron transfer [11].

Figure 4 indicates the deconvoluted curve of the catechol compound, which reveals the alignment of the maximum point of the forward peak and the minimum point of the backward one and the two points equals to the formal redox potential (E^0). Also, the relationship (4)

$$(dI_1/dt)_f = n^2 F^2 S C D^{1/2} v / 4RT \quad (4)$$

was used for calculation of the (D) value for fast charge transfer [21, 22], where $(dI_1/dt)_f$ is the height of the forward sweep of the deconvoluted curve, and the other terms have their usual meaning. Hence

the relationship (4), gives another accurate route for estimation of the diffusion coefficient (D). Values of (D) determined via different methods (Table 1), indicate a good comparable between the values of D estimated via these methods.

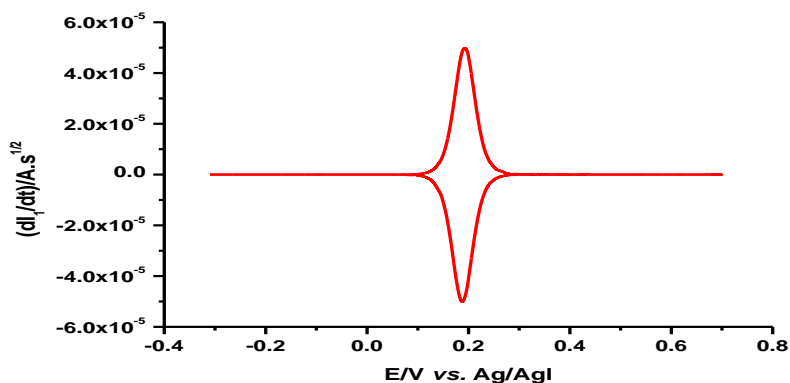


Figure 4. deconvolution current of investigated catechol in 0.5 M KNO_3 at gold electrode, sweep rate 0.1 V s^{-1} , $T = 25 \text{ }^\circ\text{C}$.

The ‘kinetic’ convolution I_2 is given by equation (5) [23]. Hence, in the I_2 transforms at t time, each division of $i(u)$ is rated by dividing upon the square root of the time which has passed from t to the

$$I_2(t) = \pi^{-1/2} \int_0^t [i(u) \exp(-kc(t-u))] / (t-u)^{1/2} du \quad (5)$$

fraction u to which the division refers and likewise is scaled by the exponential factor $\exp(-k_c(t-u))$. Accordingly, I_2 produce a plateau shape (at zero) on the return of the sweep in cyclic voltammetry and this property allows determination of k_c . The true k_c and formal potential ($E^{\circ'}$) were extracted concurrently from equation 6, [24, 25]

$$I_{\text{lim}} - I = I_2 \exp - ((E - E^{\circ'}) (nF/RT)) \quad (6)$$

where F is the faraday constant (96485 C mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and remain the symbols have their usual interpretation. Demonstration of equation 6 are summarized in Figure 5 which imply that when $E = E^{\circ'}$, the equality of $I_{\text{lim}} - I_1$ and I_2 will predominates and the intersection of the plot happen at $E^{\circ'}$ when k_c is true.

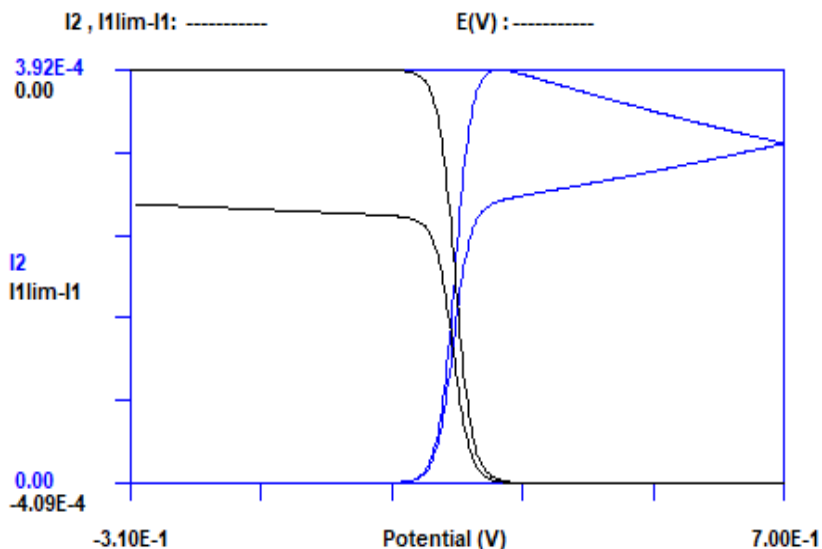
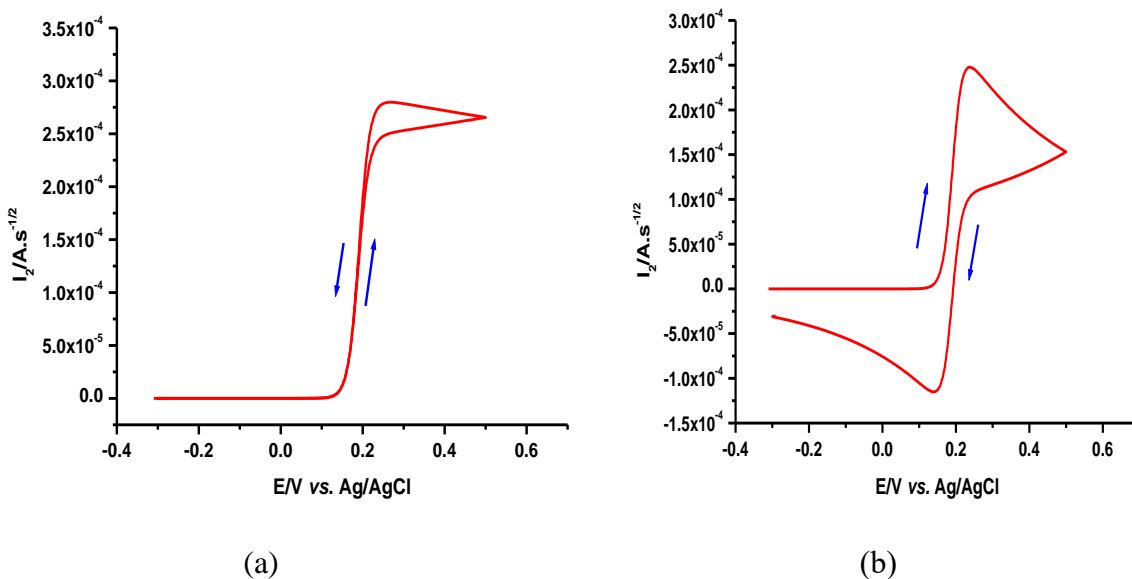


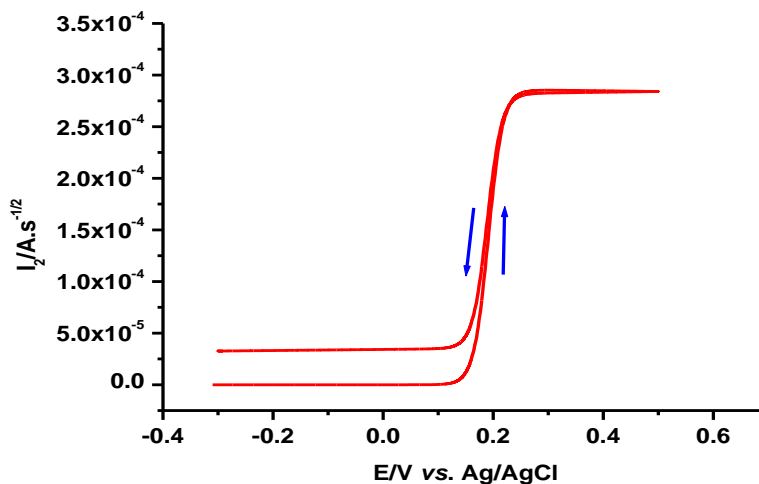
Figure 5. Combination of I_2 convolution and $I_{lim} - I_1$ of investigating catechol in existence of 4,4'-bipyridine in 0.5 M KNO_3 at gold electrode, sweep rate $0.1 \text{ V}\cdot\text{s}^{-1}$, true $k_c = 0.19 \text{ s}^{-1}$ $T = 25 \text{ }^\circ\text{C}$.

The rate constant of homogeneous chemical reaction (k_c) of catechol with 4,4'-bipyridine can be precisely evaluated via " I_2 " as explored in Figure 6 and determined from the proper value of k_c attained by putting trial value of (k_c) into the I_2 vs. E plot up till I_2 returned to zero [24]. The true k_c value extracted from I_2 convolution is 0.19 s^{-1} which compare well with the value introduced in virtual cyclic voltammograms. Figure 6 shows the true k_c value and the test k_c value of catechol with 4,4'-bipyridine in 0.5 M KNO_3 aqueous solution at gold electrode.



(a)

(b)



(c)

Figure 6. I_2 transforms of catechol in the presence of 4,4'-bipyridine in 0.5 M KNO_3 at gold electrode at the true value of k_c 0.19 s^{-1} (a), at k_c test $0.4\text{ s}^{-1} > k_c$ true (b) and at k_c test $0.05\text{ s}^{-1} < k_c$ true (c) at $0.1\text{ V}\cdot\text{s}^{-1}$ sweep rate, $T = 25\text{ }^\circ\text{C}$.

The values of peak parameters collected in Table 2 confirm that the fast rate of charge transfer of the system under investigation

Table 2. Peak parameters of the catechol extracted from voltammetric techniques and digital simulation at $0.1\text{ V}\cdot\text{s}^{-1}$.

$E_p - E_p/2 / \text{mV}$	$29^{(a)}$	$29^{(c)}$
i_p^b/i_p^f	$1.0^{(a)}$	$1.0^{(c)}$
W^p	$45^{(b)}$	$46^{(c)}$
Δe_p deconv./ mV	$0.0^{(b)}$	$0.0^{(c)}$
e_{pf} / e_{pb} (deconv)	$1.0^{(b)}$	$1.0^{(c)}$

(a) Values from CV, (b) from dl_1/dt and (c) from theoretical CV.

3.3. Digital simulation

In this work, digital simulation was achieved on PC computer via EG & G Condesim software program. The simulation process was accomplished using finite difference techniques [26 - 28]. Algorithms were coded and enforced in the Condesim package supplied via EG & G. A direct examination of the experimental parameters and the kind of electrode reaction was achieved by creating the theoretical voltammograms of the catechol. Figure 7 compares well between the theoretical and

experimental voltammograms at $0.1 \text{ V}\cdot\text{s}^{-1}$ sweep rate, which validating a fast electron transfer of the electrode reaction of the catechol.

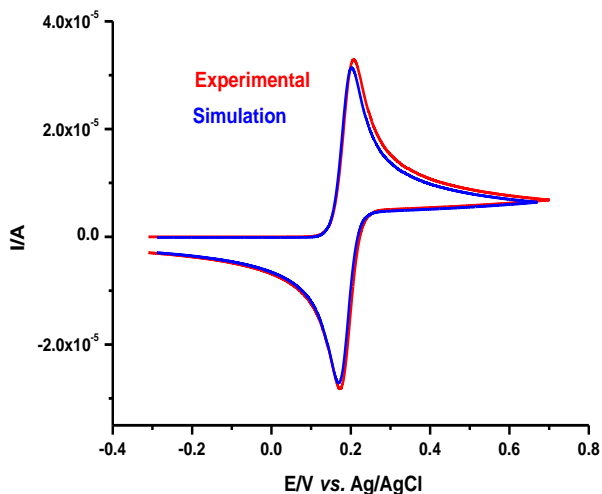


Figure 7. Shows the experimental and theoretical voltammograms of catechol are identical at a sweep rate of $0.1 \text{ V}\cdot\text{s}^{-1}$ and $T = 25 \text{ }^\circ\text{C}$.

3.4. Chronoamperometry of catechol.

The constructing of the experimental chronoamperogram is carried out by stepping the potential beginning at the initial potential (0.2 V) where no electrode reaction happens to 0.25 V and the current was plotted as a function of the duration of the experiment. Chronoamperogram of the catechol compound in 0.5 M KNO_3 at a gold electrode at starting potential step 0.2 V and end potential step 0.25 V , is exhibited in Figure 8. The heterogeneous rate of electron transfer (k_f) was calculated from equation 8 [17].

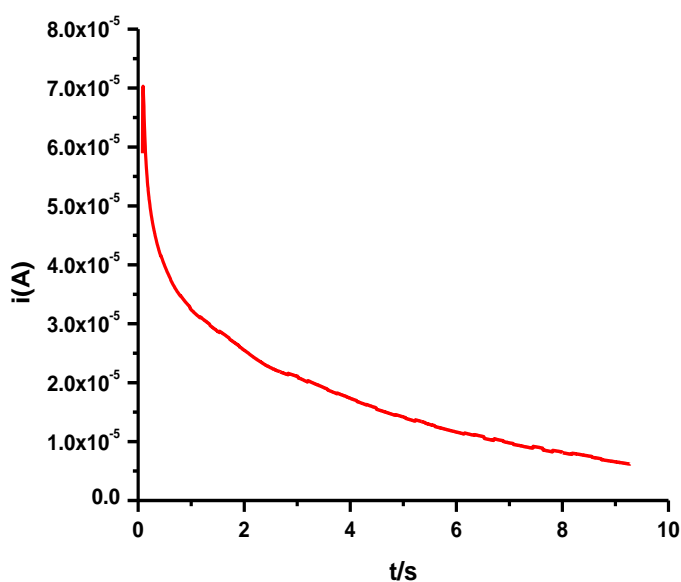


Figure 8. Chronoamperogram of catechol compound at gold electrode and at $T = 25 \text{ }^\circ\text{C}$.

$$i(t) = -\beta I_1 + u \quad (7)$$

where $u = nFSC^{\text{bulk}} k_f (D)^{1/2}$ and $\beta = k_f (D)^{1/2}$. Measurements of the intercept at $I_1 = 0$ and the slope of the straight line of $i(t)$ versus I_1 produce k_f . Here, the basic relationship between the rate constant of the electron transfer and the potential of the electrode is considered in the treatment of the Butler-Volmer relationship which can be written into the equation 8[17]

$$\ln k_f = \frac{\alpha n F}{RT} (E_f - E^{o'}) + \ln k_s \quad (8)$$

The value of α was computed from the slope of the linear line of $\ln k_f$ vs. $(E_f - E^{o'})$ and was being to be 0.5, while the value of k_s was calculated at the point at which $E_f = E^{o'}$ and was estimated to be $4.65 \times 10^{-2} \text{ cm s}^{-1}$. Both values are agreed well with those computed from cyclic voltammetry and digital simulation data (Table 1).

4. CONCLUSION

In this article the electrochemistry of catechol in nonexistence of 4,4'-bipyridine and in the presence of 4,4'-bipyridine was discussed and explained at a gold electrode in 0.5M aqueous solution using cyclic voltammetry, convolutive – deconvolutive voltammetry and chronoamperometry methods. The chemical and electrochemical parameters of the catechol have been computed experimentally and confirmed theoretically. The electrode reaction was found to behave as fast speed of charge transfer and in case of existence of 4,4'-bipyridine the electron transfer is followed by slow chemical reaction step i.e., EC_{irr} mechanism.

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