

Full Paper

Determination of Adrenaline by a New Pharmacokinetic Method

Mohammad Hasanzadeh,^{1,2,*} Ghasem Karim-Nezhad,¹ Nasrin Shadjou,^{1,2} Balal Khalilzadeh,³ Lotfali Saghatforoush,¹ Maryam Hajjizadeh,² Mohammad Hossein Abnosi⁴

¹*Department of Analytical Chemistry, Faculty of Science, Payame Noor University(PNU), P.O .Box 58168- 45164, Khoy, Iran*

²*Department of Chemistry, Faculty of Science, K.N. Toosi University of Technology (KNTU), Tehran, Iran*

³*Department of Analytical Chemistry, Faculty of Science, Arak University, Arak, Iran*

⁴*Department of Biology, Faculty of Science, Arak University, Arak, Iran*

* Corresponding Author; Tel: +98-461-2344384, +98-461-2332556

Email: m.hasanzadeh2@gmail.com , m.hasanzadeh@pnu.ac.ir

Received: 30 May 2010 / Accepted: 5 June 2010 / Published: 30 June 2010

Abstract- Electrocatalytic oxidation of adrenalin was investigated on cooper electrode in alkaline solution. The process of oxidation involved and its kinetics were established by using, chronoamperometry techniques as well as steady state polarization measurements. A mechanism based on the electrochemical generation of Cu^{III} active sites and their subsequent consumption by the adrenalin in question was also investigated.

Keywords- Adrenaline, Cyclic voltammetry, Oxidation, Pharmacokinetic

1. INTRODUCTION

A detailed knowledge of the electrochemical behavior of organic compounds is of primary importance for development of appropriate sensors and for advanced electrochemical synthesis. Numerous studies deal with electrocatalytical oxidation of organic substance

should have the following properties (i) the energy of adsorption of substrate molecules and / or intermediate species formed on the catalyst surface should be sufficiently high to substantially decrease the activation energy for the dehydrogenation step, but sufficiently low for intermediate and final products to desorb easily, and (ii) the energy realized by formation of water molecular as one of the reaction products should be sufficient to compensate for the energy needed for desorption of dehydrogenated organic intermediates from the metal surface. Copper electrode is the most active and most often used electrocatalysts.

In recent years multi-electron oxidation processes, C–C bond cleavage and the generation of lower molecular weight products from organic substrates on copper-based electrodes in alkaline solutions have received considerable attention because of their analytical applications [1,2]. These include usage of copper metal [3,4] and copper containing modified electrodes (CMEs) e.g. copper oxide/copper [5] and copper oxide/carbon paste [6] modified electrodes. Even though some reports have demonstrated that the anodic oxidation of alcohols [7,8] are facilitated on these surfaces, no specific study on the use of copper electrodes for the electro-oxidation of adrenalin has appeared in the literature. The catalytic action of copper has been reported to be the result of Cu (II)/Cu (I) or at very high positive potential, Cu^{III}/Cu^{II} redox systems [9]. The oxidation potential of the Cu^{II}/Cu^{III} redox couple is generally very high and near to the oxidation of analytes, so the mechanism of analyte oxidation seems unclear.

Recently, the biological, pharmacological, and medical properties of plant polyphenols, specifically quercetin and rutin bioflavonoids have been extensively researched. They have been reported to possess various biological activities, such as antitumor, antibacterial, enzyme inhibitory, and pro or antimutagenic properties [10–13]. These protective effects have been believed to be due to the antioxidant activity of the polyphenols because, in general, oxidative damage to the living body is mainly induced by reactive oxygen species and causes various diseases. Adrenalin is bio-phenols, important neuron-transmitter compound widely distributed in the brain for message transfer in the mammalian central nervous system. Low levels of adrenalin have been found in patients with Parkinson's disease [14].

In this work, a copper electrode for electrocatalytic determination of adrenalin has been developed as a simple, sensitive, rapid and new assay method for adrenalin.

2. EXPERIMENTAL

All chemicals used were analytical grade from Merck (Darmstadt, Germany) and were used without further purification. All solutions were prepared with doubly distilled water. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT12

boards (Eco Chemie, Utrecht, The Netherlands). The system was run on a PC using GPES 4.9 softwares. A saturated Ag/AgCl (from Metrohm) and platinum wire were reference and counter electrodes, respectively. All potentials were measured with respect to the Ag, AgCl which was positioned as close to the working electrode as possible by means of a Luggin capillary. Cylindrical copper bars with the purity of 99.9% were fitted into Teflon exposing circular areas having diameters of 4 mm (surface area is $0.126/ \text{cm}^2$) to prepare stationary and working electrodes, respectively. The copper surfaces were polished with sand paper and $0.05/ \mu\text{m}$ alumina to a mirror finish and were subsequently rinsed with distilled water. All experiments were performed at ambient temperature $22\pm 3^\circ\text{C}$.

3. RESULTS AND DISCUSSION

Typical cyclic voltammogram of copper in 0.1/M NaOH solution and in the potential range of -900 to 850 mV is shown as curve an in Fig. 1 where potential sweep rate of $10/ \text{mV s}^{-1}$ has been employed.

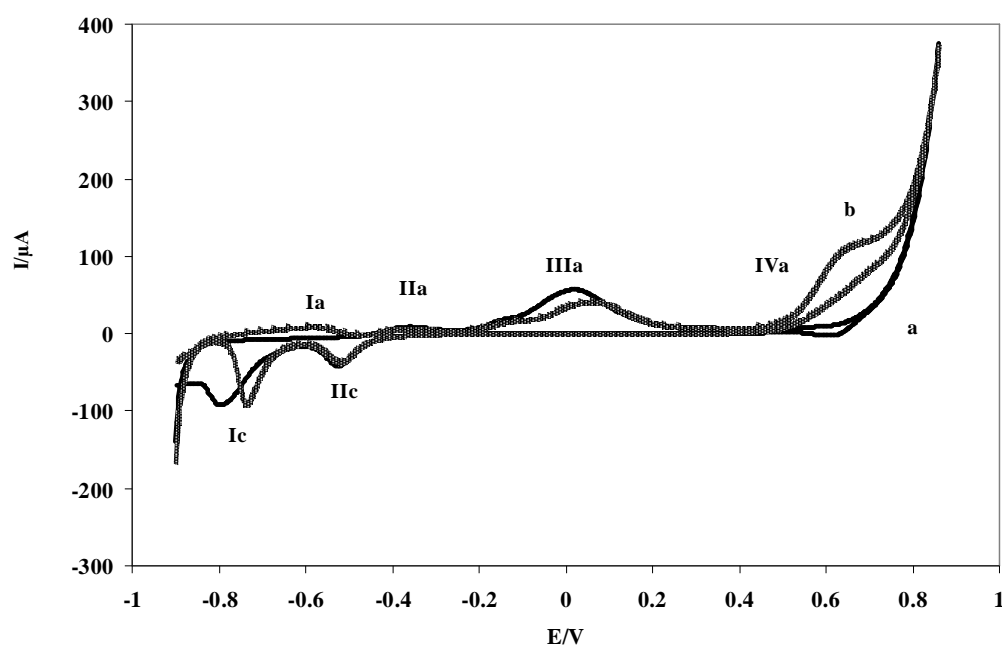


Fig. 1. Typical cyclic voltammograms of copper electrode in the potential range of -900 to 860 / mV in 0.1/ M NaOH solution in the absence (a) and presence (b) of 0.01mM adrenaline (low concentration). Potential sweep rate is $10/ \text{mV s}^{-1}$

The voltammogram is in good agreement with those reported in the literature [4,15]. A number of well-defined peaks are observed in both the anodic and cathodic half cycles. Comparing with the literature peak I_a is attributed to the $\text{Cu}/\text{Cu}^{\text{I}}$ redox couple. At the working

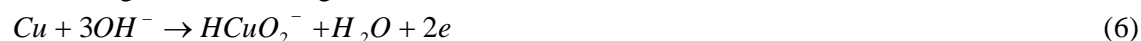
pH, copper (I) hydroxide is the main product which is transformed to the corresponding oxide upon aging [16] according to the following reactions:



Peak II_a is assigned to Cu/Cu^{II} as well as Cu^I/Cu^{II} transitions through the following:



Peaks I_c and II_c in the cathodic half cycle are assigned to the reduction of Cu^I to Cu and Cu^{II} to Cu^I respectively [15, 17, 18]. Peak III_a is related to the formation of soluble species according to the following reaction [19]:



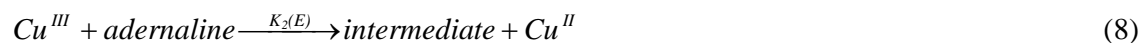
Also, an anodic peak, IV_a, just before the onset of the anodic decomposition edge of the solvent has been observed. This peak presumably corresponds to the Cu^{II}/Cu^{III} couple [15,17,20] which always appears in the course of the oxidation of copper as well as copper containing modified electrodes [21]. The participation of Cu^{III} species in the redox process signified by peak IV_a is supported by the consideration that the formal reduction potential of Cu^{III}/Cu^{II} in 1 /M NaOH solution stands at 560 /mV/ Ag, AgCl [7]. Similar observation has previously been reported by Miller [20] in a ring-disk voltammetric study of copper electrodes in alkaline solutions. In Miller's work, a total of three separate oxidation waves observed upon anodic sweeping of potential were shown to correspond to the Cu/Cu^I, Cu/Cu^{II} and Cu^{II}/Cu^{III} redox couples. It should be noted that the characteristics of the voltammograms of copper in alkaline solutions are strongly dependent on pH, potential sweep rates, mass transport regime as well as other experimental conditions and their complex appearance has further roots in the complexity of the reaction mechanism.

Cyclic voltammogram of copper electrode in the presence of adrenalin at 10/mM concentration in the electrolyte is presented in Fig. 1(curve b). A small diminution of peaks I_a–IV_a, I_c and II_c has been witnessed. Also, a small rise in the onset potential of Cu^{II}/Cu^{III} transition which implies a strong interaction of adrenalin with the surface already covered by CuO has been observed. In addition, two anodic peaks in the entire domain of the anodic sweep of potential are observed. The appearance of an anodic peak in the anodic as well as in the reverse scan is the distinct feature of adrenalin electro-oxidation on noble metals in both acidic and alkaline solutions. It should be mentioned that adrenalin is inactive at copper electrode at low potentials and it must dissociate prior to oxidation and group IB metals are not well capable of dissociative adsorbing adrenalin. So, it seems that adrenalin initially chemisorbs on the lower valence state oxides of copper and further oxidizes through reactive species. Moreover, the peak due to adrenalin oxidation was reproducible with no evidence of film formation or electrode passivation.

There is ample evidence in the literature regarding the role of Cu^{III} species in the oxidation of organic substrates [5–7,15,21,22]. This species that is generated at positive potentials has been reported to have the role of a redox mediator in the oxidation of several compounds at copper electrodes [3,7,23] and the electrode reaction may take place with a mechanism involving a rate limiting step where a reaction intermediate is formed upon a chemical reaction with a Cu^{III} species. Fleischmann et al. [7,24–25] have postulated that the oxidation of amines and alcohols on nickel, copper, silver and cobalt oxide surfaces requires, in a first step, the stripping of a hydrogen atom from the substrate and that further reactions proceed through mechanisms involving the formation of free radicals. Marioli and Kuwana [15] have suggested a different route for the oxidation of carbohydrates on copper oxide since a remarkable diminution of copper (II) oxide peak has been observed upon adding the substrate.

Figs. (2A, 3) show that upon increasing adrenalin concentration its irreversible oxidation develops in the region of the electrochemical formation of Cu^{III} . Thus, it is likely that the electro-generated Cu^{III} species is the active moiety which efficiently speeds up the oxidation of adrenalin. Any increase in the concentration of adrenalin causes a proportional almost linear enhancement of the anodic wave, Fig. 2B. It is worth to emphasize that the anodic formation of Cu^{III} seems to be an irreversible process, Fig. 1a, and the regeneration of the surface is through a chemical redox reaction. The involvement of the catalytically active Cu^{III} species is supported by the anodic response of adrenalin oxidation in the early stages of the reverse, cathodic, sweep Fig. 1(curve b).

Without going into the details of the structure of surface Cu^{III} species we assume that it originates from the surface Cu^{II} species of one kind or another and go on to propose the following mechanism for the electro-oxidation of adrenalin in alkaline solutions:



Where the intermediate is further oxidized to the product through a similar electro oxidation process:



As for the nature of Cu^{III} entities, species ranging from copper oxy-hydroxide, CuOOH , to Cu^{III} radical depicted as $\text{CuOO}^\circ\text{H}$ have been proposed [7,24]. Wells and Johnson [23] have proposed an O-transfer mechanism for cyanide oxidation on CuO films that required both CuOOH sites and adsorbed hydroxyl radicals. Catalytically active species participating as electron transfer mediators can be electrogenerated via the following reactions:



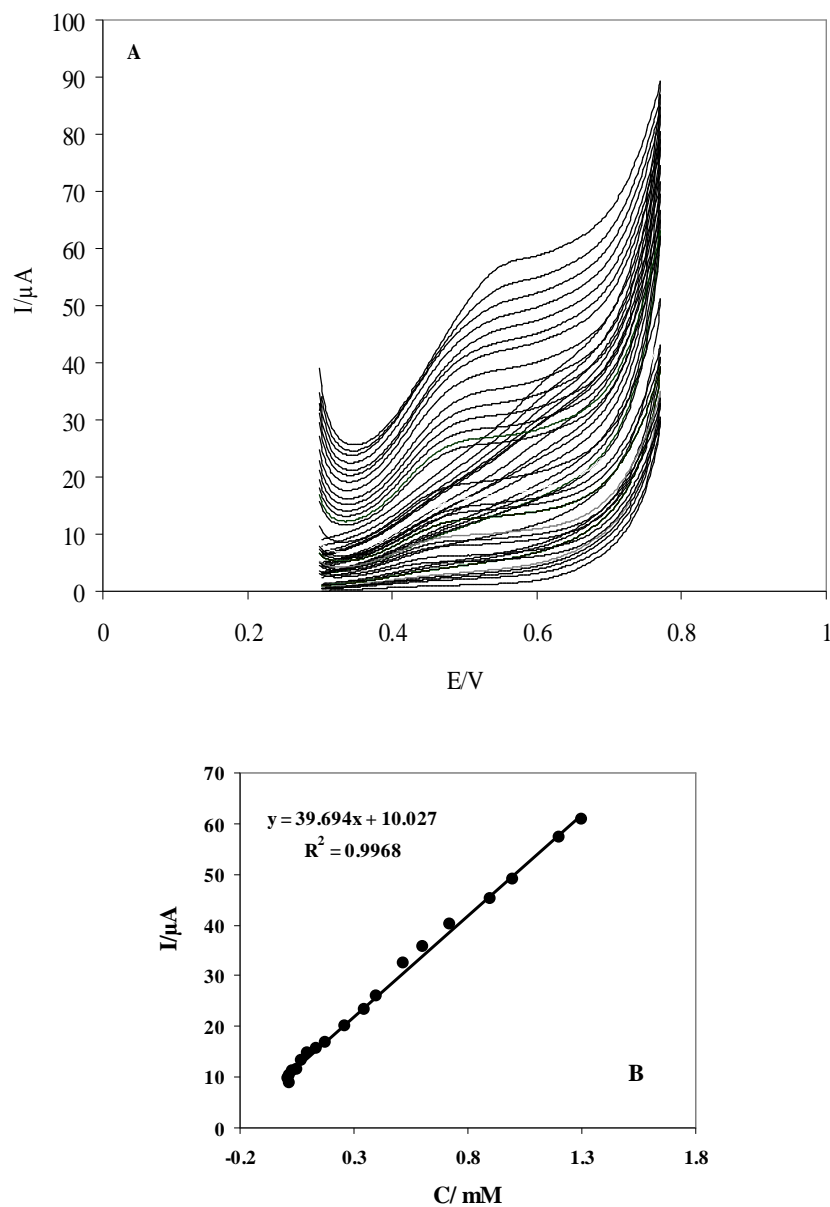


Fig. 2. A: Cyclic voltammograms of copper electrode in 0.1M NaOH solution in the presence of different concentrations of adrenalin in copper electrode. From inner to the outer: 0.01(a), 0.015(b), 0.02 (c), 0.03 (d), 0.05 (e), 0.07 (f), 0.08(g), 0.09(h), 0.1 (i), 0.2 (j), 0.3 (k), 0.4 (l), 0.5(m), 0.6 (n), 0.7 (o), 0.8 (p), 0.9 (q), 1 (r), 1.2(s), and 1.3 / mM (t) , respectively. The potential sweep rate is $10 / \text{mV s}^{-1}$. **B:** Dependency of peak current on the concentration of adrenalin

The electro-oxidation of adrenalin occurs not only in the anodic but also continues in the initial stages of the cathodic half cycle, Fig. 1(curve b). Adrenalin molecules adsorbed on Cu^{II} sites are oxidized at higher potentials parallel to the electrooxidation of Cu^{II} to Cu^{III} sites.

The latter process has the consequence of decreasing the number of sites for adrenalin adsorption that along with the poisoning effect of the products/intermediates of the reaction tends to decrease the overall rate of adrenalin electro-oxidation. The anodic current thus passes through a maximum as the potential is anodically swept. In the reverse half cycle, the electro-oxidation of adrenalin continues and its corresponding current goes through a maximum due to the regeneration of Cu^{II} surface species that are active sites for the adsorption of adrenalin. Surely the rate of adrenalin oxidation as signified by the anodic current in the cathodic half cycle drops as the unfavorable cathodic potentials are approached.

Chronoamperograms were recorded by setting the working electrode potentials to the desired values and measuring the catalytic rate constant on the copper electrode surface. In Fig. 4A shows chronoamperograms for the copper electrode in the absence (curve a) and presence (curves b–i) of over the concentration range adrenalin 0.5–1.3/mM. The applied potential step was 586/ mV. Plotting the net currents versus the minus square roots of time results in linear dependencies (Fig. 4B). Therefore, a diffusion-controlled process is dominant for electrooxidation of ascorbic acid, as was demonstrated previously using cyclic voltammetry (Fig. 2).

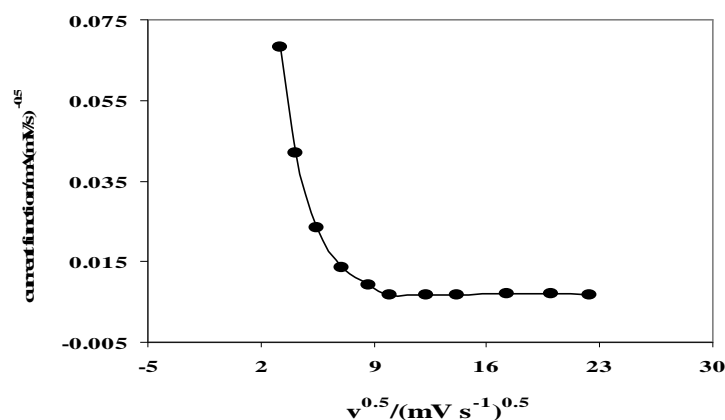


Fig. 3. Current function vs. $v^{-0.5}$ for 0.1 / M NaOH solution in the presence of 1.5/ mM adrenalin

The rate constants of the reactions of adrenalin and the ensued intermediates with the redox sites of the copper electrode can be derived from the chronoamperograms according to [26]:

$$\frac{I_{\text{catal}}}{I_d} = \lambda^{1/2} \left[\pi^{1/2} \text{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}} \right] \quad (12)$$

where I_{catal} is the catalytic current in the presence of adrenalin, I_d the limiting current in the absence of adrenalin and $\lambda = k C_m t$ (k , C and t are the catalytic rate constant, bulk

concentration of adrenalin and the elapsed time, respectively) is the argument of the error function. For $\lambda > 1.5$, $\text{erf}(\lambda^{0.5})$ almost equals unity and Eq. (12) reduces to:

$$\frac{I_{\text{catal}}}{I_d} = \lambda^{1/2} \pi^{1/2} = \pi^{1/2} (kCt)^{1/2} \quad (13)$$

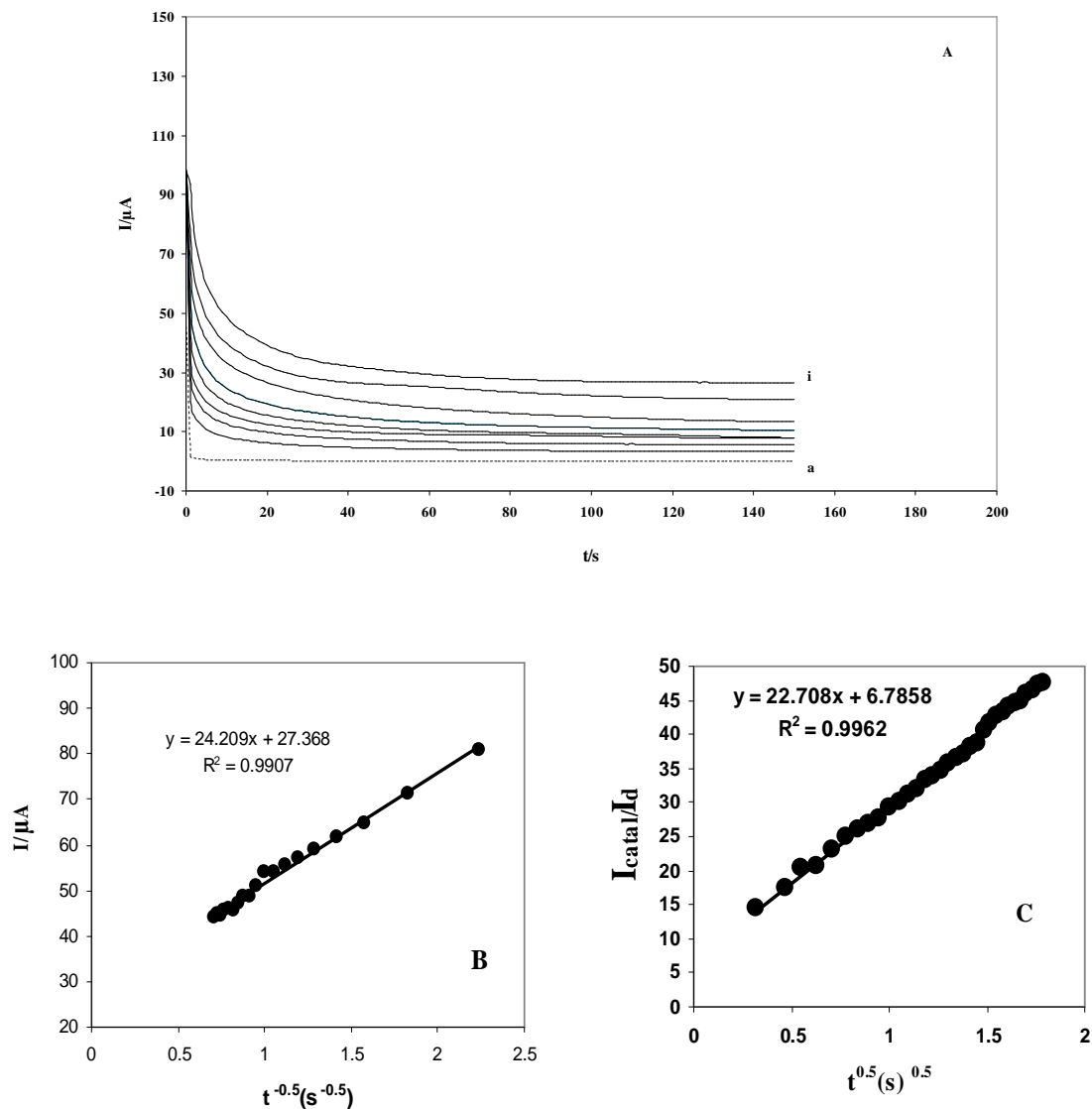


Fig. 4. A: chronoamperograms of copper electrode in the absence (a) and the presence of 0.5(b), 0.6 (c), 0.7 (d), 0.8 (e), 0.9 (f), 1 (g), 1.2(h), and 1.3/mM (i) adrenalin in 100mM NaOH solution. A potential step was 600 mV. B: Dependency of transient current on $t^{-0.5}$. C: Dependence of I_{catal}/I_d on $t^{0.5}$ derived from the data of chronoamperograms of (a) and (i) in main pane

From the slope of the I_{catal}/I_d plot the value of k at a given concentration of adrenalin is derived. Fig. 4C presents the graphs both in the absence and presence of adrenalin at 1.3/mM concentration. The mean value of k in the concentration range of 0.5–1.3/mM was found to

be $1.263 \times 10^5 / \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It should be pointed out that k is either k_2 or k_3 whichever is smaller.

The rate law for the Cu^{III} mediated oxidation of adrenalin (Eqs. (7) and (8)) is derived through:

$$v_1 = k_1 \Gamma \theta_{\text{II}} - k_{-1} \Gamma \theta_{\text{III}} \quad (14)$$

$$v_2 = k_2 \Gamma \theta_{\text{III}} C_m \quad (15)$$

where Γ is the total number of adsorption sites per unit area of the electrode surface, θ 's represent the fractional surface coverages of copper of different valence states and C_m is the bulk concentration of adrenalin. With only the 2 and 3 valence states of copper prevailing one has:

$$\theta_{\text{II}} + \theta_{\text{III}} = 1 \quad (16)$$

and the rates of changes of their surface coverages as well as that of the intermediate compounds are:

$$\frac{d\theta_{\text{II}}}{dt} = -\frac{d\theta_{\text{III}}}{dt} = -k_1 \theta_{\text{II}} + k_{-1} \theta_{\text{III}} + k_2 \theta_{\text{III}} C_m + k_3 \theta_{\text{III}} C_i \quad (17)$$

$$\frac{dC_i}{dt} = k_2 \theta_{\text{III}} C_m - k_3 \theta_{\text{III}} C_i \quad (18)$$

where C_i is the concentration of the intermediate. Assuming that the steady state dominates

$$\frac{d\theta_{\text{II}}}{dt} = -\frac{d\theta_{\text{III}}}{dt} = 0 \quad (19)$$

$$\frac{dC_i}{dt} = 0 \quad (20)$$

one arrives at the values if the coverages:

$$\theta_{\text{II}} = \left(\frac{k_{-1} + 2k_2 C_m}{k_1 + k_{-1} + 2k_2 C_m} \right) \quad (21)$$

$$\theta_{\text{III}} = \left(\frac{k_1}{k_1 + k_{-1} + 2k_2 C_m} \right) \quad (22)$$

and subsequently:

$$v_1 = \left(\frac{2k_1 \Gamma k_2 C_m}{k_1 + k_{-1} + 2k_2 C_m} \right) \quad (23)$$

On the basis of this rate equation the faradic current will be:

$$i_f = \left(\frac{2FAk_1 \Gamma k_2 C_m}{k_1 + k_{-1} + 2k_2 C_m} \right) \quad (24)$$

where A is the surface area of the electrode and the rate constants k_1 and k_{-1} are obviously potential dependent and are of the forms:

$$k_1(E) = k^0 \exp \left[\frac{\alpha n F E}{RT} \right] \quad (25)$$

$$k_{-1}(E) = k_{-1}^0 \exp\left[\frac{(\alpha - 1)nFE}{RT}\right] \quad (26)$$

where k^0 's are the chemical rate constants measured at $E/\text{Ag}, \text{AgCl} = 0$ with α being the anodic transfer coefficient and other parameters have their usual meanings. Eq. (24) is well suited for the calculation of rate constants and the validity test of the kinetics and mechanism of the oxidation process.

The pseudo-steady state polarization curves of the electro-oxidation of adrenalin on copper electrode at a number of adrenalin concentrations are presented in Fig. 5.

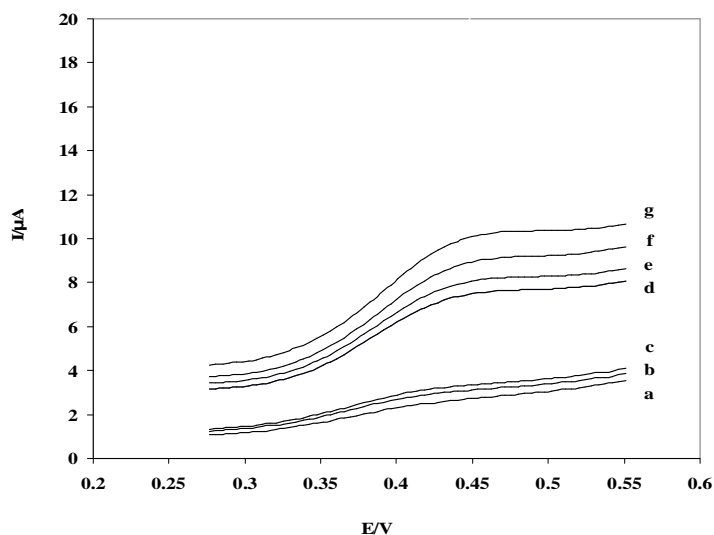


Fig. 5. Typical pseudo-steady state polarization curves of copper electrode obtained in: [0.01(a), 0.03 (b), 0.05 (c) (low concentrations)], [0.8 (d), 1 (e), 1.2(f), and 1.3 /mM (g) (high concentrations)], adrenalin, respectively

The rotation rate of the electrode is maintained at 3000 /rpm to avoid the interference of the mass transfer in the kinetics measurements. The oxidation process was found to begin at nearly 580 / mV/ Ag, AgCl and to reach a plateau at 615 / mV/ Ag, AgCl while the oxygen evolution starts at still higher potentials. In the course of reaction the coverage of Cu^{III} increases and reaches a saturation (steady state) level and the oxidation current follows accordingly. According to Eq. (24) the plots of the inverse of current against the inverse of adrenalin concentration should be linear:

$$i_f^{-1} = (FAk_1\Gamma)^{-1} + \left[\frac{k_1 + k_{-1}}{2FAk_1k_2\Gamma}\right] c_m^{-1} \quad (27)$$

Fig. 6A presents the i^{-1} versus C_m^{-1} dependencies where straight lines at various potentials have been obtained. Both the intercepts and slopes of the straight lines appearing in this figure were potential dependent. The slopes are plotted against $\exp(-nFE/RT)$ with $n = 1$ and the graph is presented in Fig. 6B. Using this graph along with Eq. (27) reveals that the rate constant of reaction 8, $k_2\Gamma$ and the ratio of k_{-1}^0/k_1^0 are $2 \times 10^{-12}/\text{cm s}^{-1}$ and 4.86×10^3 , respectively. Fig. 6C presents the variation of the intercepts of the lines in Fig. 5A with the applied potential in a semi-log scale. Using this graph and Eq. (27) the magnitudes of $k_1^0\Gamma$ and the anodic transfer coefficient of $6.435 \times 10^{-11} / \text{mol s}^{-1} \text{cm}^{-2}$ and 0.47 have been obtained. From the above findings the value of $k_{-1}^0\Gamma$ was worked out to be $3.13 \times 10^{-7} / \text{mol s}^{-1} \text{cm}^{-2}$.

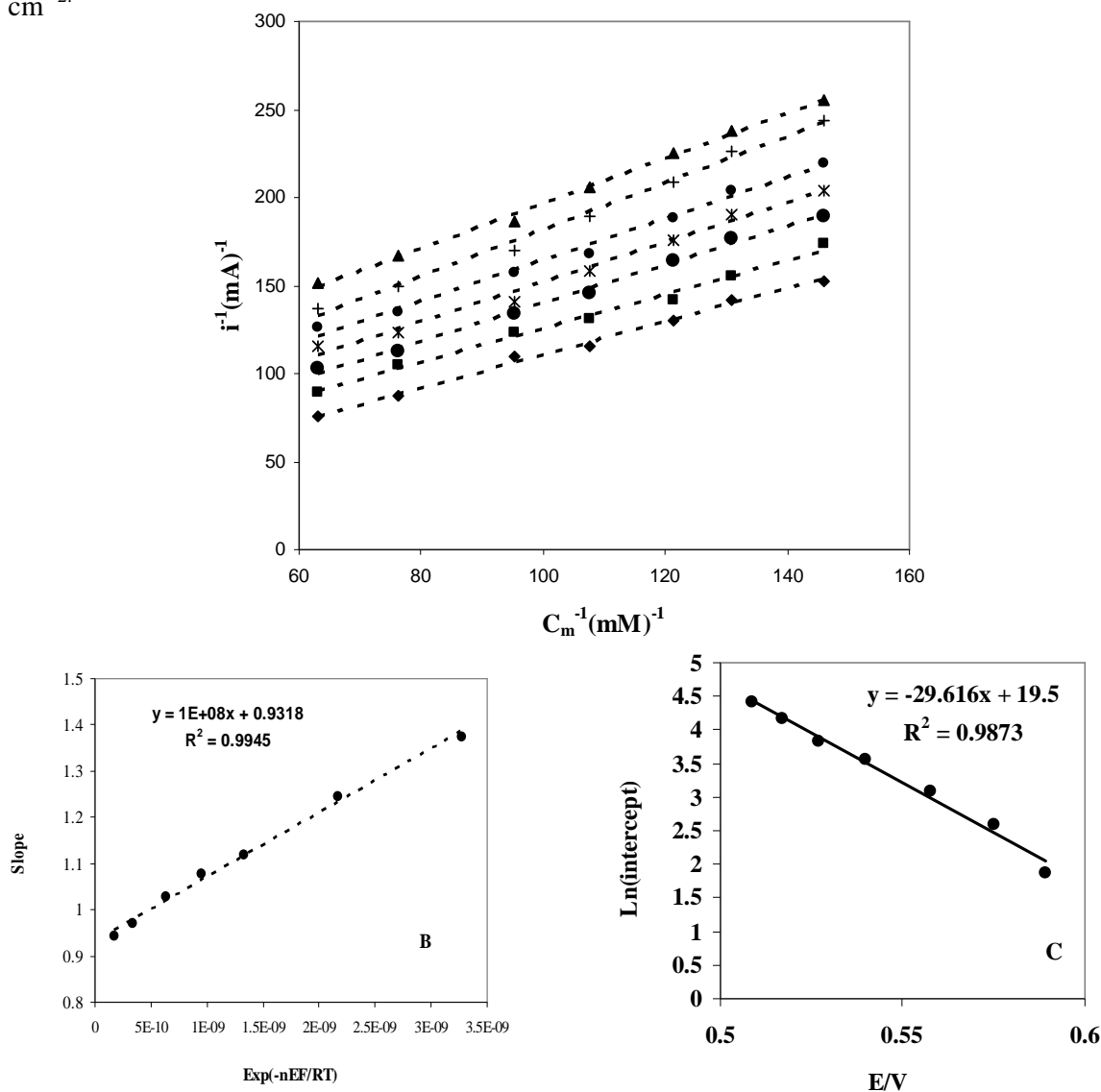


Fig. 6. A: Plot of i^{-1} (from polarization curves in Fig. 5) against C_m^{-1} at various potentials: 520, 530, 540, 550, 560, 570, 580/ mV/Ag, AgCl as curves (a–g). **B:** Plot of the slopes (of curves in A) vs. $\exp(-nFE/RT)$. **C:** Plot of the $\text{Ln}(\text{intercept})$ (of curves in A) vs. applied potential.

The calibration curve for adrenalin in 100/mM NaOH was obtained by differential pulse voltammetry (DPV). Fig. 7 shows typical DPV curves for different concentrations of adrenalin in alkaline solution.

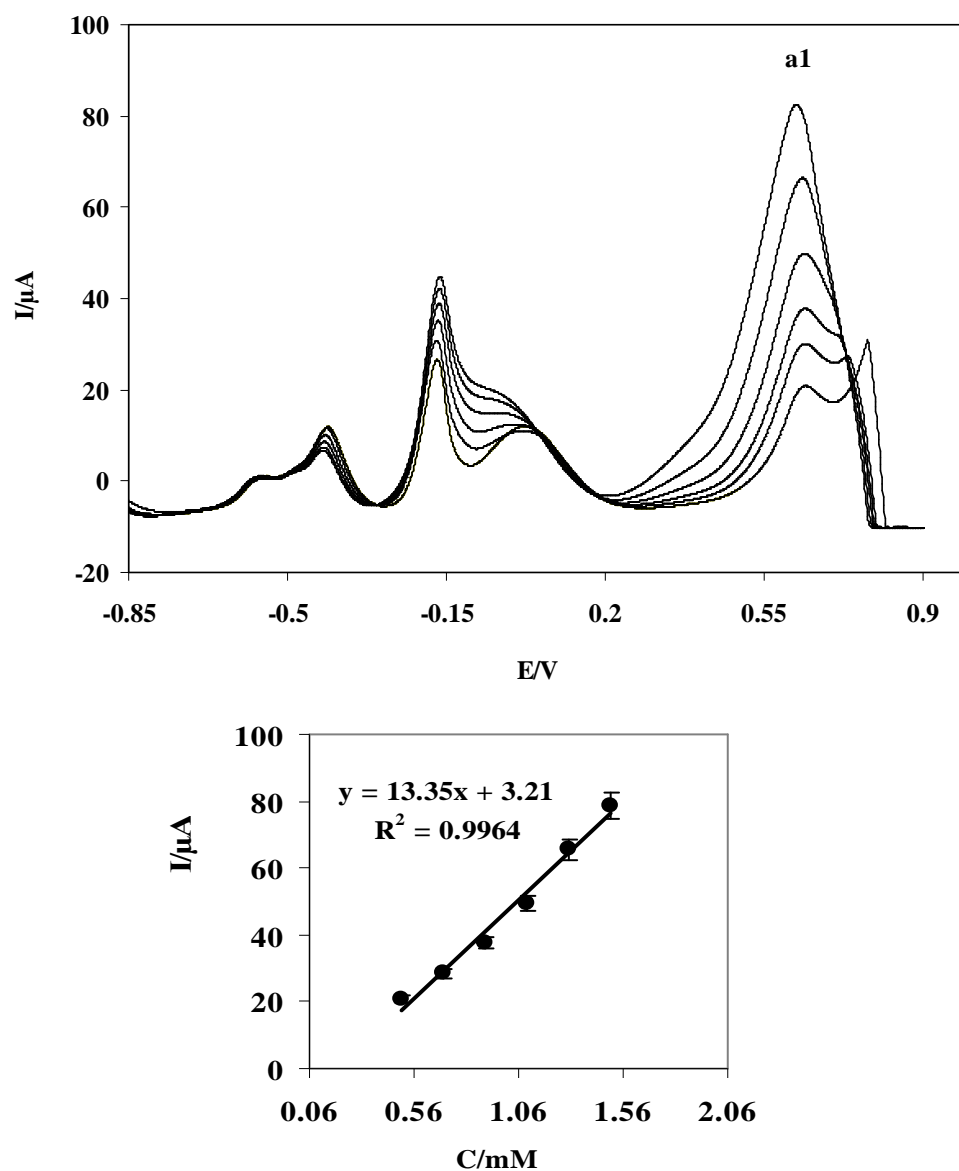


Fig. 7. Main panel: Differential pulse voltammograms obtained for determination of adrenalin in 100/ mM NaOH. Adrenalin concentrations from inner to outer are: 0.5, 0.7, 0.9, 1.2, 1.3 and 1.4 /mM. Insets: The related calibration graph for peak a1

The dependency between peak current and adrenalin concentration was rectilinear for peak a1 within the range of 0.08 to 1.50 mM (with a regression equation of $y=13.35x+3.21$, $R^2=0.9964$, $n=6$, Figure 7, inset. The limits of detection (LOD) and quantitation (LOQ) of the

procedure were calculated according to the $3 S.D/m$ criteria where S.D. is the standard deviation of the blank and m is the slope of the calibration curves [27]. The limits of detection and quantitation were found to be $5.79 \times 10^{-6} /M$ and $9.41 \times 10^{-6} /M$ for peak a1. Precision and accuracy were assessed by performing replicate analyses of adrenalin samples. The precision of the method was calculated as the relative standard deviation (RSD). The procedure was repeated on the same day on the same solutions at concentrations in the range of the standard series. The intra-assay RSDs of the proposed method determined on the basis of peak current for 10 replications, was 1.63% for peaks a1, and showed good repeatability. The analytical parameters obtained for the analyzed samples are summarized in Table 1.

Table 1. Results obtained for adrenalin analysis from 100 mM NaOH

Linear range /μM	50-1500
Slope/$\mu A M^{-1}$	0.0133
Intercept/M	3.40×10^{-5}
RSD(%)^a	1.63
LOD/μM^b	5.79
LOQ/μM^c	9.41

^a Each value was obtained from ten experiments.

^b LOD is the limit of detection

^c LOQ is the limit of quality

4. CONCLUSION

This work presents the electro-oxidation of adrenalin on poly-crystalline copper in alkaline solutions. It is concluded that the electro-oxidation of adrenalin that starts around 500 /mV/Ag,AgCl occurs through a mediated electron transfer mechanism catalyzed by Cu^{III} species which form in the same potential region. The kinetics of the reaction based on the above mechanism has been developed and the magnitudes of the rate constants, anodic transfer coefficient of the electro-oxidation reaction have been obtained.

Acknowledge

We gratefully acknowledge the support of this work by Payame Noor University.

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