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Electrocatalytic Detection of Isoproterenol at a Ferrocene-Multiwall Carbon Nanotubes Paste Electrode

Ali A. Ensafi[*], *Elaheh Khoddami and Hassan Karimi-Maleh*

Department of Chemistry, Isfahan University of Technology, Isfahan 84156–83111, Iran
[*]E-mail: Ensafi@cc.iut.ac.ir

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A sensitive and selective electrochemical method for the determination of isoproterenol (ISPT) was developed by using a ferrocene multi wall carbon nanotubes paste electrode (FCMWCNTPE). The fabrication of FCMWCNTPE and its electrocatalytic effect for electrochemical oxidation of ISPT were investigated by electrochemical impedance spectroscopy (EIS) and voltammetric methods. The cyclic voltammetric results indicate that multi wall carbon nanotubes (MCNTs) remarkably enhance the oxidation of ISPT in wide *pH* range of 2.0–5.0, which is leading to considerable improvement of anodic peak current for ISPT, and allow the development of a highly sensitive voltammetric sensor for determination of ISPT in pharmaceutical and urine samples. It has been found that under optimum condition (*pH* 5.0) in cyclic voltammetry, the oxidation of ISPT occurred at a potential about 140 mV less positive than that unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, α and catalytic reaction rate constant, k_h were also determined using electrochemical approaches. Finally, differential pulse voltammetry (DPV) exhibited two wide linear dynamic ranges and a lower detection limit of 0.07 µmol L^{-1} for ISPT.

Keywords: Isoprpterenol, carbon nanotubes paste electrode, ferrocene, electrocatalytic, electrochemical impedance spectroscopy

1. INTRODUCTION

Isoprenaline or isoproterenol 4-[1-hydroxy-2-[(1-methylethyl)-amino] ethyl]-1, 2-benzenediol (scheme 1) is a catecholamine drug that the drug affects the heart by increasing inotropic and chronotropic activity. In addition, isoproterenol causes arterial and bronchial dilation, and is sometimes administered via aerosolization as a bronchodilator to treat bronchial asthma and bronchospasm. It is also supplied in ampoules under the brand name isuprel for injection and in sublingual pill form for treatment of asthma, chronic bronchitis and emphysema. The plasma half-life for isoproterenol is approximately two hours [1]. The cardiovascular effects of isoprenaline are compared with the

adrenaline and noradrenaline, which can relax almost every kind of the smooth musculature that receives adrenergic nervous, but this effect is pronounced in the musculature of bronchus and also in the gastrointestinal tract [2]. Therefore, determination of this compound is very important. Various methods including gas chromatography [3], chemiluminescence [4-6], spectrophotometry [7-11], and electrochemical methods [12-14] have been used for the detection of ISPT.

Carbon nanotubes (CNTs) have been proved to be a novel type of nanostructure with unique structural electronic and mechanical properties and have drowned extensive since their discovery [15-17]. Research over the past decade has revealed that the CNTs constituted a new form of carbon materials that are finding striking application in many filed, such as energy conversion and storage [18,19], chemical actuators [20,21], and chemical sensing [22-25].

In this study the application of FC was discussed as a suitable mediator for the determination of ISPT in aqueous media using differential pulse voltammetric (DPV) method. The suitability of ferrocene modified carbon nanotubes paste electrode (FCMWCNTPE) in the electrocatalysis determination of isoproterenol is discussed by DPV and EIS methods. Finally, in order to demonstrate the catalytic ability of the modified electrode in the electrooxidation of ISPT in real samples, we examined this method for the voltammetric determination of ISPT in urine and ampoule samples.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. Ferrocene was used from Fluka and ISPT from Aldrich, all used as received.

A 1.0×10^{-2} mol L^{-1} ISPT solution was prepared daily by dissolving 0.062 g isoproterenol in water and the solution was diluted to 25 mL with water in a 25–mL volumetric flask. The solution was kept in the refrigerator at 4 ^{o}C in the dark. More dilute solutions were prepared by serial dilution with water.

Phosphate buffer (sodium dihydrogen phosphate and disodum monohydrogen phophate plus sodium hydroxide, 0.1 mol L^{-1}) solutions with different *pH* values were used.

Multiwall carbon nanotubes (>90% MWCNT basis, d×l = (110–70 nm) × (5–9 μm)) from Fluka were used as the substrate for the preparation of the carbon paste electrode as a working electrode. Spectrally pure graphite powder (particle size <50 μm) from Merck and high viscose paraffin oil (density = 0.88 Kg L^{1}) from Merck were used for the preparation of the carbon paste electrode (CPE).

2.2. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed in an analytical system, Micro-Autolab, potentiostat/galvanostat connected to a three electrode cell,

Metrohm Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and with micro-Autolab software. In addition, impedance spectroscopy were performed in an analytical system using an Autolab PGSTAT 12, potentiostat/galvanostat connected to a three-electrode cell, Metrohm Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and with Autolab software. The system was run on a PC using GPES and FRA 4.9 software. For impedance measurements, a frequency range of 100 kHz to 1.0 Hz was employed. The AC voltage amplitude used was 5 mV, and the equilibrium time was 10 minutes. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode was used. The working electrode was either an unmodified carbon nanotubes paste electrode (CNPE) or a carbon nanotubes paste electrode modified with ferrocene (FCMWCNTPE). The prepared electrodes with carbon nanotubes and with the modifier were characterized by scanning electron microscopy (SEM) (XLC Philips).

A *pH*-meter (Corning, Model 140) with a double junction glass electrode was used to check the pH of the solutions.

2.3. Preparation of the electrode

1.0 mg ferrocene hand mixed with 89 mg of graphite powder and 10 mg of carbon nanotubes in a mortar and pestle. Using a syringe, 0.88 g paraffin was added to the mixture and mixed well for 40 min until a uniformly-wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. The unmodified carbon paste electrode (CPE) was prepared in the same way without adding ferrocene and carbon nanotubes to the mixture to be used for comparison purposes.

2.4. Preparation of real samples

Ampoule (0.2 mg mL^{-1}) prepared and then 0.1 mL of the solution plus 10 mL of 0.1 mol L^{-1} buffer (*pH* 5.0) was used for the analysis.

The urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 10 min at 2000 rpm. The supernatant was filtered using a 0.45 μm filter and then diluted 5 times with universal buffer *pH* 5.0. The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. Standard addition method used for the determination of ISPT in real samples.

2.5. Recommended procedure

The multiwall carbon nanotubes paste electrode was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of buffer solution (PBS, *pH* 5.0), was transferred into an

electrochemical cell. The initial and final potentials were adjusted to –0.00 and +0.50 V *vs*. Ag/AgCl, respectively. The DPV was recorded with pulse height and width of 100 mV and 0.7 mV to give the balnk signal and labled as I_{pb}. Then different amounts of ISPT solution were added to the cell, using a micropipette, and the DPV was recorded again to get the analytical signal (I_{ps}). Calibration curves were constructed by plotting the catalytic peak current *vs*. the ISPT concentration.

3. RESULTS AND SISCUSSION

3.1. Electrochemical behavior of FCMWCNTPE

Cyclic voltammetry was employed for investigation of the electrochemical properties of FCMWCNTPE in a pure buffered aqueous solution (*pH* 5.0) at a various scan rates (Fig. 1. Insert).

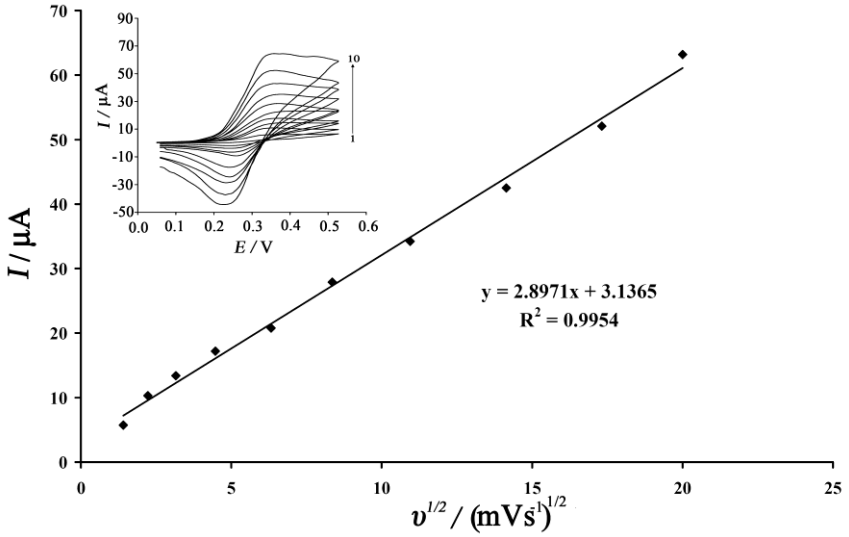

Figure 1. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of FCMWCNTPE. Insert cyclic voltammograms of at various scan rates: (1) 2; (2) 5; (3) 10; (4) 20; (5) 40, (6) 70, (7) 120, (8) 200, (9) 300, and (10) 400 mV s^{-1} in 0.1 mol L^{-1} buffer solution (*pH* 5.0).

The cyclic voltammogram exhibits anodic and corresponding cathodic peaks with E_{pa}=0.350V and E_{pc}=0.220V vs. Ag/AgCl/KCl_3 M. The experimental results show well-defined and reproducible anodic and cathodic peaks related to a Fc/Fc^+ redox couple with a quasireversible behavior because the peak separation potential, $\Delta E_p=(E_{pa}–E_{pc})$, is greater than that of the 59/*n* mV expected for a reversible system. Also, the obtained result from cyclic voltammetry of this modified electrode in various buffered solutions does not show any shift in the anodic and cathodic peak potentials. Therefore, the electrochemical behavior of the redox process of Fc/Fc^+ in FCMWCNTPE is independent of the *pH* of aqueous solution. In addition, the plot of the anodic peak current was linearly

dependent on $\upsilon^{1/2}$ with a correlation coefficient of 0.9954 at all scan rates (Fig. 1). This behavior indicates that the nature of the redox process is diffusion controlled [26].

3.2. Catalytic effect

Figure 2 shows cyclic voltammetric responses from the electrochemical oxidation of 800 μmol L^{-1} ISPT at FCMWCNTPE (curve c), ferrocene modified carbon paste electrode (FCMCPE) (curve b), and carbon nanotubes paste electrode (CNTPE) (curve d) and carbon paste electrode (CPE) (curve e).

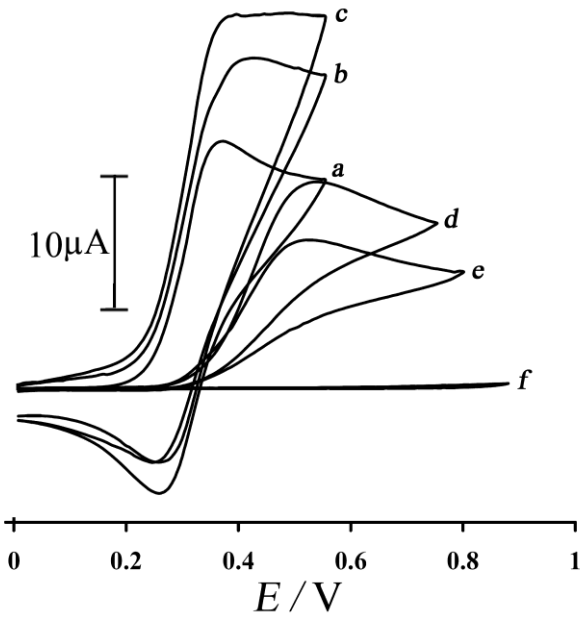

Figure 2. Cyclic voltammograms of FCMWCNTPE in 0.1 mol L^{-1} *PBS* (*pH* 5.0) at a scan rate of 10 mV s^{-1} in the absence (a) and in the presence of 800 μmol L^{-1} ISPT (c). (b) as (c) for an FCMCPE. (d) as (c) and (e) as (b) for the unmodified electrode. Curve (f) show a bare carbon paste electrode in *PBS pH* 5.0.

As can be seem, the catalytic peak potential for ISPT oxidation at FCMWCNTPE (curve c) and FCMCPE (curve b) were about 370 and 400 mV respectively, while at the CNTPE (curve d) and CPE (curve e), the peaks potential were about 510 and 525 mV respectively. From these results, it was concluded that the best electrocatalytic effect for ISPT oxidation was observed at FCMWCNTPE (curve c). For example, when we comparing the oxidation of ISPT at FCMWCNTPE (curve c) and FCMCPE (curve b) a dramatic enhancement of the anodic peak current at FCMWCNTPE relative to that obtained at the FCMCPE was observed. In other hand, the data clearly show that the combination of multi wall carbon nanotubes and mediator definitely improve the characteristics of ISPT oxidation. FCMWCNTPE, in 0.1 M PBS (*pH* 5.0) and without ISPT, exhibited a well-behaved redox reaction (curve a).

The effect of scan rate on the electrocatalytic oxidation of 400 µmol L^{-1} ISPT at FCMWCNTPE was investigated by cyclic voltammetry (Fig 3 insert). The oxidation peak potential shifts with increasing scan rates towards a more positive potential, confirming the kinetic limitation of the electrochemical reaction. Also, a plot of peak height (I_p) against square root of scan rate ($v^{1/2}$), in range of 2 – 17 mV s^{-1}, was constructed (Fig. 3), which was found to be linear, suggesting that at sufficient over-potentials the process is diffusion rather than surface controlled.

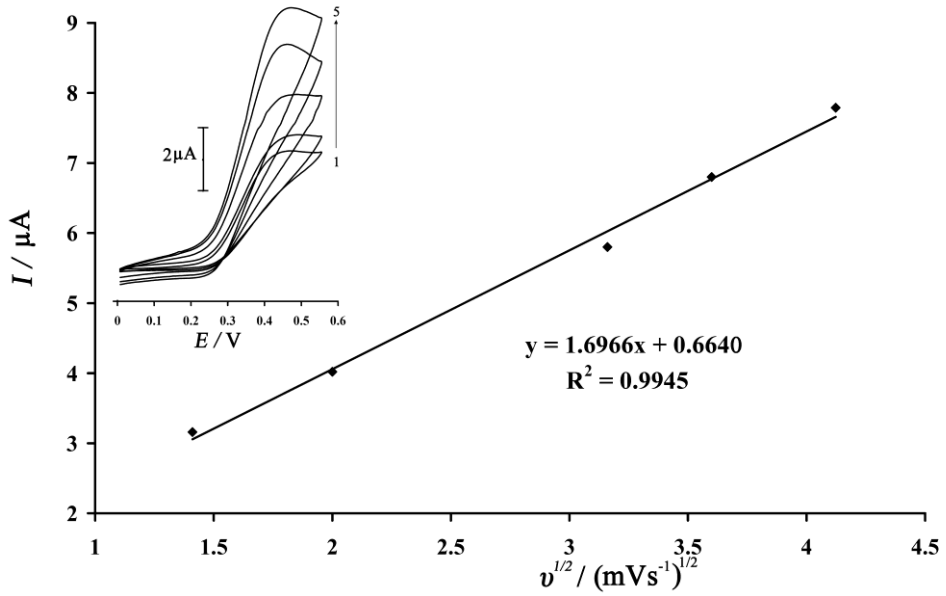

Figure 3. Variation of electrocatalytic current (I_p) with the square scan rate. (Insert) Cyclic voltammograms of FCMWCNTPE in PBS (pH 5.0) containing 400 µmol L^{-1} ISPT at different scan rates. The number of 1–5 corresponds to 2, 4, 10, 13 and 17 mV s^{-1}, respectively.

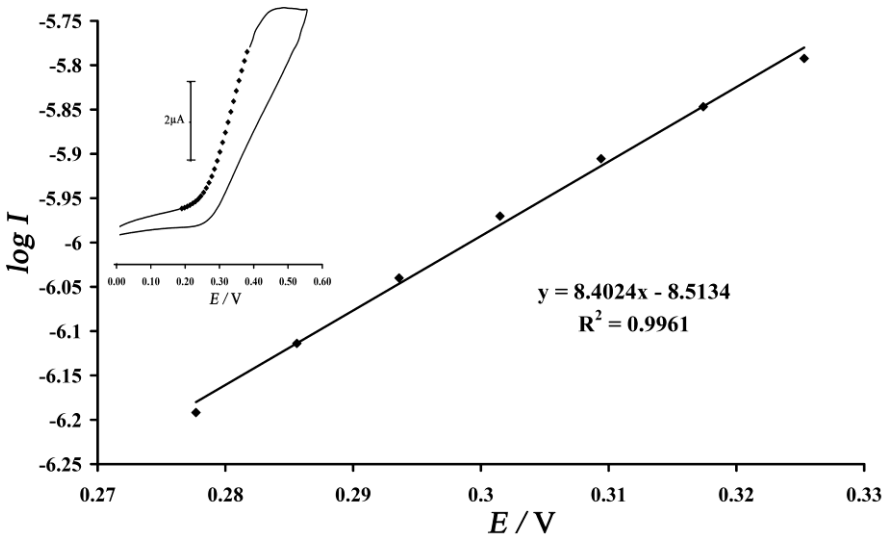

Figure 4. Tafel plot for FCMWCNTPE in 0.1 mol L^{-1} PBS (*pH* 5.0) at a scan rate of 17 mV s^{-1} in the presence of 400 µmol L^{-1} ISPT.

Figure 4 depicts a Tafel plot for FCMWCNTPE using the data derived from the raising part of the current–voltage curve in presence of 400 μmol L^{-1} ISPT. The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ which comes up to 8.4024 V $decade^{-1}$. We obtained α equal to 0.75.

3.3. Chronoamperometric study

Double step potential chronoamperometry was also employed to investigation of electrochemical behavior of aqueous buffered solution (*pH* 5.0) (Fig. 5).

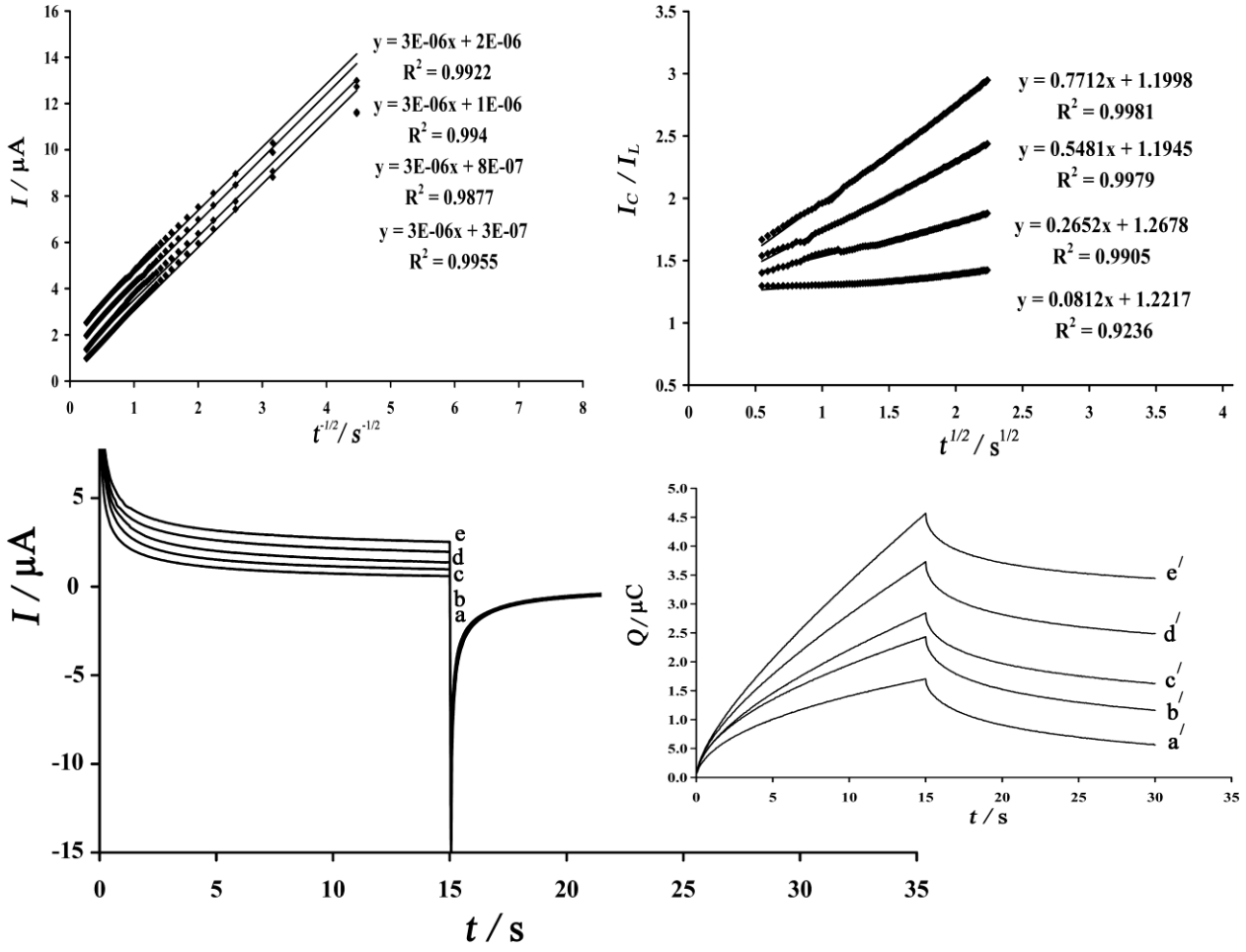

Figure 5. Chronoamperograms obtained at FCMWCNTPE in the absence a) and in the presence of b) 100, c) 200, d) 400 and e) 600 μmol L^{-1} ISPT in a buffer solution (*pH* 5.0). Insert A) Cottrell's plot for the data from the chronoamperograms and insert B) Dependence of Ic/I_L on the $t^{1/2}$ derived from the chronoamperogram data. Insert C) Shows the charge-time curves: (a') for curve (a), (b') for curve (b), (c′) for curve (c), (d′) for curve (d) and (e′) for curve (e).

Chronoamperometric measurements of different concentrations of ISPT at FCMWCNTPE were done by setting the working electrode potential at 0.0 mV and 400 mV. In chronoamperometric

studies, we have determined the diffusion coefficient, *D*, of ISPT. The experimental plots of *I* versus $t^{-1/2}$ with the best fits for different concentrations of ISPT were employed (Fig. 5. Insert A). The slopes of the resulting straight lines were then plotted versus the ISPT concentrations, from whose slope and using the Cottrell equation [27]:

$$I = nFAD^{1/2} C_b \pi^{-1/2} t^{-1/2} \qquad (1)$$

We calculated a diffusion coefficient of 3.1×10^{-6} cm^2 s^{-1} for ISPT.

The rate constant for the chemical reaction between ISPT and redox sites in FCMWCNTPE, k_h, can be evaluated by chronoamperometry according to the method of Galus [28]:

$$I_C/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_b t)^{1/2} \qquad (2)$$

Where I_C is the catalytic current of ISPT at FCMWCNTPE, I_L the limited current in the absence of ISPT and t is the time elapsed (*s*). The above equation can be used to calculate the rate constant of the catalytic process k_h. Based on the slope of the I_C/I_L versus $t^{1/2}$ plots (Fig. 5, Inset B), k_h can be obtained for a given ISPT concentration. From the values of the slopes an average value of k_h was found to be $k_h = 1.72 \times 10^2$ M^{-1} s^{-1}. The value of k_h explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of ISPT at the surface of FCMWCNTPE. Double potential step chronocoloumetry, as well as other electrochemical methods, was also employed for the investigation of electrode processes at FCMWCNTPE. Forward and backward potential step chronocoloumetry on the modified electrode in a blank buffer solution showed very symmetrical chronocolougrams. These had about an equal charge consumed for both oxidation and reduction of the Fc/Fc^+ redox system in FCMWCNTPE. However, in the presence of ISPT, the charge value associated with forward chronocoloumetry was significantly greater than that observed for backward chronocoloumetry (Fig. 5, Inset C). This behavior is typical of that expected for electrocatalysis at chemically modified electrodes (Diagram 1) [29].

3.4. Electrochemical impedance spectroscopy study

Electrochemical impedance spectroscopy (EIS) is a powerful technique for determining conveniently kinetic as well as mass-transport parameters and charge transfer coefficient using minor electrochemical perturbation, as compared with other transient electrochemical techniques [30,31]. Therefore, we use this method for more investigation.

For study of catalytic effect, we compare value charge transfer coefficient modified electrode in absence and presence of 1000 μmol L^{-1} ISPT (Fig. 6). Results show, in the presence of ISPT, the diameter of the semicircle decreases, confirming the electrocatalytic capability of the mentioned electrocatalyst for oxidation of ISPT. This is due to the instant chemical reaction of ISPT with the high-valence FCMWCNTPE species. The catalytic reaction of oxidation of ISPT that occurred via the participation of FCMWCNTPE species virtually caused an increase in the surface concentration of low valence species of electrocatalyst, and the charge transfer resistance declined, depending on the

concentration of ISPT in the solution. This behavior is consistent with the result of cyclic voltammetry and chronoamperometry (see Figs. 2 and 5).

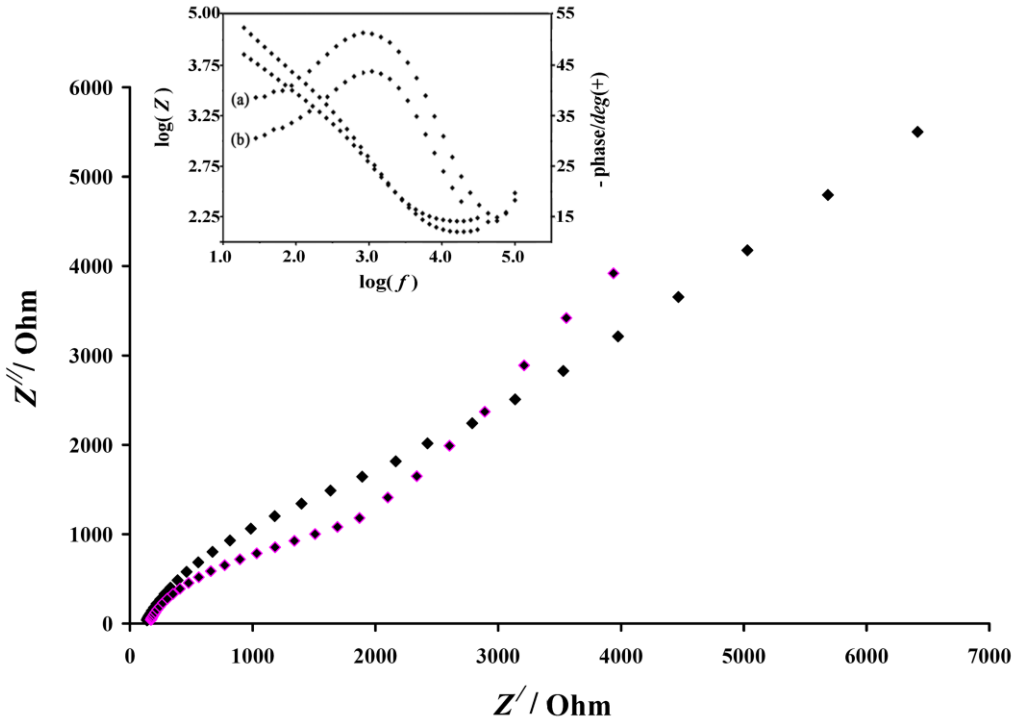

Figure 6. Nyquist diagrams of FCMWCNTPE in the absence (a) and in the presence of (b) 100.0 μmol L^{-1} ISPT at *pH* 5.0. Bias is 0.25 V with E_{ac} = 5 mV with a frequency range of 10 kHz to 0.1 Hz. Insert show bod plot derivative from Nyquist diagrams.

3.5. Stability and reproducibility

The repeatability and stability of FCMWCNTPE was investigated by cyclic voltammetry measurements of 1.0 μmol L^{-1} ISPT. The relative standard deviation (*RSD*) for ten successive assays is 1.7%. When using four different electrodes, the *RSD* for five measurements is 2.1%. When stored in a libratory, the modified electrode retains 97% of its initial response after a week and 93% after 30 days. These results indicate that FCMWCNTPE has good stability and reproducibility, and could be used for ISPT.

4. CALIBRATION PLOT AND LIMIT OF DETECTION

Differential pulse voltammetry was used to determine the concentration of ISPT. The pulse height and width of 100 mV and 0.7 mV were selected in order to get the best sensitivity under the specific conditions. The results show two linear segments with different slop. For ISPT concentration;

namely, for 0.1 – 0.6 µmol L^{-1} of ISPT, the regression equation was I_p(µA) = (84.250±0.3)C_{ISPT} + (17.751±0.2) (r^2 = 0.995, n = 5) and for 0.6 – 5.0 µmol L^{-1} of ISPT, the regression equation was I_p(µA) = (16.645±0.2)C_{ISPT} + (69.126±0.1) (r^2 = 0.991, n = 5) where C_{ISPT} is µmol L^{-1} concentration of ISPT .

The detection limit was determined at 0.07 µmol L^{-1} for ISPT according to the definition of $Y_{LOD} = Y_B + 3\sigma$ [32].

5. INTERFERENCE STUDIES

Interference studies were carried out with several species, prior to the application of the proposed method for the assay of ISPT in spiked urine samples and ampoule.

Table 1. Interference study for the determination of 5 µmol L^{-1} ISPT under the optimized conditions respectively.

Species	Tolerante limits ($W_{substance}$ / W_{ISPT})
Citric acid, glycine, valine, lucine, alanine, phenylalanine, methionine	1000
Thiourea, urea, glucose, fructose, lactose, sucrose, tartaric acid	800
I^-, SCN^-, $C_2O_4^{2-}$, Br-,Mg^{2+}, SCN^-, F^-	600
Starch	Saturation
Ascorbic acid	1

* Although ascorbic acid is interference, but interference from ascorbic acid can be minimized by using ascorbic oxidase enzyme.

The potential interfering substances were chosen from the group of substances commonly found with ISPT in pharmaceuticals and in biological fluids. The influence of various substances as potential interference compounds on the determination of 1.0 µmol L^{-1} ISPT under the optimum conditions was studied. Tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than 5% for determination of ISPT. The results are given in Table 1, which shows the peak current of ISPT is not affected by all conventional cations, anions, and organic substances. Although ascorbic acid show interference, but interference from ascorbic acid can be minimized by using ascorbic oxidase enzyme, which exhibits high selectivity to oxidation of ascorbic acid, if necessary.

6. REAL SAMPLE ANALYSIS

The voltammetric sensor was tested by determining isoproterenol in ampoule and in urine samples to evaluate the applicability of the proposed method for the determination of isoproterenol in real samples. For the ampoule, each sample was analyzed in triplicate by standard addition using the proposed method. The potential was controlled between 0.0 V and 0.50 V. I_{pa} was measured at the oxidation potential of ISPT. The average concentration of ISPT in the injection was 2.0 µmol L^{-1}, which corresponded quite well with the specified value. This procedure was repeated four times to obtain a relative standard deviation of 2.5%. Different standard concentrations of ISPT were added to the diluted ISPT injection solution, with recoveries between 98.0% and 98.3% for the two measurements. A typical DPV for the determination of ISPT in an ampoule sample is shown in Fig. 7.

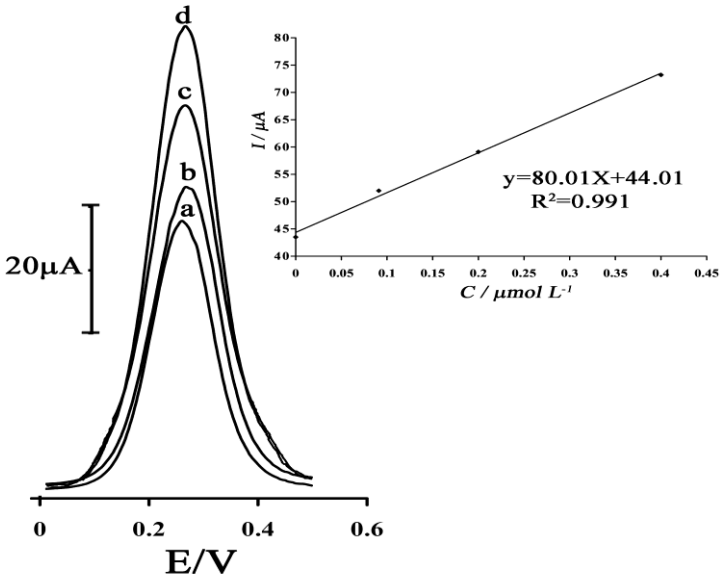

Figure 7. Differential pulse voltammograms of FCMWCNTPE in a solution containing 0.50 µmol L^{-1} ISPT (*pH* 5.0). ISPT added as a) 0.00, b) 0.09, c) 0.200, and d) 0.400 µmol L^{-1}.

Table 2. Determination of ISPT in urine sample.

Urine sample	added(µmol L^{-1})	expected(µmol L^{-1})	found(µmol L^{-1})	Rsd(%)
1			Detection limit	
2	0.50	0.50	0.53+0.01	1.80
3	2.50	3.50	3.56+0.02	2.10
4	1.50	5.00	4.96+0.01	1.80

For the urine sample, each sample was analyzed in triplicate by standard addition using the proposed method. The samples were centrifuged and diluted five times with water without any further pretreatment. The results are given in Table 2. The results indicate that the determination of

isoproterenol using the electrode is effective and can be applied for their detection of isoproterenol in real samples.

7. CONCLUSION

This work demonstrates the application of an organo-metallic compound (ferrocene) for determination of isoproterenol at a surface of multi wall carbon nanotubes paste electrode as a mediator. The results show that the oxidation of isoproterenol is catalyzed by the mediator at *pH* 5.0, whereas the peak potential of isoproterenol is shifted by 140 mV to a less positive potential at the surface of FCMWCNTPE. The catalytic peak current obtained by DPV was linearly dependent on the isoproterenol concentrations and the lower quantitation of 0.07 mol L^{-1}. Current sensitivity, low detection limit, and high selectivity of FCMWCNTPE for the detection of isoproterenol prove its potential sensing applications for the determination of isoproterenol in real samples such as urine and ampoule.

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