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Voltammetric determination of isoproterenol using multiwall carbon nanotubes-ionic liquid paste electrode

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A sensitive and selective electrochemical method for the determination of isoproterenol (ISPT) was developed using multiwall carbon nanotubes and a room temperature ionic liquid (i.e. 1-butyl-3-methylimidazolium hexafluoro phosphate, ([C4mim]-[PF6])). This multiwall carbon nanotubes ionic liquid electrode (MWCNTILEE) is a very good alternative to previously described electrodes because the electrocatalytic effect is achieved without any electrode modification. The oxidation peak potentials in cyclic voltammogram of ISPT on MWCNTILEE was occurred around 470 mV *vs* Ag/AgCl (at pH 6.0) while this peak potential at carbon paste electrode was appeared around 605 mV at the same scan rate of 100 mV s^{-1}. The electrochemical parameters such as diffusion coefficient and charge transfer resistance were determined using cyclic voltammetry and electrochemical impedance spectroscopy. Under the optimized conditions, the peak current was linear to ISPT concentration over the concentration range of 1.0 to 520 μmol L^{-1} using differential pulse voltammetry. The detection limit was 0.85 μmol L^{-1}. The proposed method was successfully applied to the determination of ISPT in both ampoules and urine samples.

Keywords: isoproterenol; ionic liquid; multiwall carbon nanotubes paste electrode; voltammetry

Introduction

Isoproterenol (ISPT) or isoprenaline is a sympathomimetic beta adrenergic agonist medication. It's been used for bradycardia or heart block. By activating β1–receptors on the heart, it induces positive chronotropic, dromotropic, and inotropic effects.[1] ISPT has positive inotropic and chronotropic effects on the heart. In skeletal muscle arterioles it produces vasodilatation. Its inotropic and chronotropic effects elevate systolic blood pressure, while its vasodilatory effects tend to lower diastolic blood pressure. This drug is used to treat bronchitis, cardiac events, and heart attack. Nevertheless, the excess of this substance can causes heart failure and arrhythmia.[2] Therefore, determination of this compound is very important. Various methods including gas chromatography,[3] chemiluminescence,[4–6] spectrophotometry,[7–11] electrochemical methods,[12–14] and flow injection analysis[15,16] have been used for the detection of ISPT. To the best of our knowledge, two electrochemical methods[12,13] based on modified electrode for the determination of ISPT have been reported with a detection limit of 8×10^{-5} mol L^{-1} and 1.6×10^{-7} mol L^{-1}, respectively. On the other hand, no study is reported in the literature on the determination of ISPT, using ionic liquid carbon nanotubes paste electrode.

Ionic liquids have been generating increasing interest over the last decade.[17] In one of the earlier reports, McEwen *et al*. explored electrochemical properties of some common room temperature ionic liquids (RTILs) with an eye towards their applications in electrochemical capacitor.[18] Later, in a series of papers published, detailed preliminary investigations of the potential of RTILs towards electroanalytical applications were reported by many research groups.[19–24]

Since the discovery of carbon nanotubes (CNTs) in 1991,[25] they have been the target of numerous investigations due to their unique properties.[26,27] Distinctive properties of CNTs, such as a high surface area, ability to accumulate analyte, minimization of surface fouling, and electrocatalytic activity are very attractive for electrochemical sensing.[28,29] Recent studies demonstrated that CNTs exhibit strong electrocatalytic activity for a wide range of different compounds such as 6-thioguanine,[30] epinephrine,[31] glutathione,[32] dopamine and uric acid,[33] ascorbic acid,[34] and cytochrome c.[35] Most of the CNT-based electrodes for electroanalytical applications are based on physical adsorption of CNTs onto electrode surfaces, usually glassy carbon.[36] However, it is important to note that CNTs dispersed in mineral oil[30–32] or consolidated into Teflon[37] have been recently used.

In this study we describe a novel strategy for the determination of ISPT using paste electrode containing of multiwall carbon nanotubes plus a room temperature ionic liquid (i.e. 1-butyl-3-methylimidazolium hexafluoro phosphate, ([C4mim]-[PF6])), MWCNTILE. This electrode shows good electrocatalytic and accumulative effect on ISPT. This novel approach shows advantages in terms of high sensitivity, reproducibility, and selectivity. Moreover, the stability is enhanced greatly due to the introduction of ionic liquid as a binder. The analytical feasibility of the approach is examined by measuring ISPT content in different real samples with satisfactory results.

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Experimental

Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. ISPT was from Aldrich. Other reagents were used without further purification.

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

Phosphate buffer solution (sodium dihydrogen phosphate and disodum monohydrogen phophate plus sodium hydroxide, 0.1 mol L^{-1}), PBS, with different pHs were used.

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

Apparatus

Cyclic voltammetry (CV), chronoamperomtry, 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 was 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 min. 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 multiwall carbon nanotubes paste electrode (MWCNTPE) or MWCNTILE. The prepared electrodes with multiwall carbon nanotubes and carbon paste 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.

Fabrication of the modified electrode

To eliminate any metal oxide within multiwall carbon nanotubes, multiwall carbon nanotubes were refluxed in 2.0 mol L^{-1} HNO_3 for 15 h, then they were washed with distilled water and dried at room temperature. MWCNTPE was prepared by hand-mixing 0.900 g of graphite powder and 0.100 g multiwall carbon nanotubes plus paraffin at a ratio of 70/30 (*w*/*w*) and mixed well for 40 min until a uniformly wet 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. MWCNTILE was prepared by mixing of 0.200 g of n-butyl-3-methylimidazolium hexafluoro phosphate, 0.300 g of the liquid paraffin, 0.100 g of multiwall carbon nanotubes, and 0.400 g of graphite powder. Then the mixture was mixed well for 40 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare MWCNTILE.

Preparation of real samples

Ampoule (0.20 mg mL^{-1}) prepared and then 0.10 mL of the solution plus 10 mL of 0.1 mol L^{-1} buffer (pH 6.0) was used for the analysis.

Urine samples were stored in a refrigerator (at 4 °C) 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 it was diluted 5 times with the phosphate buffer pH 6.0. 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.

Recommended procedure

MWCNTILE was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of buffer solution (PBS, pH 6.0), was transferred into an electrochemical cell. The initial and final potentials were adjusted to 0.20 and 0.85 V *vs* Ag/AgCl, respectively. The differential pulse voltammogram (DPV) was recorded with pulse height and pulse width of 100 mV and 5 mV to give the blank 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.

Results and Discussion

Optimization of modified electrode

To obtain the best conditions for the modified electrode, we optimized the ratio of MWCNTs and ionic liquid in MWCNTILE. The oxidation signal of 150 mol L^{-1} ISPT was used for the optimization. The results showed that by increasing the percentage of MWCNTs from 2% to 10% (relative to the other substances present in the modified electrode), the peal current of ISPT increased and then it's levelled off. In addition, the percentages of IL changed from 5% to 30%. Maximum oxidation peak current of ISPT was achieved at 20% IL. Although addition of IL (up to 20%) increased the oxidation peak current of ISPT, but the double-layer charging for the system increased. We selected 10% MWCNTs and 20% IL for the preparation of the modified electrode.

Characteristics of the MWCNTILE using SEM, IR, and cyclic voltammetry

Typical SEM images of different electrodes are shown in Figure 1. It can be seen that at the surface of CPE (Figure 1A), the layer of irregularly flakes of graphite powder was present and isolated with each other. By addition of MWCNTs to the carbon paste, it can be seen that MWCNTs were distributed homogeneously on the electrode with a special three-dimensional structure (Figure 1B), indicating that MWCNTs were mixed well with IL to make a homogeneous mixture on MWCNTILE.

IR spectra of MWCNTs, [C4mim]-[PF6] and MWCNTILE showed that the pretreated MWCNTs presented absorption peaks at 1867 and 1574 cm^{-1}, indicating that MWCNTs bear carboxylic and carboxylate groups.[38] The peaks at 1123 and 3418 cm^{-1} could be ascribed to the stretching vibrations of C–OH and O–H. IR spectrum of [C4mim]-[PF6] film was similar to that reported previously.[39] The strong absorption band at 838 cm^{-1} was caused by PF_6^-. When [C4mim]-[PF6] and MWCNTs form paste, their IR

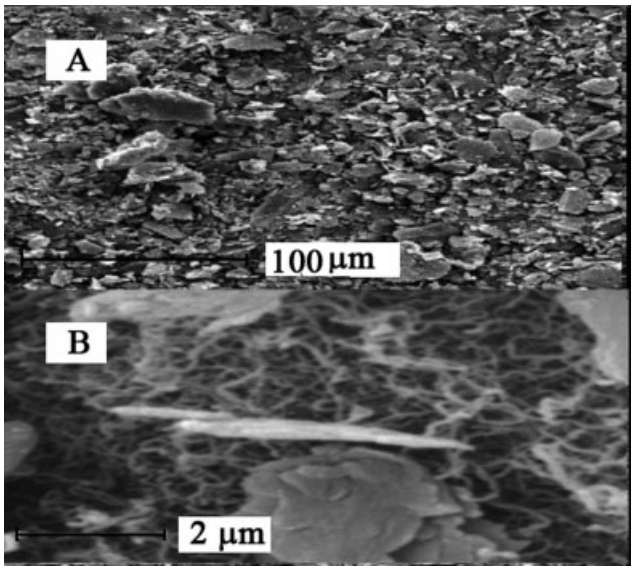


Figure 1. SEM images of CPE (A) and MWCNTILE (B).

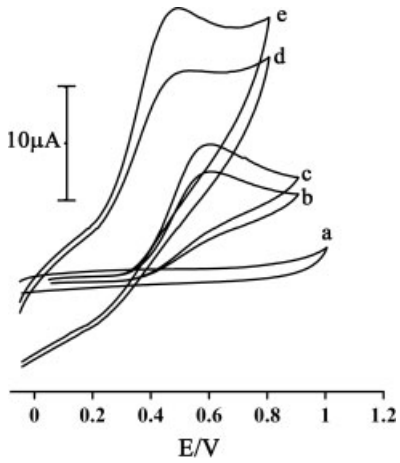


Figure 2. Cyclic voltammograms of (a) CILE in a buffer solution (pH 6.0) in the absence of ISPT; (b) 200 µmol L^{-1} ISPT (pH 6.0) at CPE; (c) 200 µmol L^{-1} ISPT (pH 6.0) at MWCNTs/CPE; (d) 200 µmol L^{-1} ISPT (pH 6.0) at CILE; and (e) 200 µmol L^{-1} ISPT (pH 6.0) at MWCNTILE.

spectrum showed the absorption peaks of [C4mim]-[PF6] and MWCNTs. However the peak at 3418 cm^{-1} shifts to 3125 cm^{-1} and its intensity decreased. This is related to the interaction between MWCNTs and [C4mim]-[PF6].

The direct electrochemistry of ISPT at the surface of the modified electrode was investigated using cyclic voltammetry. Figure 2 shows a typical cyclic voltammograms of different electrodes in a buffer solution (pH 6.0) in the absence or presence of 200 µmol L^{-1} ISPT. In the absence of ISPT no electrochemical responses was obtained on the bare carbon ionic liquid electrode (CILE) (curve a) that indicating no electroactive substance existed on the electrode surface. For the carbon paste electrode (CPE), an electrochemical signal of ISPT was obtained with the oxidation peak current (I_{pa}) of 9.47 µA and an oxidation potential (E_{pa}) of 0.605 V (Figure 2, curve b). On the other hand, at MWCNTs/CPE, the oxidation peak current (I_{pa}) was obtained as 11.97 µA and the oxidation potential (E_{pa}) appeared at 0.590 V (Figure 2, curve c). These small changes in the peak potential indicated that MWCNTs/CPE showed a little catalytic activity to the oxidation of ISPT. In addition, at the surface of bare CILE (without MWCNTs), the oxidation peak of ISPT appeared at 0.505 V with the peak current of 18.4 µA (Figure 2, curve d). That confirmed that presence of ionic liquids (ILs) in CPE could enhance the peak currents and decrease the oxidation potential (decreasing the overpotential). The advantages of CILE had been elucidated with higher conductivity, fast electron transfer rate, good anti-fouling properties and inherent catalytic ability of ILs. So the oxidation peak current increased with decreasing of the overpotential at CILE, while on MWCNTILE, the oxidation peak of ISPT appeared at 0.470 V with the oxidation peak current of 24.0 µA (Figure 2, curve e). The results indicated that the presence of MWCNTs on CILE had greatly improved the electrochemical response of the electrode, which was partly due to excellent characteristics of MWCNTs such as good electrical conductivity, high chemical stability, and high surface area.

The influence of pH on the ISPT electro-oxidation at MWCNTILE was studied. The results showed that the peak current and potential were changed by changing the solution pH (Figure 3, inset, and Scheme 1). It can be seen that maximum value of the peak current was appeared at pH 6.0, so this value was selected throughout the experiments. The formal potential ($E^{0/}$) of the oxidation peak was pH dependent, with a slope of −59.9 mV/pH unit at 25 °C which was equal to the anticipated Nernstian value for a two electrons, two protons electrochemical reaction (Figure 4B). This result is agreed with the oxidation mechanism of ISPT as shown in Scheme 1.

The active surface areas of the modified electrodes are estimated according to the slope of the I_P versus $\nu^{1/2}$ plot for a known concentration of $K_3Fe(CN)_6$, based on the Randles–Sevcik equation:

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

where I_{pa} refers to the anodic peak current, n the electron transfer number, A the surface area of the electrode, D_R the diffusion coefficient, C_0 the concentration of $K_3Fe(CN)_6$ and ν is the scan rate. For 1.0 mmol L^{-1} $K_3Fe(CN)_6$ in 0.10 mol L^{-1} KCl electrolyte (with n = 1 and $D_R = 7.6 \times 10^{-6}$ cm s^{-1}) from the slope of the $I_{pa} - \nu^{1/2}$ relation, the microscopic areas were calculated. They were 0.0041, 0.003, 0.0023 and 0.0012 cm^2 for MWCNTILE, MWCNTs/CPE, CILE and CPE respectively. Those results show that presence of MWCNTs and IL together cause increasing the active surface of the electrode.

The dependence of the oxidation peak current of 200 µmol L^{-1} ISPT on the potential scan rate was evaluated by varying the scan rate from 10 to 400 mV s^{-1} (Figure 4, inset). Figure 4 shows that there was a linear relationship between the peaks current (I_p) and the square root of the scan rate ($\nu^{1/2}$). This indicates that the oxidation of ISPT at MWCNTILE is a diffusion-controlled process.

Chronoamperommetry study

The oxidation of ISPT at surface of MWCNTILE was also studied using chronoamperometry (Figure 5). Chronoamperometric measurements of different concentrations of ISPT at a surface of the electrodes were performed by setting the working electrode potential at a 0.45 V *vs* $Ag/AgCl/KCl_{sat}$. From the chronoamperommetric study the diffusion coefficient, D, of ISPT was determined in aqueous solution. The experimental plots of I *vs.* $t^{-1/2}$ for different concentrations of ISPT were employed (Figure 5, inset). The slops of the resulting straight lines were then plotted *vs* the ISPT concentration. From the slope of the resulting plots and using the Cottrell equation, we calculated D as 5.22×10^{-4} cm^2 s^{-1}.

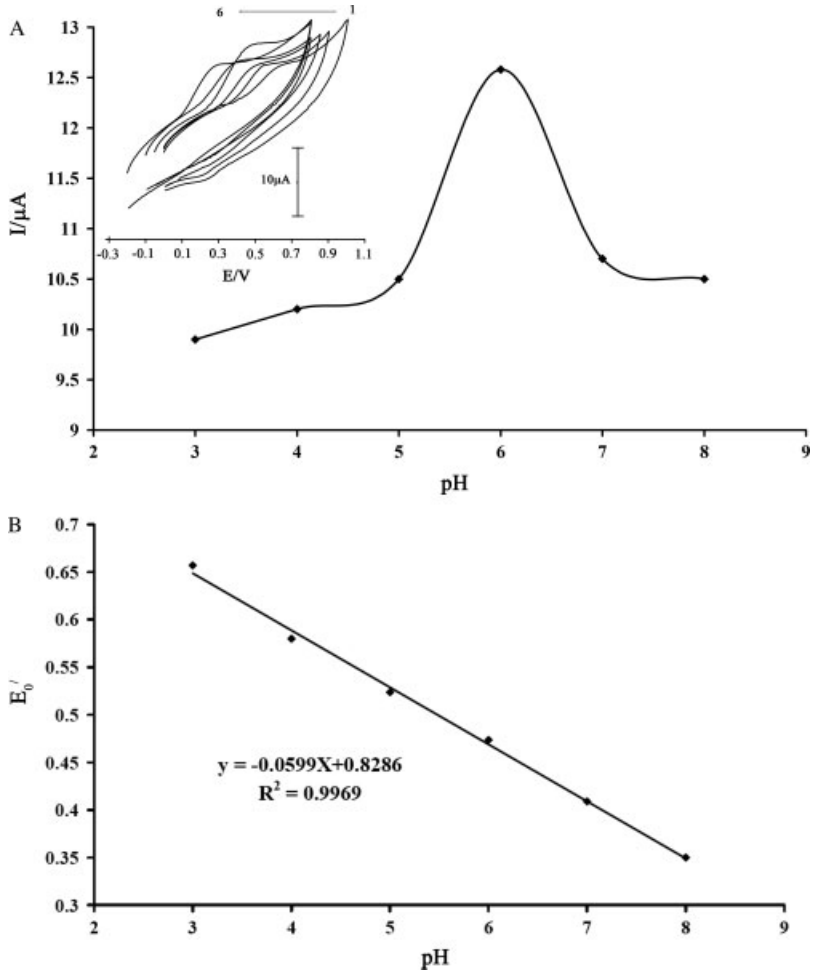
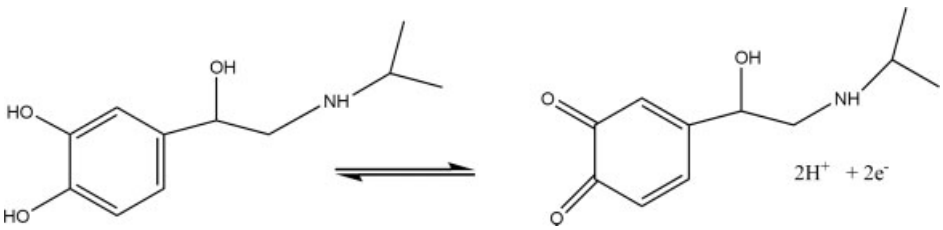


Figure 3. (A) Current–pH curve for electrooxidation of 150.0 μmol L^{-1} ISPT at MWCNTILEE with a scan rate of 100 mV s^{-1}; (Inset) influence of pH on cyclic voltammograms of ISPT at a surface of the modified electrode, (1–6: pH 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0, respectively). (B) Dependence of oxidation formal potential of ISPT vs. pH at the surface of the modified electrode in the presence of 150.0 μmol L^{-1} ISPT.



Scheme 1. Proposed ISPT reaction at the surface of modified electrode in 0.1 mol L^{-1} PBS.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was also employed as a powerful method to investigate the oxidation of ISPT at MWCNTILE. Figure 6 shows typical EIS results of different modified electrodes in 700 μmol L^{-1} ISPT solution. The charge transfer resistance (R_{ct}) value of the bare CPE was achieved as 85.0 ± 0.20 KΩ (Figure 6, curve a). The R_{ct} value of MWCNTs/CPE was decreased to 63.1 ± 0.21 KΩ (Figure 6, curve b), indicating that the presence of high conductive MWCNTs on the CPE cause decreasing the resistance and facilitated the electron transfer of the electrochemical probe. While on the carbon paste ionic liquid electrode, the R_{ct} value was 6.24 ± 0.06 KΩ (Figure 6, curve c) indicating the presence of high ionic conductive (ionic liquid) in the carbon paste could greatly enhance the conductivity of the electrode. For MWCNTILE a nearly straight line appeared with a R_{ct} value of 1.59 ± 0.02 KΩ (Figure 6, curve d). This result indicated that MWCNTs were successfully immobilized on the carbon paste ionic liquid electrode surface and the synergistic effect of MWCNTs and ionic liquid on the modified electrode effectively increased the conductivity of the electrode and promoted the electron transfer.

Stability and reproducibility

The repeatability and stability of MWCNTILE were investigated by cyclic voltammetric measurements of 10.0 μmol L^{-1} ISPT. The relative standard deviation (RSD%) for ten successive assays

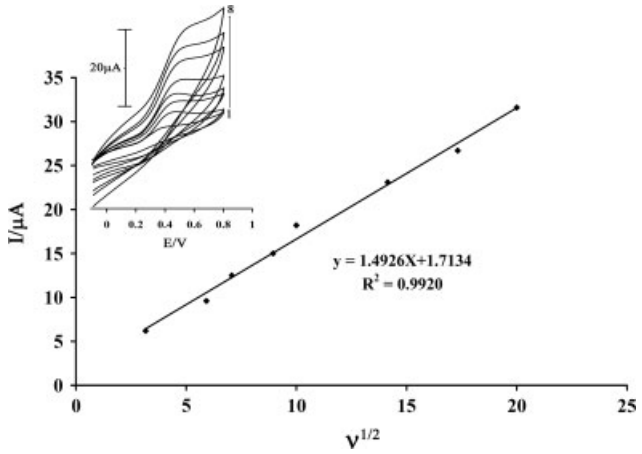


Figure 4. Cyclic voltammograms of ISPT (1.0×10^{-3} mol L^{-1}, pH 6.0) at MWCNTILE with different scan rates of 10, 35, 50, 80, 100, 200, 300, and 400 mV s^{-1}.

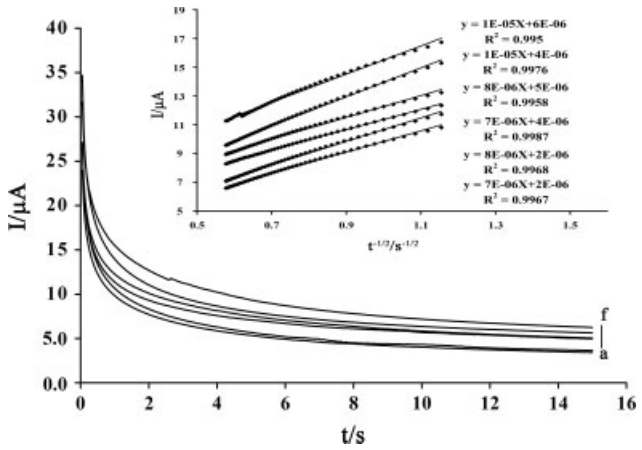


Figure 5. Chronoamperograms obtained at the MWCNTILE in the presence of (a) 650; (b) 700; (c) 750; (d) 800; (e) 900; and (f) 1000 μmol L^{-1} ISPT in the buffer solution (pH 6.0). Inset: Cottrell's plot for the data from the chronoamperograms.

was 0.72%. When using four different electrodes, the RSD% for five measurements was 1.9%. When the electrode stored in the laboratory, the modified electrode retains 98% of its initial response after a week and 93% after 45 days. These results indicate that MWCNTILE has a good stability and reproducibility, and could be used for ISPT analysis.

Analytical Features

Differential pulse voltammetry (DPV) was used to estimate the range of detection and determination of ISPT. The results showed two linear segments with different slopes for ISPT concentration in the ranges of 1.0 to 110, and 110 to 520 μmol L^{-1}. The regression equations were $I_p(\mu A) = 0.1016C_{ISPT} + 26.466$ ($r^2 = 0.9944$, n = 12) for 1.0 to 110 μmol L^{-1} ISPT, and $I_p(\mu A) = 0.0273C_{ISPT} + 35.923$ ($r^2 = 0.9960$, n = 8) for 110–520 μmol L^{-1} ISPT, where C_{ISPT} is μmol L^{-1} concentration of ISPT.

The detection limit of 0.85 μmol L^{-1} ISPT was obtained by DPV method.

Interference Studies

The influence of various substances as potentially interfering compounds for the determination of ISPT was studied under the optimum conditions with 10.0 μmol L^{-1} ISPT at pH 6.0. The potential interfering substances were chosen from the group of substances commonly found with ISPT in pharmaceuticals and/or in biological fluids. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ±5% for the determination of ISPT. After the experiments, we found that neither 800-fold of glucose, sucrose, lactose, fructose, and citric acid, nor 600-fold of Ca^{2+}, Mg^{2+}, Al^{3+}, NH_4^+, and ClO_4^-, nor 300-fold methionine, alanine, phenylalanine, valine, and glycine affected the selectivity. Nor did saturation solution of starch; neither 100-fold of urea and thiourea were interfered with the determination of ISPT.

Analytical Applications

In order to evaluate the applicability of the proposed method for the determination of ISPT in real samples, its utility was tested by determining ISPT in ampoule, and in urine samples. For the ampoule, each sample was analyzed in triplicate by standard addition method using the proposed method. I_{pa} was measured at the oxidation potential of ISPT. The average concentration of ISPT in the injection was 9.50 ± 0.50 μmol L^{-1}, which corresponded quite well with the corresponding value (= 9.47 μmol L^{-1}). This procedure was repeated five times and the relative standard deviation was calculated as 1.8%. Different standard concentrations of ISPT were added to the diluted solution of ISPT injection sample. Then, the ISPT contents were measured. The results showed good recoveries between 97.5% and 102.6% (n = 4).

For the urine samples, each sample was analyzed in triplicate by standard addition method using the proposed method. The samples were centrifuged and diluted five times with water without any further pretreatment. The results are given in Table 1. The recovery ratio indicates that the determination of ISPT using the modified electrode is effective and can be applied for their detection of ISPT in real samples.

Conclusion

MWCNTILE combines the features of carbon nanotubes and room temperature ionic liquid to play a good voltammetric sensor. Hence it shows high sensitivity and reproducibility in sensing of ISPT. Compared with traditional CPE, a decrease of overpotential of oxidation of ISPT was about 135 mV with 2.5-fold increment in the oxidation peak current when using MWCNTILE. Under the optimum conditions, the oxidation peak current was proportional to the ISPT concentration in the range of 1.0 to 520 μmol L^{-1} with the detection limit of 0.85 μmol L^{-1}. The proposed method was successfully applied to the ISPT detection in real samples such as drug and urine.

Acknowledgments

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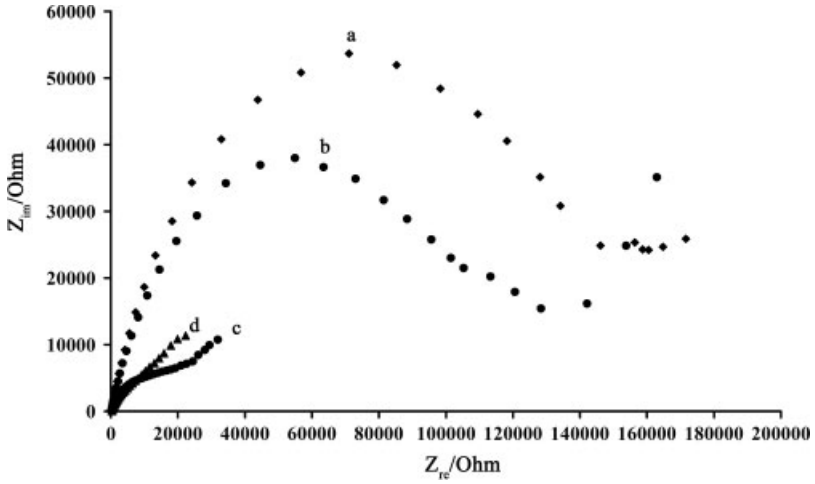

Figure 6. Nyquist plots of (a) CPE, (b) MWCNTs/CPE, (c) CILE and (d) MWCNTILE in the presence of 700 μmol L^{-1} ISPT at the optimum condition.

Table 1. Determination of ISPT in urine samples

Sample	ISPT added (μmol L^{-1})	ISPT expected (μmol L^{-1})	ISPT found (μmol L^{-1})	RSD(%)
1 Urine*	–	–	<detection limit	–
2	20.0	20.0	20.2 ± 0.06	1.0
3	30.0	50.0	50.1 ± 0.04	0.6
4 Urine†	–	–	<detection limit	–
5	10.0	10.0	10.3 ± 0.04	1.1
6	20.0	30.0	30.1 ± 0.05	0.7

* Male urine.
†Female urine.
Average of five replicate measurements.

References

[1] S. Howard, *Illustrated Pharmacology Memory Cards: PharMnemonics*, Minireview LLC: Twinsburg, OH, **2008**, p. 5.
[2] D. Voet, J. G. Voet, *Biochemistry*, Wiley: New York, **1995**, p. 1268.
[3] J. R. Watson, R. C. Lawrence, *J. Pharm. Sci.* **1977**, *66*, 560.
[4] G. J. Zhou, G. F. Zhang, H. Y. Chen, *Anal. Chim Acta* **2002**, *463*, 257.
[5] C. Zhang, J. Huang, Z. Zhang, M. Aizawa, *Anal. Chim. Acta.* **1998**, *374*, 105.
[6] A. A. Al-Warthan, S. A. Al-Tamrah, A. Al-Akel, *Anal. Sci.* **1994**, *10*, 449.
[7] K. O. Lupetti, I. C. Vieira, O. Fatibello-Filho, *Talanta* **2002**, *57*, 135.
[8] P. Solich, C. K. Polydorou, M. A. Koupparis, C. E. Efstathiou, *J. Pharm. Biomed. Anal.* **2000**, *22*, 781.
[9] J. J. B. Nevado, J. M. L. Gallego, P. B. Laguna, *Anal. Chim. Acta* **1995**, *300*, 293.
[10] H. A. El-Obeid, *Anal. Lett.* **1984**, *17*, 771.
[11] R. M. V. Camanas, J. M. S. Mallols, J. R. T. Lapasio, G. Ramis-Ramos, *Analyst* **1995**, *120*, 1767.
[12] V. G. Bonifacio, L. H. Macolino Jr, M. F. S. Teixeira, O. Fatibello-Filho, *Microchem. J.* **2004**, *78*, 55.
[13] A. Kutluary, M. Aslanoglu, *Acta Chim. Slov.* **2010**, *157*, 157.
[14] F. Mashige, Y. Matsushima, C. Miyata, R. Yamada, H. Kanazawa, I. Sakuma, N. Takai, N. Shinozuka, A. Ohkubo, K. Nakahara, *Biomed. Chromatogr.* **1995**, *9*, 221.
[15] J. C. Huang, C. X. Zhang, Z. J. Zhang, *China Chem. Lett.* **1998**, *9*, 843.
[16] O. Nozaki, T. Iwaeda, H. Moriyama, Y. Kato, *Luminescence* **1999**, *14*, 123.
[17] P. Wasserschied, T. Welton (Eds) *Ionic Liquids in Synthesis*, VCH–Wiley: Weinheim, **2002**.
[18] A. B. McEwen, H. L. Ngo, K. LeCompte, J. L. Goldman, *J. Electrochem. Soc.* **1999**, *146*, 1687.
[19] A. Safavi, N. Maleki, S. Momeni, F. Tajabadi, *Anal. Chim. Acta.* **2008**, *625*, 8.
[20] W. Sun, R. Gao, K. Jiao, *J. Phys. Chem. B* **2007**, *111*, 4560.
[21] F. Xiao, C. Ruan, L. Liu, R. Yan, F. Zhao, B. Zeng. *Sens. Actuators B* **2008**, *134*, 895.
[22] W. Sun, X. Li, Yan Wang, X. Li, C. Zhao, K. Jiao, *Bioelectrochemistry* **2009**, *75*, 170.
[23] W. Sun, Y. Li, Y. Duan, K. Jiao, *Electrochim. Acta.* **2009**, *54*, 4105.
[24] L. Lu, T. Kang, S. Cheng, X. Guo, *Appl. Surf. Sci.* **2009**, *256*, 52.
[25] S. Iijima, *Nature* **1991**, *354*, 56.
[26] P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787.
[27] E. Katz, I. Willner, *Chem. Phys. Chem.* **2004**, *5*, 1085.
[28] J. Wang, G. Liu, M. R. Jan, *J. Am. Chem. Soc.* **2004**, *126*, 3010.
[29] F. Patolsky, Y. Weizmann, I. Willner, *Angew. Chem. Int. Edit.* **2004**, *43*, 2113.
[30] A. A. Ensafi, H. Karimi-Maleh, *J. Electroanal. Chem.* **2010**, *640*, 75.
[31] H. Beitollahi, M. Mazloum Ardakani, B. Ganjipour, Hossein Naeimi, *Biosens. Bioelectron.* **2008**, *24*, 362.
[32] A. A. Ensafi, M. Taei, T. Khayamian, H. Karimi-Maleh, F. Hasanpour, *J. Solid State Electrochem.* **2010**, *14*, 1415.
[33] A. A. Ensafi, E. Khoddami, B. Rezaei, H. Karimi-Maleh, *Colloid. Surface B* **2010**, *81*, 42.
[34] Z. H. Wang, J. Liu, Q. L. Liang, T. M. Wang, G. Luo, *Analyst* **2002**, *127*, 653.
[35] J. Wang, M. Li, Z. Shi, N. Li, *Anal. Chem.* **2002**, *74*, 1993.
[36] B. Rezaei, S. Damiri, *Sens. Actuators B* **2008**, *134*, 324.
[37] J. Wang, M. Musameh, *Anal. Chem.* **2003**, *75*, 2075.
[38] J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P.C. Eklund, R. C. Haddon, *Science* **1998**, *282*, 95.
[39] Y. U. Paulechka, G. J. Kabo, A. V. Blokhin, O. A. Vydrov, *J. Chem. Eng. Data* **2003**, *48*, 457.