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Original Scientific Article

Electrochemical Behavior and Electrochemical Determination of Tiamulin Fumarate at an Ionic Liquid Modified Carbon Paste Electrode

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Abstract. The electrochemical behavior of tiamulin fumarate (TF) at ionic liquid *N*-Butylpyridinium hexafluorophosphate ($BPPF_6$) modified carbon paste electrode ($BPPF_6$/CPE) was investigated and further used for tiamulin fumarate sample determination. $BPPF_6$/CPE showed an enhanced electrochemical response towards the electrochemical oxidation of TF. A well-defined and sensitive oxidation peak was observed at $BPPF_6$/CPE in 0.10 M phosphate buffer solution (PBS, pH = 6.80). The oxidation peak current of TF increased significantly at $BPPF_6$/CPE compared with that at carbon paste electrode and the $BPPF_6$/CPE was characterized by the electrochemical impedance spectroscopy (EIS). At the same time, the electrochemical kinetics parameters of TF on the $BPPF_6$/CPE were evaluated. Under the optimized conditions, the oxidation peak currents were linearly dependent on the concentration of TF in the range of 0.3–9.0 µM and 9.0–0.3 mM, with a detection limit of 0.16 µM (S/N = 3). The proposed method has been successfully applied in the electrochemical quantitative determination of TF content in commercial injection samples.

Keywords: Tiamulin fumarate, Ionic liquid modified carbon paste electrode, Electrochemistry, Electrochemical determination

INTRODUCTION

Tiamulin or 14-deoxy-14-[(diethylaminoethyl)mercaptoacetoxy] (Figure 1) mutilin hydrogen fumarate is a semi-synthetic derivative of the natural antibiotic pleuromutilin, isolated from basidio-mycete pleurotus mutilus.[1] It is highly active *in vitro* against staphylococci, streptococci, mycoplasma, and isolates of erysipelothrix pasteurella and treponema hyodysenteriae. The latter being the primary causal agent of swine dysentery. Because of its stability and water-soluble properties, this chemotherapeutic agent is ideally suited for administration to swine in feed, in drinking water, or by injection.[2] It is currently widely used as an antimicrobial agent in veterinary medicine to treat infections in farm animals in many countries, such as in China, over 8000 t of antibiotics are used as feed additives each year.[3] Therefore, to control the drug quality, the development of various techniques for the determination of antibiotics is very important.

To date, several methods for the analysis of tiamulin in animal tissues, milk and plasma have been reported using high-performance liquid chromatography (HPLC),[4] HPLC with ultra violet detection (HPLC-UV),[5] liquid chromatography,[6] reversed-phase liquid chromatography,[7] liquid chromatography/mass spectrometry (LC-MS),[3] liquid chromatography/tandem mass spectrometry (LC-MS-MS,[8] liquid chromatography with diode array or electrospray ionization mass spectrometry detection (LC-DAD-ESI-MS),[9] gas chromatography[10] and so on. However, none of electrochemical techniques determination was reported in the literature to the best of our knowledge.

Room-temperature ionic liquids (RTILs), which are stable salts composed of an organic cation and an inorganic anion, have been shown to exhibit many specific physicochemical properties, such as high chemical and thermal stability, high ionic conductivity, negligible vapor pressure and wide electrochemical windows.[11,12] To date, RTILs have been used in different fields of

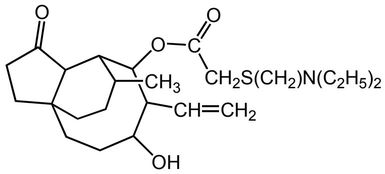

Figure 1. Structure of Tiamulin.

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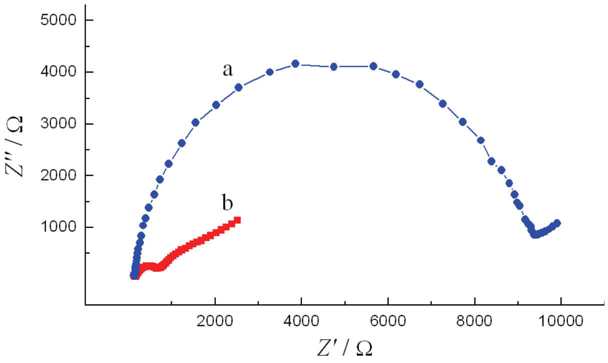

Figure 2. EIS of CPE (a), and BPPF$_6$/CPE (b) in 1.0 mM $Fe(CN)_6^{3-/4-}$ + 0.10 M KCl.The frequency range is 1–10^5 Hz.

chemistry such as analytical chemistry and electrochemistry.[13–18] In the field of electroanalytical chemistry, RTILs could be used as binders for carbon paste electrodes,[19] supporting electrolytes for electrochemical measurements[20] and membrane materials for modified electrodes.[21,22] For example, Zheng *et al.*[23] fabricated an ionic liquid of 1-amyl-3-methylimidazolium bromide modified carbon paste electrode and investigated the voltammetric determination of rutin. Sun *et al.*[24–26] also combined butylpyridinium hexafluorophosphate (BPPF$_6$) with graphite powder to fabricate RTILs modified electrode and was applied in the electrochemical determination of different inorganic, organic and biomolecules. Dong *et al.*[27] declared that the electrodes modified by enzyme-RTILs could allow the efficient transfer of electron between the electrode and the protein. Safavi *et al.*[28,29] fabricated an ionic liquid of octylpyridinium hexafluorophosphate (OPFP) modified carbon paste electrode and investigated the electrochemical oxidation of some phenolic compounds.

As a continuation of our previous work,[30,31] we had used hydrophobic ionic liquid *N*-Butylpyridinium hexafluorophosphate (BPPF$_6$) as a modifier to fabricate BPPF$_6$/CPE and investigated the electrochemical behaviors and electrochemical kinetics of tiamulin fumarate (TF) at BPPF$_6$/CPE. In this work we have found that the oxidation peak currents of TF were increased greatly at BPPF$_6$/CPE compared with that at CPE. The experimental results indicated that BPPF$_6$/CPE could enhance TF electrochemical responses greatly. At the same time, a quantitative electrochemical determination was developed which was successfully used to determine TF in commercial injection samples.

EXPERIMENTAL

All electrochemical experiments were carried out using an Electrochemistry Workstation CHI660A (CH Instrument, USA). The working electrodes were carbon paste electrode (CPE) and *N*-Butylpyridinium hexafluorophosphate (BPPF$_6$) modified carbon paste electrode (BPPF$_6$/CPE). A CHI115 platinum wire and a CHI150 saturated calomel electrode (SCE) served as the auxiliary electrode and reference electrode, respectively. All potentials measured and reported in this work were versus a SCE.

Tiamulin fumarate (Batch No. 20090903) were from Ningxia Duowei Tairui Pharmaceutical Corporation (Yinchuan, China) and used as received and without further purification. Tiamulin fumarate Injection (Batch No. 08040201) from Ganzhou Bailing Pharmaceutical Corporation (Jiangxi, China), *N*-Butylpyridinium hexafluorophosphate (BPPF$_6$) from Chengjie Chemical Reagent Ltd. (Shanghai, China, Purity 99 %), and all solutions were prepared by using deoxygenated and doubly distilled water. All Other chemicals were of analytical grade and also used as received. All experiments were carried out at room temperature.

Carbon paste electrode was prepared as following: 1.50 g of graphite and 0.50 mL of paraffin oil were mixed in a mortar to form a homogeneous mixture. The mixture was pressed by hand into the end cavity of a polytetrafluoroethylene (PTFE) cylindrical electrode body and the surface was polished on a piece of weighing paper. BPPF$_6$/CPE was prepared as followings: 0.50 g of BPPF$_6$ was first dissolved in 2.0 mL of DMF, and then added in 1.50 g of graphite powder in a mortar, ground until DMF totally volatilized, and finally mixed with 0.5 mL of paraffin oil in a mortar. The mixture was pressed by hand into the end cavity of a polytetrafluoroethylene (PTFE) cylindrical electrode body and the surface was polished on a piece of weighing paper.

RESULTS AND DISCUSSION

Electrochemical impedance spectroscopy (EIS) can generally provide useful information on the impedance changes of the electrode surface during the fabrication process.[32] By using $Fe(CN)_6^{3-/4-}$ redox couples as the electrochemical probe, Figure 2 shows the impedance spectra in the form of Nyquist diagrams for different electrodes with the frequencies from 1 Hz to 100 kHz. The diameter of the semicircle is usually equal to the electron transfer resistance (Rct).[33] From the Figure 2, It could be seen that the whole profile for BPPF$_6$/CPE exhibited a quasi-semicircle portion with much smaller diameters (curve b), which was attributed to the good ionic conductivity of IL in the carbon paste and the least charge transfer resistance of BPPF$_6$/CPE. For the CPE an obvious semicircle was observed (curve a), and the diameter of the semicircle CPE (curve a) was much larger than that of BPPF$_6$/CPE. This might be due to the presence of nonconductive paraffin oil in the carbon paste, which played an important role in hindering the electron transfer and made it more difficult for the electron transfer reaction to take place, thus increased the resistance to $Fe(CN)_6^{3-/4-}$ redox couple.[34] The results indicated that the BPPF$_6$/CPE showed markedly different properties from that of the CPE.

The electrochemical behavior of 0.10 mM of TF in 0.10 M PBS were investigated at CPE and BPPF$_6$/CPE at scanning rate of 50 mV s^{-1} over the potential range from 0.0–1.0 V, and the cyclic voltammogram (CV) curves are shown in Figure 3. At the CPE, the cyclic voltammogam of TF (curve a) showed a less sensitive oxidation peaks, with the oxidation peak potential (E_{pa}) at 0.785V, and the oxidation peak current (I_{pa}) was 2.20μA. However, the oxidation peaks current were significantly increased at BPPF$_6$/CPE (curve b) and the peak shape is well-defined, the oxidation peak potential is 0.753 V, and the oxidation peak current (I_{pa}) was 7.52μA. The experimental results indicated that BPPF$_6$/CPE showed a good enhancing effect on the electrochemical oxidation of TF, which was attributed to the specific advantages of RTILs including high conductivity, fast electron transfer rate,[34] therefore, the BPPF$_6$/CPE is more active to TF and can greatly enhance the electrode sensitivity compared with that of the CPE. As a result, the direct oxidation process of TF on the BPPF$_6$/CPE can be greatly improved. In addition, no corresponding reduction peak was observed in the reverse scanning indicating the irreversibility of electrochemical oxidation.

The effect of various media on the peak currents and potentials of TF could be easily observed from CV. The voltammetric behaviors of TF at scanning rate of 50 mV s^{-1} in different electrolyte solutions such as aqueous NaCl, NaAc, $NaNO_3$, Na_2SO_4 and NaAc/HAc, B/R, Na_2HPO_4/NaH_2PO_4 (PBS) solutions had been investigated. The experimental results showed that in 0.10 M aqueous PBS solution, TF had a well-defined electrochemical behavior. Thus, 0.10 M aqueous PBS solution was chosen as a supporting electrolyte.

The effect of solution pH on the oxidation peak potential and peak current for TF were studied in 0.10 M PBS over the range from pH = 2.0–8.5. From Figure 4, it can be seen that with the increasing pH, the oxidation peak potential shifted linearly to negative direction, a linear regression equation was obtained as $E_{pa} = -0.068\text{pH} + 1.235$ (Figure 4a), with a correlation coefficient of 0.9975. The slope was found to be –0.068V was close to the theoretical value of –0.059 V/pH at 25 °C, which indicated that the electron-transfer number and the number of protons taking part in the electrode reaction process was the same. Figure 4b shows the dependence of the oxidation peak currents on the solution pH, it was found that the oxidation peak currents slightly increased from pH = 2.0–3.5, then decreases from 3.5–7.0, and from 7.0–8.5, the anodic peak current almost keep constant.

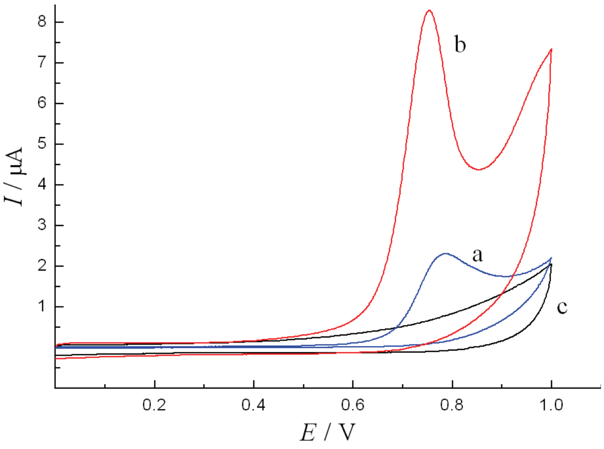

Figure 3. Cyclic voltammograms of BPPF$_6$/CPE in 0.10 M PBS (c), and in the presence of 0.10 mM TF at CPE (a), and at BPPF$_6$/CPE (b). Scanning rate: 50 mV s^{-1}. Accumulation time: 120 s, accumulation potential: 0.30 V.

The effect of scanning rate on the electrochemical behavior of 0.10 mM TF at BPPF$_6$/CPE at different scan rates of 20 to 800 mV s^{-1} were investigated by CV. With the potential scanning rate increasing, the peak currents increased and the peak potentials shifted positively which implied the irreversible nature of the electrode reaction processes. The oxidation peak currents versus the scanning rate were a straight line and the linear regression equation is expressed as $I_{pa}/\mu A = 2.185 + 0.0637v/\text{mV s}^{-1}$, with a correlation coefficient of 0.9983. The results indicated that the electrode process was adsorption controlled one. The electrochemical kinetic parameters are connected by the Laviron's equations:[35]

$$I_p = \frac{n^2F^2vA\Gamma_T}{4RT} = \frac{nFQv}{4RT}, \qquad Q = nFA\Gamma_T \qquad (1)$$

Where n is the number of electron transferred, F is the Faraday's constant (C mol^{-1}), A is the electrode area (cm^2), Q is the peak area (calculated by the charges in C) and v (V s^{-1}) is the scanning rate. Based on the rela-

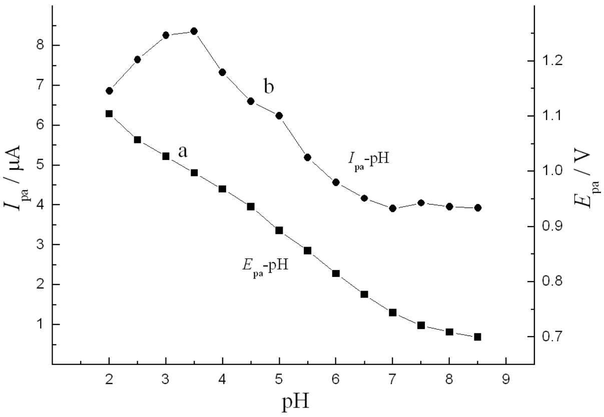

Figure 4. Dependence of E_{pa} (a) and I_{pa} (b) on pH.

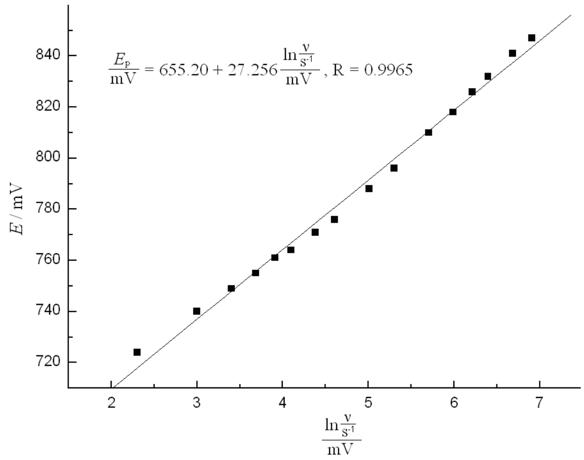

Figure 5. Dependence of the peak potentials on logarithm of scanning rates (ln*v*).

tionship of I_p with v, the values of n was obtained with the results between 1.85 and 2.01, therefore, the values of n is approximately 2.

In addition, the peak potential all shifted positively with the increase of the scanning rate. According to Laviron's equation:[35]

$$E_p = E^0 + \frac{RT}{(1-\alpha)} \ln v \qquad (2)$$

Where α is the charge-transfer coefficient and the other symbols have same meanings as above. The dependency of E_{pa} on ln$v$ for the oxidation of TF at BPPF$_6$/CPE is depicted in Figure 5, its linear regression equation is expressed as $E_{pa}(v) = 655.200 + 27.256 \ln v$, with a correlation coefficient of 0.9965. The E_{pa} - ln$v$ slope is 27.256, the number of electrons involved in the reaction of TF is 2, So it gives the charge- transfer coefficient $\alpha = 0.53$.

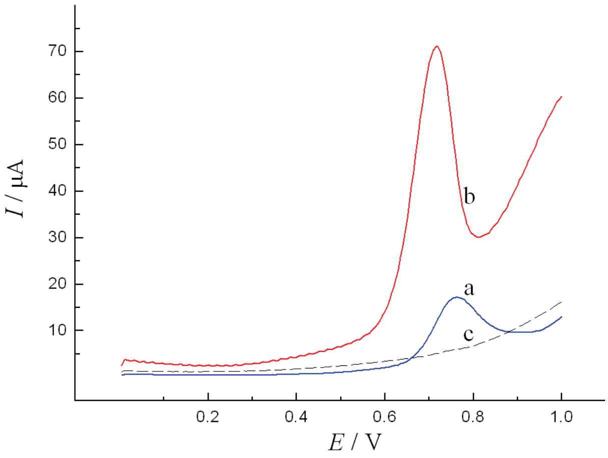

Figure 6. The SWV of BPPF$_6$/CPE in 0.10 M PBS (c), and in the presence of 0.10 mM TF at CPE (a) and at BPPF$_6$/CPE (b). Accumulation time is 120 s; accumulation potential is 0.30 V.

The electrode reaction rate constant (k_f) can be determined by Chronoamperometry (CA) using the following:[36]

$$I(t) = nFAk_fC[1 - 2H\sqrt{t}/\sqrt{\pi}] \qquad (3)$$

In which $H = k_f/D_{Ox}^{1/2} + k_b/D_{Rd}^{1/2}$. For the totally irreversible electrochemical reaction, the value of k_b is 0, therefore $H = k_f/D_{Ox}^{1/2}$. When t approaches to 0, the plot of $I(t)$ *vs.* $t_{1/2}$ gives a good straight line; therefore, k_f can be calculated from the intercept of CA curve, the intercept of CA at BPPF$_6$/CPE is 8.09×10^{-6}. The resulting value of k_f is 7.22×10^{-3} s^{-1}.

The square wave voltammetry responses are markedly depended on the parameters of the excitement signals. Therefore, optimization of pulse amplitude, frequency, and the scanning potential increment were investigated in the experiment. The dependence of the oxidation peak current on pulse amplitude was examined in the range 10–85 mV. Between 10 and 60 mV, the variation of the peak currents with the pulse amplitude was a linear increasing, after 60 mV the variations remained almost constant. Thus, the pulse amplitude of 60 mV was chosen to improve the sensitivity without peak distortion. With a 60 mV pulse amplitude, the frequency was varied in the range 10–85 Hz. From the experimental results we found that between 10 and 65 Hz, the peak current increased linearly with increasing frequency, after 65 Hz, the variation of the current with the frequency remained almost constant. A value of 65 Hz was chose. Also with a 60 mV pulse amplitude and a 65 Hz frequency, a scanning potential increment of 6 mV was found to develop a well-defined peak and a higher current response.

The SWV behaviors of 0.10 mM TF at BPPF$_6$/CPE in the 0.10 M aqueous PBS solution under the optimal experimental conditions (pulse amplitude of 60 mV, frequency of 65Hz, and scanning potential increment of 6 mV) was shown in Figure6. From the curves, it can be seen that TF itself showed a weak SWV response at CPE, but the electrochemical response could be greatly enhanced at BPPF$_6$/CPE. The experimental result was in a quite good agreement with that of CV.

The relationship between oxidation peak currents for TF and its concentration were investigated at BPPF$_6$/CPE. Linear calibration curves are obtained over the range 0.30 to 9.0 μM and 9.0 μM to 0.3 mM in 0.10 M PBS solution with a linear fitting regression equation of I_{pa}/μA = 1.030 + 1846.754C/10^{-3} M and I_{pa}/μA = 17.731 + 241.037C/10^{-3} M with a correlation coefficient of 0.9978 and 0.9947, respectively. The detection limit was 0.16 μM (S/N = 3) for TF under the optimized experimental conditions.

Table 1. TF determination results of the injection samples (n = 6)

Samples	Labeled	Found / g	Added / g	Total / g	RSD / %	Recoverage / %
1	0.125 g / 5 mL	0.124	0.042	0.166	1.3	100.0
2		0.127	0.125	0.255	3.2	102.4
3		0.125	0.208	0.337	1.9	101.4

The influences of various possible interferents were also examined by analyzing a standard solution of 0.10 mM TF at BPPF$_6$/CPE. The amount of the foreign species tolerated was that which caused a change in the responding signal of ±5 %. The interferences of some metal ions and organic compounds have been examined. The experimental results showed that 1000-fold of inorganic ions K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}, 500-fold of glucose, saccharose, citric acid and tartaric acid does not affect TF currents response.

In order to inspect the reproducibility of the electrode, ten times of the parallel determination were made by one BPPF$_6$/CPE, almost the same results were obtained. A relative standard deviation (RSD) of about 3.5 % was obtained by measuring the oxidation peak current for TF electrochemical oxidation. The experimental results showed a good reproducibility for the modified electrode.

The proposed method was successfully applied in the determination of TF in the commercial pharmaceutical samples, the results are shown in Table 1. The 0.10 mM TF sample was prepared by doubly distilled water, and 0.03 mM TF samples were analyzed with the proposed one. An acceptable reproducibility with a relative standard deviation of 1.3–3.2 % was obtained for six parallel measurements. The determination was performed by the standard addition. In addition, the recoverages on the basis of the method were in the range of 100.0–102.4 %. The result indicated that the proposed one can be used as an effective electrochemical determination of TF in the commercial injection samples.

CONCLUSION

In this work, an ionic liquid modified carbon paste electrode with BPPF$_6$ as modifier was fabricated and characterized by EIS. The electrochemical behaviors of TF at BPPF$_6$/CPE were investigated in 0.10 M phosphate buffer solution (PBS), compared with its response at CPE, the electrochemical sensitivity of TF at the modified electrode was improved dramatically, revealing some advantages of BPPF$_6$/CPE over CPE such as high conductivity and fast electron transfer. Under the optimized conditions, a sensitive and simple method for the determination of TF was established and it had been successfully applied to the determination of TF in the commercial injection samples. At the same time, the electrochemical kinetic parameters (the number of electron transferred n, charge-transfer coefficient α, and the electrode reaction rate constant k_f) were determined. In addition, the modified electrode exhibited a distinct advantage of simple preparation, easy surface renewal, good reproducibility and good stability.

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REFERENCES

1. R. L. Hanson, J. A. Matson, D. B. Brzozowski, T. L. LaPorte, D. M. Springer, and R. N. Patel, *Org. Proc. Res. Dev.* **6** (2002) 482–487.
2. B. Cancho Grande, M. S. García Falcón, C. Pérez-Lamela, M. Rodríguez Comesaña, and J. Simal Gándara, *J. Chrom. Suppl.* **53** (2001) 460–463.
3. W. W. Ben, Z. M. Qiang, C. Adams, H. Q. Zhang, and L. P. Chen, *J. Chromatogr. A* **1202** (2008) 173–180.
4. D. Howard and T. Cowen, *Analyst* **107** (1982) 319–323.
5. M. Juhel-Gaugain, B. Anger, and M. Laurentie, *J. AOAC. Int.* **82** (1999) 1046.
6. J. R. Markus, J. Sherma, *J. AOAC. Int.* **76** (1993) 447–448.
7. W. Chan, G. C. Gerhardt, and C. D. Salisbury, *J. AOAC. Int.* **77** (1994) 331–333.
8. M. P. Schlüsener, Kai. Bester, and M. Spiteller, *Anal. BioAnal. Chem.* **375** (2003) 942–947.
9. M. J. Nozal, J. L. Bernal, M. T. Martín, J. J. Jiménez, J. Bernal, and M. Higes, *J. Chromatogr. A* **1116** (2006) 102–108.
10. J. R. Markus and J. Sherma, *J. AOAC. Int.* **76** (1993) 451–458.
11. J. L. Anderson, D. W. Armstrong, and G. T. Wei, *Anal. Chem.* **78** (2006) 2892–2902.
12. M. C. Buzzeo, R. G. Evans, and R. G. Compton, *Chem. Phys. Chem.* **5** (2004) 1106–1120.
13. J. S. Moulthrop, R. P. Swatloski, G. Moyna, and R. D. Rogers, *Chem.Commun.* **5** (2005) 1557–1559.
14. M. C. Buzzeo, C. Hardacre, and R. G. Compton, *Anal. Chem.* **76** (2004) 4583–4588.
15. Z. Y. Li, H.T. Liu, Y. Liu, P. He, and J. H. Li, *J. Phys. Chem. B* **108** (2004) 17512–17518.
16. P. Du, S. Liu, P. Wu, and C. X. Cai, *Electrochim. Acta* **52** (2007) 6534–6547
17. X. M. Wu, P. Du, P. Wu, andC. X. Cai, *Electrochim. Acta* **54** (2008) 738–743
18. X. M. Wu, B. Zhao, P. Wu, H. Zhang, and C. X. Cai, *J. Phys. Chem. B* **113** (2009) 13365–13373
19. W. Sun, R. F. Gao, and K. Jiao, *Electroanal.* **19** (2007) 1368–1374.
20. S. F. Wang, T. Chen, Z. L. Zhang, X. C. Shen, Z. X. Lu, D. W. Pang, and K. Y. Wong, *Langmuir* **21** (2005) 9260–9266.
21. A. Safavi, N. Maleki, O. Moradlou, and M. Sorouri, *Electrochem. Commun.***10** (2008) 420–423.
22. P. Du, S. N. Liu, P. Wu, and C. X. Cai, *Electrochim. Acta* **52** (2007) 6534–6547.
23. Y. Zhang and J. B. Zheng, *Talanta* **77** (2008) 325–330.

24. W. Sun, R. F. Gao, K. Jiao, *J. Phys. Chem. B* **111** (2007) 4560–4567.
25. W.Sun, R. F. Gao, X. Q. Li, D. D Wang, M. X.Yang, and K. Jiao, *Electroanal.* **20** (2008) 1048–1054.
26. W. Sun, Y. Z. Li, Y. Y. Duan, and K. Jiao, *Biosens. Bioelectron.* **24** (2008) 988–993.
27. F. Zhao, X. Wu, M. K. Wang, Y. Liu, L. X. Gao, and S. J. Dong, *Anal.Chem.***76** (2004) 4960–4967.
28. A. Safavi, N. Maleki, O. Moradlou, and F. Tajabadi, *Anal. Biochem.* **359** (2006) 224–229.
29. A. Safavi, N. Maleki, and F. Tajabadi, *Analyst* **132** (2007) 54–58.
30. L. H. Liu and Z. N. Gao, *Chin. J. Pharm. Anal.* **30** (2010). 438–442
31. W. You, Z. N. Gao, *Chin. J. Antibiot* **34** (2009) 422–424.
32. J. J. Feng, G. Zhao, J. J. Xu, and H. Y. Chen, *Anal. Biochem.* **342** (2005) 280–286.
33. E. Katz and I. Willner, *Electroanal.* **15** (2003) 913–947.
34. W. Sun, M. X. Yang, and K. Jiao, *Anal. BioAnal. Chem.* **389** (2007) 1283–1291.
35. E. J. Laviron, *J. ElectroAnal. Chem.* **101** (1979) 19–28.
36. H. Q. Wu and Y. F. Li, *Electrochemical kinetics*, Higher Education Press(Ch), Bei Jing, 1998, p.96.

SAŽETAK

Elektrokemijsko ponašanje i elektrokemijsko određivanje tiamulin fumarata na ugljik-pasta elektrodi modificiranoj s ionskom tekućinom

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U ovom radu, istraženo je elektrokemijsko ponašanje tiamulin fumarata (TF) na ugljik-pasta elektrodi (BPPF$_6$/CPE) modificiranoj s ionskom tekućinom, *N*-butilpiridinij heksafluorofosfatom (BPPF$_6$), korištenom u određivanju uzoraka tiamulin fumarata. BPPF$_6$/CPE pokazuje pojačan elektrokemijski odgovor prema elektrokemijskoj oksidaciji TF. Dobro definiran i osjetljiv pik oksidacije opažen je na BPPF$_6$/CPE u 0,10 M otopinu fosfatnog pufera (PBS, pH = 6,80). Električna struja oksidacijskog pika TF značajno je povećana na BPPF$_6$/CPE u usporedbi s onom od ugljik-pasta elektrode te je BPPF$_6$/CPE okarakteriziran elektrokemijskom impendancijskom spektroskopijom (EIS). Istovremeno, provjereni su elektrokemijski kinetički parametri TF na BPPF$_6$/CPE. Pod optimiranim uvjetima, struje oksidacijskog pika ovisile su linearno o koncentraciji TF u rasponu od 0,3–9,0 μM i 9,0 μM do 0,3 mM, uz granicu detekcije od 0,16 μM (S/N = 3). Predložena metoda uspješno je primjenjena u kvantitativnom elektrokemijskom određivanju sadržaja TF u komercijalnim uzorcima.