



Electrochemical behavior and determination of rutin on a pyridinium-based ionic liquid modified carbon paste electrode

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ABSTRACT

In this paper the electrochemical behavior of rutin on a pyridinium-typed ionic liquid modified carbon paste electrode (IL-CPE) was investigated and further used for rutin sample determination. The IL-CPE showed strong electrocatalytic effects to the oxidation of rutin. In phosphate buffer solution (PBS, pH 2.5; 0.1 M) a pair of well-defined cyclic voltammetric redox peaks of rutin appeared with the redox peak located at 512 mV (Epa) and 448 mV (Epc) (vs. SCE), respectively. The redox peak current was increased about 27.5 times more than that on traditional carbon paste electrode (CPE). The electrochemical parameters of rutin on the IL-CPE were calculated with the results of the charge transfer coefficient (α), the number of electron transfer (n) and the electrode reaction rate constant (k_s) as 0.53, 1.80 and 2.39 s^{-1} , respectively. The cathodic peak currents increased linearly with the concentration of rutin in the range from 5.0×10^{-7} to 1.0×10^{-4} M with the detection limit as 3.58×10^{-7} M (3σ). The relative standard deviation (RSD) of 10 successive detection of 5.0×10^{-5} M rutin was 4.2%. The method was successfully applied to the determination of rutin content in tablets samples with good recovery. The modified electrode showed good stability and reproducibility without the influence of the coexisting substances.

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1. Introduction

Rutin (3',4',5,7-tetrahydroxyflavone 3 β -D-rutinoside, the corresponding chemical structure shown in Fig. 1) is one kind of the most bioactive flavonoid glycosides, which are often used clinically as anti-tumor, anti-inflammatory, anti-oxidants, haemostat and anti-bacterial, etc. As a naturally occurring compound widely presented in plants such as *Flos Sophorae* buds and the leaves of some plants, rutin is often used as a therapeutic medicine with the functions in a wide range of circulatory problems, which can dilute the blood, reduce capillary permeability and lower blood pressure [1]. So it is necessary to develop simple, economic and sensitive methods for rutin determination in pharmaceutical drugs or plants. Many methods have been proposed for the determination of rutin, such as UV-vis spectrophotometry [2], high-performance liquid chromatography (HPLC) [3], flow injection analysis (FIA) [4], capillary electrophoresis (CE) [5], chemiluminescence [6], electrochemical methods [7–9] and sequential injection analysis [10]. Rutin is an electroactive compound, which can be easily subject to either oxidation or reduction on different working electrodes, hence rutin

can be investigated by electrochemical methods. Compared with other methods, electrochemical methods have the advantages such as simple, sensitive, selective with small amounts of sample. Also electrochemical sensors can be fabricated with small dimensions and suitable for placement directly into biological samples. Kang et al. [11] used glassy carbon electrode (GCE) for the rutin determination and further applied to Chinese medicines samples with satisfactory results. Ghica and Brett [12] investigated the electro-oxidation mechanism of rutin on GCE and disclosed a complex and pH-dependent process. Xu et al. [13] used a 2-aminoethanethiol self-assembled monolayer modified gold electrode for the direct determination of rutin without the interference from coexisting ascorbic acid. Wei et al. [14] fabricated a CeO₂ nanoparticle-modified electrode for the rutin determination and demonstrated a strong catalytic effect of nanoparticle towards electrochemical oxidation of rutin. Mousty et al. [15] investigated the feasibility of amperometric detection of rutin at a biosensor using polyphenol oxidase (PPO) and obtained a better sensitivity for rutin.

Room temperature ionic liquids (RTILs) are entirely composed of ions and exist as liquids at room temperature with the characteristics of negligible vapor pressure, good solubility and chemical stability. As a new "green" media, RTILs have many unique electrochemical properties such as high ionic conductivity and wide electrochemical windows [16–18]. They have been recognized as a

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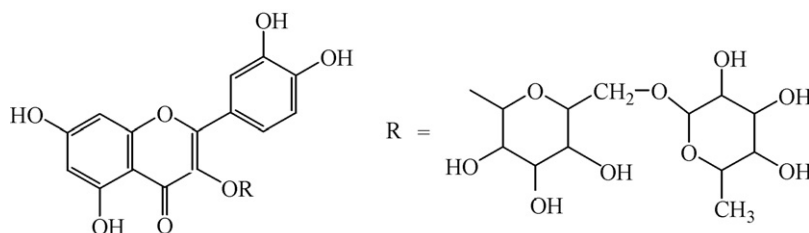


Fig. 1. The molecular structure of rutin.

useful non-aqueous media for various electrochemical processes [19,20]. Recently RTILs have been also used as new modifiers for chemically modified electrodes. Zhao et al. [21] prepared a RTILs/carbon nanotube (CNT) film modified electrode for the voltammetric determination of dopamine (DA) in the presence of uric acid (UA). Li et al. prepared a RTILs modified glassy carbon electrode for the voltammetric determination of chlorpromazine (CPZ) [22] and promethazine [23]. RTILs can also be utilized as a new kind of binder to make modified carbon paste electrode (CPE). Safavi et al. [24] fabricated an ionic liquid of octylpyridinium hexafluorophosphate (OPFP) modified carbon paste electrode and investigated the electrochemical oxidation of some phenolic compounds [25]. Yan et al. [26] established a voltammetric method for UA detection with multi-walled carbon nanotube (MWCNT)/ionic liquid paste coated glassy carbon electrode (GCE). Sun et al. also fabricated a IL modified carbon paste electrode and used it as the basal electrode for protein electrochemistry [27,28] or neurotransmitter detection [29,30].

In this paper a RTILs modified carbon paste electrode (IL-CPE) was used for the investigation of electrochemical behavior of rutin. It was found that IL-CPE showed good electrocatalytic activity for the oxidation of rutin with the increase of the redox peak current in the phosphate buffer solution. The electrochemical behaviors of rutin on the IL-CPE were carefully investigated and a sensitive voltammetric method for rutin determination was further established, which showed no interferences from the coexisting ascorbic acid (AA).

2. Experimental

2.1. Apparatus

All the electrochemical experiments were performed on a LK 98A microcomputer-based electrochemical analyzer (Tianjin Lanlike Chemical and Electron High Technology Company, China). Traditional three-electrode system was used, which was composed of a homemade IL-CPE ($\Phi = 4.4$ mm) as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. All the measurements were carried out at 25 ± 1 °C. A pH S-25C pH meter (Shanghai Lida Instrument, China) was used to adjust the pH of phosphate buffer solution. The solutions were purged with highly purified nitrogen for about 10 min prior to a series of experiments, and a nitrogen environment was kept during the measurements.

2.2. Reagents

Rutin (Shanghai 2nd Reagent Company, China), N-butylpyridinium hexafluorophosphate (BPPF₆, Hangzhou Kemer Chemical Limited Company, China), graphite powder (average particle size 30 μ m, Shanghai Colloid Chemical Plant, China), ascorbic acid (Tianjin Basifu Chemical Limited Company, China) were used as received. 0.1 M phosphate buffer solution (PBS) of

various pH values were used as supporting electrolyte. All other chemicals were of analytical reagent grade and doubly distilled water was used in the experiments. The compound rutin tablets were purchased from Shanxi Linfen Qilin Pharmaceutical Co. Ltd. (050907, 050506), Shanghai Fuxing Zhaohui Pharmaceutical Co. Ltd. (107319) and Shanxi Yunpeng Pharmaceutical Co. Ltd. (108620), respectively, with the specified amount of 20 mg per tablet.

2.3. Procedure

The traditional carbon paste electrode (CPE) was prepared by hand-mixing of graphite powder with paraffin oil at a ratio of 70/30 (w/w). The IL-CPE was fabricated with the following procedures: 3.0 g of graphite powder and 1.0 g of BPPF₆ were mixed thoroughly in a mortar to form a uniform carbon ionic liquid paste and further heated at 80 °C for about 1 h. A portion of the resulted carbon paste was filled into one end of a glass tube ($\Phi = 4.4$ mm) and a copper wire was inserted through the opposite end to establish an electrical contact. The IL-CPE surface was smoothed on a piece of polishing paper just before use [30].

All the cyclic voltammetric experiments were carried out at a quiescent PBS with the scan rate of 100 mV s⁻¹ unless otherwise stated. The procedure for preparing rutin samples were as following: Two pieces of 20 mg rutin tablets were carefully ground in the agar, transferred to a 10 mL calibrated tube and diluted to the scale with ethanol. A 100 μ L portion of the solution was taken and diluted with pH 2.5 PBS in 10 mL calibrated tube, and then the cyclic voltammogram was recorded in the potential range from 0.1 to 0.8 V with the scan rate of 100 mV s⁻¹.

3. Results and discussion

3.1. Electrochemical response of rutin on IL-CPE

Since RTILs have high viscosity and ionic conductivity, the ionic liquid carbon paste modified electrode shows excellent electrochemical behavior such as high conductivity, wide electrochemical windows, good mechanic property and stability [31]. Fig. 2 showed the cyclic voltammograms of rutin on different working electrodes. It can be seen that on the traditional CPE a pair of redox peaks appeared (curve a) with the redox peak potential located at 488 mV (E_{pa}) and 440 mV (E_{pc}) (vs. SCE). The anodic (I_{pa}) and cathodic (I_{pc}) peak current was 5.27 and -4.12 μ A, respectively, and the ratio of redox peak current (I_{pa}/I_{pc}) was calculated as 1.28. Curve b was the cyclic voltammogram of IL-CPE in 0.1 M PBS. Since the electrode was made up of graphite powder and IL, the presence of IL could lie on the surface of graphite powder and fill in the void spaced between the graphite powder. So the observed big background current may be due to the accessible capacitance of the IL on the carbon surface [32]. Curve c was the cyclic voltammogram of IL-CPE in rutin solution. A pair of well-defined redox peaks was observed with good electrochemical behaviors. The redox peak potential located

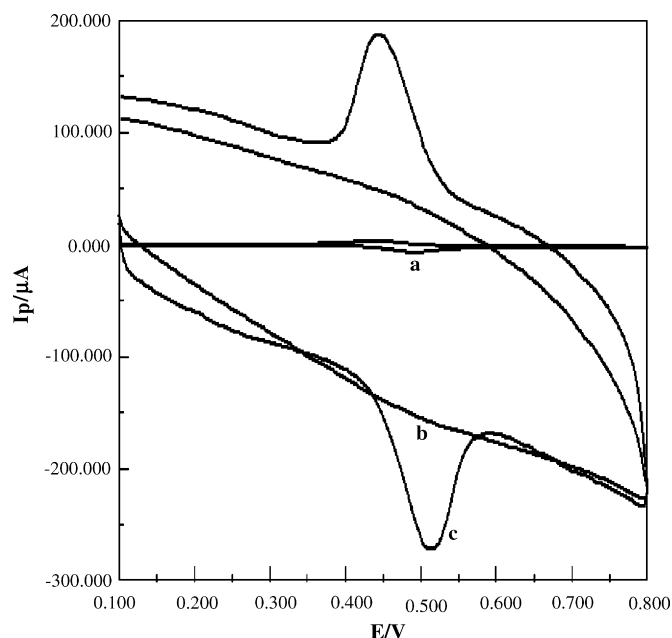


Fig. 2. Cyclic voltammograms of (a) CPE and (c) IL-CPE in pH 2.5 PBS containing 5.0×10^{-5} M rutin, (b) IL-CPE in the buffer solution. Scan rate: 100 mV s^{-1} .

at 512 mV (E_{pa}) and 448 mV (E_{pc}) (vs. SCE). The anodic peak current (I_{pa}) was $145.18 \mu\text{A}$ and the cathodic peak current (I_{pc}) was $-124.92 \mu\text{A}$, which was 27.5 times higher than that on CPE. The ratio of redox peak current (I_{pa}/I_{pc}) was calculated to be 1.16, indicating a more reversible electrode reaction. It is well-known that the increase of the redox peak current and the decrease of the overpotential are the typical indicative of an electrocatalytic reaction. When ILs were mixed with graphite powder, it not only acted as a binder to bind the graphite powder together, but also filled into the void spaces between the graphite powders to form an excellent charge-transfer bridge in the bulk of the CPE. A layer of IL was also formed on the surface of IL-CPE. So the significant improvement of the reversibility and sensitivity was achieved on the IL modified carbon paste electrode.

3.2. Effect of scan rate

The effect of scan rate on the electrochemical response of 5.0×10^{-5} M rutin was also investigated in the range from 30 to 500 mV s^{-1} and the results were shown in Fig. 3. It can be seen that with the increase of the scan rate, the redox peak current increased gradually along with the slight shift of redox potential. The relationship of redox peak currents with the scan rates was constructed and the results showed the redox peak currents were proportional to the square root of scan rate ($\nu^{1/2}$) in the range from 30 to 500 mV s^{-1} , which indicated the electron transfer reaction of rutin on the IL-CPE was diffusion-controlled process in the solution.

The electrochemical parameters of the rutin on the IL-CPE were further calculated. From Fig. 3, it can be seen that the redox peak potentials were also moved with the increase of the scan rate and the peak-to-peak separation increased. The relationship of the peak potentials with scan rate was further constructed, which could be used for the calculation of the electrochemical parameters of rutin. According to the Laviron's equation [33]:

$$E_{pc} = E^{0'} - \frac{RT}{\alpha nF} \ln \nu \quad (1)$$

$$E_{pa} = E^{0'} + \frac{RT}{(1-\alpha)nF} \ln \nu \quad (2)$$

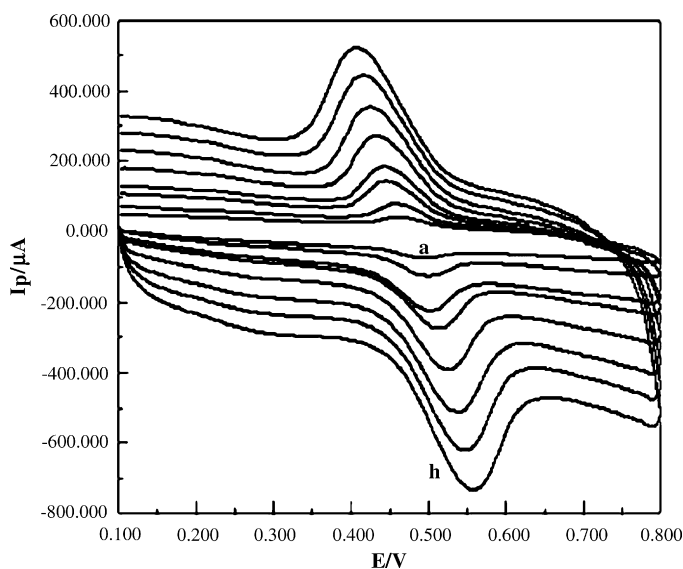


Fig. 3. Cyclic voltammograms of 5.0×10^{-5} M rutin on IL-CPE with different scan rates (a-h: 30, 50, 80, 100, 150, 200, 250, 300 mV s^{-1}) in pH 2.5 PBS.

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha) \log \alpha - \log \frac{RT}{nF\nu} - \frac{(1-\alpha)\alpha nF \Delta E_p}{2.3RT} \quad (3)$$

where α is the charge transfer coefficient, n the number of electron transfer, k_s the electrode reaction constant, ν the scan rate, $E^{0'}$ the formal potentials and F the Faraday's constant.

A linear relationship between the E_p with the $\ln \nu$ was established and two straight lines were got with two linear regression equations as $E_{pa} (\text{V}) = 0.0298 \ln \nu + 0.583$ ($n=6$, $\gamma=0.993$) and $E_{pc} (\text{V}) = -0.0275 \ln \nu + 0.383$ ($n=6$, $\gamma=0.997$). According to the Eqs. (1) and (2) the values of α and n were calculated to be 0.53 and 1.8, respectively. Based on the Eq. (3) the value of k_s was further calculated to be 2.39 s^{-1} .

3.3. Effect of buffer pH

The effect of buffer pH on the electrochemical responses of rutin on the IL-CPE was investigated in the pH range from 2.0 to 8.0 by cyclic voltammetry. From Fig. 4 it could be seen that the maximum

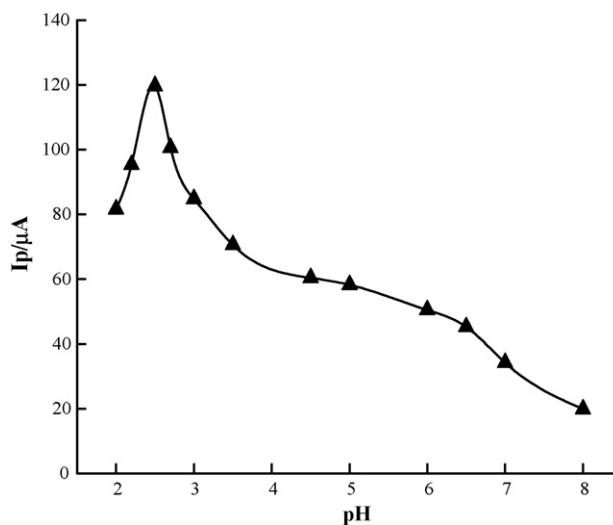


Fig. 4. pH dependence of reduction peak currents with 5.0×10^{-5} M rutin. Scan rate: 100 mV s^{-1} .

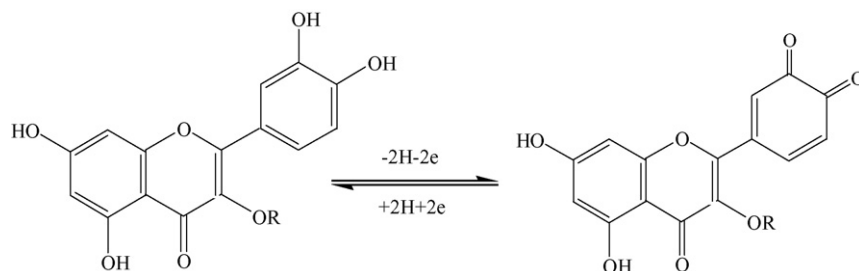
Table 1
Determination results of rutin with different analytical methods.

Methods	Linear range	Detection limit	References
HPLC	4.5×10^{-9} to 1.5×10^{-6} M	1.13×10^{-9} M	[3]
Flow injection analysis	3.0×10^{-8} to 1.2×10^{-5} M	1.0×10^{-8} M	[4]
Capillary electrophoresis	5.0×10^{-6} to 1.0×10^{-3} M	5.11×10^{-7} M	[5]
Chemiluminescence	1.5×10^{-10} to 4.5×10^{-8} M	4.5×10^{-11} M	[6]
Sequential injection analysis	3.0×10^{-6} to 3.0×10^{-5} M	2.25×10^{-6} M	[10]
Differential pulse voltammetry	5.0×10^{-7} to 5.0×10^{-4} M	2.0×10^{-7} M	[14]
Cyclic voltammetry	5.0×10^{-7} to 1.0×10^{-4} M	3.58×10^{-7} M	This paper

value of reduction peak current was got at the pH value of 2.5 and decreased gradually with the further increase of buffer pH. The peak potential was also found to be negatively shifted with the increase of pH value. The results indicated that proton could participate in the electrochemical reaction. Therefore pH 2.5 PBS was chosen as the optimal supporting electrolyte for rutin determination in the following experiments.

The effect of the buffer pH on the formal peak potential (E^0) was also investigated. In the pH range from 2.0 to 8.0, the value of E^0 shifted to the negative direction with the increase of the buffer pH. A linear regression equation was obtained as E^0 (V) = $-0.054\text{pH} + 0.602$ ($n = 12$, $\gamma = 0.995$). The slope of -0.054 was close to the theoretical value of -0.059 V/pH at 25°C . According to the equation: $-0.054x/n = -0.059$, where n is the electron transfer number and x is the number of hydrogen ion participating in the reaction, so the uptaking of electron was accompanied by an equal number of hydrogen ion and $x = n = 2$.

According to the above results the electro-oxidation reaction of rutin on IL-CPE was a two-electron two-proton process and the electrode reaction equation was expressed as follows. The mechanism of electro-oxidation for rutin is first a predissociation of a proton to give the monoanionic species, which is then oxidized to form a radical anion. The radical anion undergoes a second reversible $1e^-$ oxidation to form dehydro-rutin. The latter species is rapidly dehydrated to yield the final product of 3',4'-diquinone.



3.4. Chronocoulometric response

Since the electrode process was diffusion-controlled, the diffusion coefficient could be calculated by chronocoulometric experiment. According to the equation given by Anson [34]:

$$Q = \frac{2nFAD^{1/2}Ct^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$

where n is the number of electron transferred, F (C mol^{-1}) is the Faraday constant, A (cm^2) is the area of the electrode, D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of species, C (mM) is the bulk concentration of species, t (s) is the potential pulse width, Q_{dl} (C) is the double-layer charge, Q_{ads} (C) is the faradic component due to the oxidation of adsorbed species. The parameter D can be calculated from the slope of Q vs. $t^{1/2}$ plot if the values of A , n and C are known.

The relationship between Q and $t^{1/2}$ was constructed with a good linear regression equation as Q (μC) = $13.90t^{1/2} + 17.67$ ($n = 5$, $\gamma = 0.998$). From the slope the diffusion coefficient of rutin was

calculated as $9.16 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which was much larger than previously reported [35]. The result indicated that the electrochemical reaction was accelerated on the IL-CPE.

3.5. Analytical application

Based on the relationship of the oxidation peak current with the rutin concentration, a working curve for rutin determination was established in the range of 5.0×10^{-7} to 1.0×10^{-4} M. The linear regression equation was $I_{pc} (\mu\text{A}) = -1.775C(\mu\text{M}) - 19.58$ ($n = 10$, $\gamma = 0.993$) and the detection limit was estimated as 3.58×10^{-7} M (3σ), which could be used for sensitive quantification of rutin. The comparison of this method with some other different methods for rutin determination was listed in Table 1. As seen from Table 1, HPLC and chemiluminescence showed lower detection limits than the proposed method in this paper. However, the two methods require sophisticated instrumentation, complicated operation and high cost. In this paper, the proposed method showed a significant improvement with simple electrode preparation and low cost.

3.6. Reproducibility and stability

To investigate the precision of the determination, the IL-CPE was applied to the 10 parallel determinations of 5.0×10^{-5} M rutin and

the relative standard deviation (RSD) was calculated as 4.2%. The results indicated that IL-CPE showed good reproducibility. The

Table 2
Influence of coexisting substances on the determination of 5.0×10^{-5} M rutin ($n = 3$).

Coexisting substance	Concentration	Relative error (%)
Glucose	10.0 mg L^{-1}	2.22
Glycine	10.0 mg L^{-1}	1.35
Citric acid	10.0 mg L^{-1}	4.03
L-Arginine	10.0 mg L^{-1}	0.54
HSA ^a	10.0 mg L^{-1}	-4.62
SDS ^b	10.0 mg L^{-1}	-0.27
RNA ^c	10.0 mg L^{-1}	1.42
Mg ²⁺	1.0×10^{-5} M	-5.70
Cu ²⁺	1.0×10^{-5} M	-3.87
K ⁺	1.0×10^{-2} M	4.22
Cl ⁻	1.0×10^{-2} M	4.22

^a Human serum albumin.

^b Sodium dodecylsulfate.

^c Ribonucleic acid.

Table 3
Determination of rutin in compound rutin tablets and the recovery data ($n=5$).

Sample	Specified (mg)	Detected (mg)	RSD (%)	Added (mg)	Detected (mg)	Recovery (%)
050907-1	20.0	19.3	2.95	0.133	0.127	95.5
050907-2	20.0	19.9	1.67	0.133	0.139	104.5
050506-1	20.0	20.2	3.23	0.133	0.130	97.8
050506-2	20.0	19.6	3.17	0.133	0.139	104.5
107319-1	20.0	19.9	2.61	0.133	0.136	102.2
107319-2	20.0	20.2	1.45	0.133	0.133	100.0
108620-1	20.0	19.4	1.37	0.133	0.136	102.2
108620-2	20.0	19.7	3.01	0.133	0.132	99.3

stability of IL-CPE was also studied. After the IL-CPE was stored for 3 weeks, no apparent decrease of the electrochemical response to rutin was observed, which indicated the good stability of the IL-CPE.

3.7. Interference study

The influences of some foreign substances on the determination of 5.0×10^{-5} M rutin were tested according to the general procedure and the results were shown in Table 2. It can be seen that most of them did not interfere with the determination.

Ascorbic acid is the main coexisting substance in compound rutin tablet samples, so the electrochemical responses of rutin in the presence of AA on the IL-CPE were studied. The typical cyclic voltammogram of AA on IL-CPE was shown in Fig. 5 (curve a) and the oxidation peak appeared at 164 mV (vs. SCE). Compared with that of rutin in Fig. 2, it can be seen that the oxidation peak was located at the different potential position and did not interfere with each other. Curve b was the cyclic voltammogram of AA and rutin mixture solution on the traditional CPE. A rather broad oxidation peak was obtained, which showed that the oxidation peak could not be distinguishable due to the oxidation of AA and rutin simultaneously and the peak potentials of them were indistinguishable. So the presence of AA often shows the potential interference to rutin determination and it is impossible to determine the individual substance from the broad anodic peak. While on IL-CPE, two separated oxidation peaks appeared on the cyclic voltammogram with the potentials at 160 and 516 mV

(vs. SCE), which was attributed to that of AA and rutin, respectively (curve c). The oxidation peak potential separation was 356 mV for AA and rutin. These separations were large enough for simultaneously determinations of rutin and AA in the mixed solution.

3.8. Samples determination

The proposed method was further applied to the compound rutin tablet samples determination with the determination results shown in Table 3. It can be seen the current method was sensitive for rutin determination with a good recovery in the range of 95.5–104.5%.

4. Conclusion

In this paper the IL-CPE was used to investigate the electro-oxidation behavior of rutin and the electrochemical parameters of rutin on the IL-CPE were calculated. Compared with traditional CPE, the redox peak current was increased 27.5 times for 5.0×10^{-5} M rutin on the IL-CPE compared with that of traditional CPE. Under the selected conditions, the reduction peak current was proportional to the rutin concentration in the range from 5.0×10^{-7} to 1.0×10^{-4} M with the detection limit as 3.58×10^{-7} M (3σ). The presence of coexisting substances such as AA and amino acids, etc. showed no interferences to the determinations. The proposed method was further applied to rutin tablet samples and demonstrated a new method for rutin determination, which showed good electrochemical characteristics and analytical performance with lower detection limit and higher sensitivity.

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References

- [1] J. van der Geer, J.A.J. Hanraads, R.A. Lupton, J. Sci. Commun. 163 (2000) 51–59.
- [2] H.N.A. Hassan, B.N. Barsoum, I.H.I. Habib, J. Pharm. Biomed. Anal. 20 (1999) 315–320.
- [3] I. Kazuo, F. Takashi, K. Yasuji, J. Chromatogr. B 759 (2001) 161–168.
- [4] C.X. He, X.Y. Zhao, H.Z. Zhao, G.W. Zhao, Anal. Lett. 32 (1999) 2751–2759.
- [5] G. Chen, J.X. Zhang, J.N. Ye, J. Chromatogr. A 923 (2001) 255–262.
- [6] Z.H. Song, S. Hou, Talanta 57 (2002) 59–67.
- [7] G.J. Volikakis, C.E. Efstathiou, Talanta 51 (2000) 775–785.
- [8] N.E. Zoulis, C.E. Efstathiou, Anal. Chim. Acta 320 (1996) 255–261.
- [9] J.L. He, Y. Yang, X. Yang, Y.L. Liu, Z.H. Liu, G.L. Shen, R.Q. Yu, Sens. Actuators B 114 (2006) 94–100.
- [10] Z. Legnerova, D. Satinsky, P. Solich, Anal. Chim. Acta 497 (2003) 165–174.
- [11] J.W. Kang, X.Q. Lu, H.J. Zeng, H.D. Liu, B.Q. Lu, Anal. Lett. 35 (2002) 677–686.
- [12] M.E. Ghica, A.M.O. Brett, Electroanalysis 17 (2005) 313–318.
- [13] Q. Xu, R. Wang, Q.Y. Lu, W.B. Ye, X.W. Cao, X.Q. Wu, Chin. J. Anal. Chem. 34 (2006) 971–974.
- [14] Y. Wei, G.F. Wang, M.G. Li, C. Wang, B. Fang, Microchim. Acta 158 (2007) 269–274.

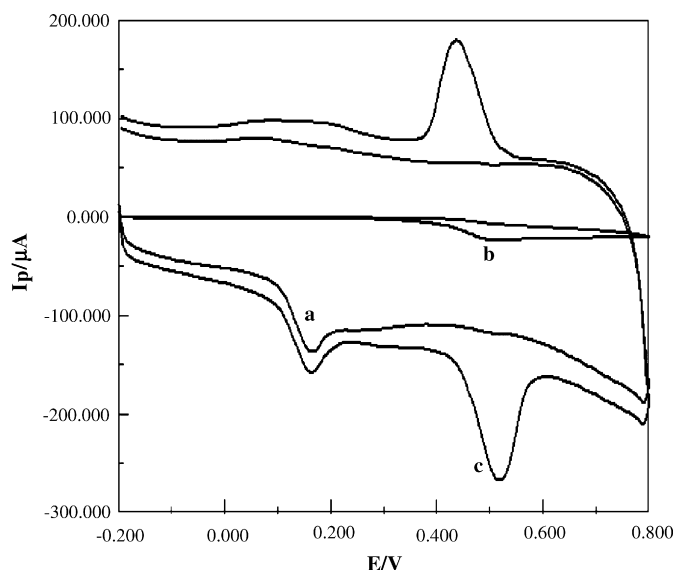


Fig. 5. Cyclic voltammograms of 1.0×10^{-4} M AA on the IL-CPE (a); the mixed solution of 1.0×10^{-4} M AA and 5.0×10^{-5} M rutin on CPE (b) and IL-CPE (c) with scan rate as 100 mV s^{-1} .

- [15] C. Mousty, S. Cosnier, M. Sanchez-Paniagua Lopez, E. Lopez-Cabarcos, B. Lopez-Ruiz, *Electroanalysis* 19 (2007) 253–258.
- [16] M.C. Buzzo, C. Hardace, R.G. Compton, *Anal. Chem.* 76 (2004) 4583–4588.
- [17] Z. Li, H. Liu, Y. Liu, P. He, H. Li, J.H. Li, *Langmuir* 20 (2004) 10260–10267.
- [18] P. He, H. Liu, Z. Li, J.H. Li, *J. Electrochem. Soc.* 152 (2005) E146–E153.
- [19] O. Hiroyuki, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, Inc, New Jersey, 2005.
- [20] M.C. Buzzo, R.G. Evans, R.G. Compton, *Chemphyschem* 5 (2004) 1106–1120.
- [21] F.Q. Zhao, L.Q. Liu, F. Xiao, J.W. Li, R. Yan, S.S. Fan, B.Z. Zeng, *Electroanalysis* 19 (2007) 1387–1393.
- [22] J.W. Li, F.Q. Zhao, P. Xiao, B.Z. Zeng, *Chin. J. Anal. Chem.* 34 (2006) S5–S9.
- [23] J.W. Li, F.Q. Zhao, B.Z. Zeng, *Microchim. Acta* 157 (2007) 27–33.
- [24] A. Safavi, N. Maleki, O. Moradlou, F. Tajabadi, *Anal. Biochem.* 359 (2006) 224–229.
- [25] A. Safavi, N. Maleki, F. Tajabadi, *Analyst* 132 (2007) 54–58.
- [26] Q.P. Yan, F.Q. Zhao, G.Z. Li, B.Z. Zeng, *Electroanalysis* 18 (2006) 1075–1080.
- [27] W. Sun, R.F. Gao, K. Jiao, *J. Phys. Chem. B* 111 (2007) 4560–4567.
- [28] W. Sun, D.D. Wang, R.F. Gao, K. Jiao, *Electrochem. Commun.* 9 (2007) 1159–1164.
- [29] W. Sun, M.X. Yang, K. Jiao, *Anal. Bioanal. Chem.* 389 (2007) 1283–1291.
- [30] W. Sun, M.X. Yang, R.F. Gao, K. Jiao, *Electroanalysis* 19 (2007) 1597–1602.
- [31] G. Shul, J. Sirieix-Plenet, L. Gaillon, M. Opallo, *Electrochem. Commun.* 8 (2006) 1111–1114.
- [32] E. Rozniecka, G. Shul, J. Sirieix-Plenet, L. Gaillon, M. Opallo, *Electrochem. Commun.* 7 (2005) 299–304.
- [33] E. Laviron, *J. Electroanal. Chem.* 101 (1979) 19–28.
- [34] F.C. Anson, *Anal. Chem.* 36 (1964) 932–934.
- [35] B.Z. Zeng, S.H. Wei, F. Xiao, F.Q. Zhao, *Sens. Actuators B* 115 (2006) 240–246.