Colloids and Surfaces A: Physicochem. Eng. Aspects 359 (2010) 25–30

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Square-wave adsorptive stripping voltammetric behaviour of entacapone at HMDE and its determination in the presence of surfactants

Rajeev Jain*, Rajeev Kumar Yadav, Ashish Dwivedi

School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India

ARTICLE INFO

Article history:
Received 29 November 2009
Received in revised form 18 January 2010
Accepted 20 January 2010
Available online 25 January 2010

Keywords:
Entacapone
Surfactants
Adsorptive stripping voltammetry
Hanging mercury dropping electrode
Pharmaceutical dosage forms
Solubilized systems

ABSTRACT

The objective of the present work is to develop a voltammetric method for the determination of entacapone based on the enhancement effect of Tween 20. Addition of neutral surfactant (Tween 20) to the entacapone containing electrolyte enhanced the reduction current signal while anionic surfactant (sodium lauryl sulphate) and cationic surfactant (cetrimide) showed an opposite effect. The reduction process was irreversible over the entire pH range studied (2.5–12). The mechanism of reduction has been postulated on the basis of controlled potential electrolysis and coulometry. The current–concentration plot was rectilinear over the range from 5×10^{-4} mol L^{-1} to 1.8×10^{-5} mol L^{-1} with a correlation coefficient of 0.996 for differential pulse voltammetry (DPV) and 1.6×10^{-4} mol L^{-1} to 1.6×10^{-5} mol L^{-1} with correlation of 0.999 M for square ware voltammetry (SWV) in Britton Robinson buffer at pH 2.5. The lower limit of quantification (LOQ) and the lower limit of detection (LOD) were found to be 0.42 ng mL^{-1} and 0.13 ng mL^{-1} respectively. The analysis of entacapone in its pharmaceutical formulation exhibited the mean recovery of 99% for the reduction peak.

1. Introduction

Entacapone is an inibitor of catechol-O-methyltransferase (COMT), used in the treatment of Parkinson's disease as an adjunct to levodopa/carbidopa therapy. It is anitrocatecole structure compound with a molecular mass of 305.29. Chemically entacapone is represented as (E)-2-cyano-3-(3,4-dihydroxy-5-nitrophenyl)-N,N-diethyl-2-propenamide (Scheme 1) [1].

When levodopa therapy is used in Parkinson's disease, degradation of the drug in the peripheral nervous system is associated with dyskinesias and motor fluctuations. Much of this degradation is produced by catechol-O-methyltransferase (COMT), an enzyme involved in the metabolism of catecholamines and catechol compounds. Inhibition of COMT activity prolongs the action of levodopa and reduces fluctuations in response. Entacapone is a selective inhibitor of COMT whose activity is primarily in the peripheral nervous system, with little effect in the central nervous system [2]. Entacapone increases the bioavailability and reduces the daily variation of plasma levodopa when administered with standard levodopa preparations [3]. The novel COMT inhibitors as entacapone, tolcapone and nitecapone are useful as adjuncts to traditional therapies as levodopa [4–7].

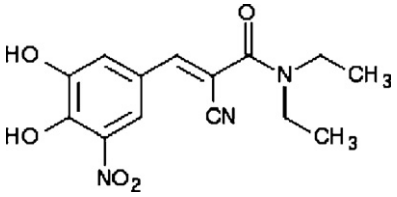
Survey of literature reveals that various spectrophotometric methods have been applied to the determination of entacapone in tablet dosage forms [8,9]. HPLC was also applied to the analysis of entacapone in pharmaceutical formulations and in biological samples [10–13]. Micellar capillary chromatography was developed for glucuronides of entacapone in urine [14,15]. Furthermore, a differential pulse polarographic method was also developed for the determination of entacapone [16]. Although above mentioned techniques offer a high degree of specificity, yet, sample preparation and instrumentation limitations preclude their use in routine analysis.

Electrochemical methods [17–28], such as differential pulse polarography (DPP), stripping voltammetry (SV), differential pulse voltammetry (DPV) and square-wave voltammetry (SWV) have been widely applied for the determination of pharmaceuticals. Furthermore there appears to be no electroanalytical method in the presence of surface active agents for the determination of entacapone in pharmaceutical formulations and in bulk form.

The use of surfactants as drug carriers makes necessary the study of interaction of drugs with micellar systems, implying the elucidation of the nature of these interactions. In the present paper, a micelle-enhanced voltammetric method for the determination of entacapone is proposed and the results obtained were promising.

* Corresponding author at: School of Studies in Chemistry, Jiwaji University, 54 Krishna Vihar, Gwalior, Madhya Pradesh 474011, India. Tel.: +91 0751 2442766, fax: +91 0751 2346209.
E-mail address: rajeevjain54@yahoo.co.in (R. Jain).

0927-7757/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2010.01.047



Scheme 1.

2. Experimental

2.1. Materials and methods

Entacapone (98% purity) was obtained from Alkem Laboratories, Mumbai, India and was used as received. Tablets containing entacapone [*Adacapone*®] labeled 200 mg was obtained from commercial source. KCl (0.1 M) solution was prepared in double distilled water and used as supporting electrolyte. Stock solutions of entacapone (1×10^{-4} mol L^{-1}) were prepared in dimethylformamide (DMF), dioxane, cetrimide, sodium lauryl sulphate (SLS) and in Tween 20. The solutions for recording of voltammograms were prepared by mixing appropriate volume of stock solution, BR buffer and 0.1 M KCl. All chemicals used were of analytical reagent grade quality and were employed without further purification.

2.2. Instrumentation

Electrochemical measurements were performed using a MICRO AUTOLAB TYPE III (Eco-Chemie B.V., Utrecht, The Netherlands) potentiostat–galvanostat with 757 VA computrace software. The utilized electrodes were hanging mercury drop electrode (HMDE) as working electrode, Ag/AgCl (3 M KCl) as reference electrode and a graphite rod as auxiliary electrode. Controlled potential coulometric experiments were carried out using an electrochemical cell i.e. Autolab Potentiostat/Galvanostat PGSTAT Metrohm 663 VA stand with GPES 4.2 (General Purpose Electrochemical Software) Software. Coulometric experiments were performed in the potentiostatic mode using Pt foil with large surface area as working electrode and a Pt wire as the counter electrode. All the solutions examined by electrochemical technique were purged for 2 min with purified nitrogen gas after which a continuous stream of nitrogen was passed over the solutions during the measurements. All pH-metric measurements were made on a Decible DB-1011 digital pH meter fitted with a glass electrode and a saturated calomel electrode as reference, which was previously standardized with buffers of known pH.

3. Results and discussion

The electrochemical behaviour of entacapone on HMDE was studied by using cyclic voltammetry (CV), differential pulse cathodic adsorptive stripping voltammetry (DPCAdSV) and square-wave cathodic adsorptive stripping voltammetry (SWCAdSV). In all electrochemical methods entacapone gave one well defined reduction peak in dioxane at −208.0 V and in Tween 20 at −149.0 V, which is attributed to the reduction of –NO_2 group at mercury electrode.

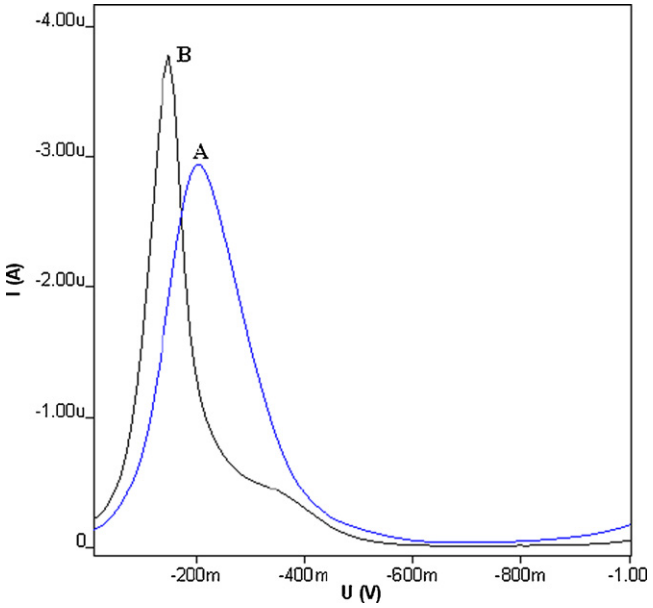


Fig. 1. Square-wave voltammograms of 1×10^{-3} mol L^{-1} entacapone solution in BR buffer, pH 2.5 (A) without the addition of 2.43×10^{-3} mol L^{-1} Tween 20 (B) after the addition of 2.43×10^{-3} mol L^{-1} Tween 20 showing enhancement in peak current.

3.1. Comparison of square-wave cathodic adsorptive stripping voltammetric behaviour of entacapone in the presence and absence of surfactants

On comparing the voltammetric behaviour of entacapone in dioxane and in the presence of surfactants (a neutral, a cationic and an anionic type), it is observed that entacapone shows substantial increase in peak current and the limit of detection is also found to be lower in neutral surfactant Tween 20 (Fig. 1), while cationic and anionic surfactants showed an opposite effect. Electrochemical parameters of entacapone determined at HMDE in solubilized systems are shown in Table 1.

3.2. Effect of pH on reduction wave

For controlling pH various electrolytes such as Britton Robinson buffer, acetate buffer, borate buffer, citrate buffer and phosphate buffer were used. The best results with respect to sensitivity accompanied with sharper response were obtained with Britton Robinson buffer. This study was made in the pH range 2.5–12 at a target concentration of 1.33×10^{-4} mol L^{-1} aqueous entacapone solution. With the rise in pH the peak potential shifted towards more negative potential which indicated the existence of a protonation reaction coupled with the entacapone process.

Fig. 2 shows the influence of pH on the peak height. The effect of pH on the voltammogram of entacapone leads to the conclusion that an acidic medium is suitable for analytical studies. The absolute values of i_p where the peak shape is well defined pass through a maximum at pH 2.5.

Table 1
Electrochemical parameters of entacapone in solubilized systems.

Electrolyte (BR buffer pH 2.5)	E_{pc} (mV) (vs. Ag/AgCl)	i_{pc} (μA)
1.0×10^{-3} mol L^{-1} entacapone + 1.48×10^{-3} mol L^{-1} cetrimide	−129.0	1.6
1.0×10^{-3} mol L^{-1} entacapone + 2.43×10^{-3} mol L^{-1} Tween 20	−149.0	3.59
1.0×10^{-3} mol L^{-1} entacapone + 1.73×10^{-3} mol L^{-1} sodium lauryl sulphate	−149.0	1.05
2.0×10^{-3} mol L^{-1} entacapone in dioxane	−208.0	2.82
2.0×10^{-3} mol L^{-1} entacapone in DMF	−228.0	2.19