Research article

Drug Testing and Analysis

Received: 14 September 2010 Revised: 3 November 2010 Accepted: 3 November 2010 Published online in Wiley Online Library: 23 February 2011

(www.drugtestinganalysis.com) DOI 10.1002/dta.240

Voltammetric quantification of tamoxifen

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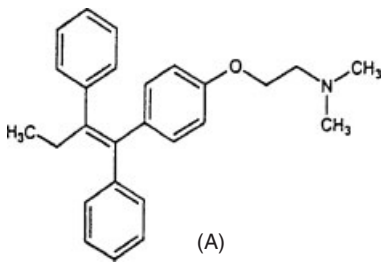
The electrochemical behaviour of tamoxifen has been investigated at gold electrode by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and squarewave voltammetric techniques. The dependence of current and potential on pH, concentration, scan rate, nature of solvent, surfactants and different surfactant concentration is investigated. Tamoxifen is oxidized in a single two-electron, irreversible and diffusion-controlled wave. Linear calibration plots are obtained over the concentration range 1.0–5.0 and 1.0–6.0 μgmL^{-1} in 1.0 M KCl and Britton Robinson buffers (pH 2.51) respectively. The procedure has been applied to the assay of the drug in tablet form with mean percentage recoveries of 99.98%. The suggested method can be successfully applied to the determination of tamoxifen in different drug formulations.

Keywords: tamoxifen; voltammetry; surfactant; pharmaceutical formulation

Introduction

Tamoxifen (A) is an oral nonsteroidal antiestrogen drug that has been widely used for treatment and prevention of breast cancer over the last 28 years.[1–3] Tamoxifen (A) has some serious side effects, such as endometrial cancer and thromboembolic diseases that limit its use in healthy woman.[4–7]



(A)

Several methods have been reported for the quantitative analysis of tamoxifen and metabolites in biological fluids and pharmaceutical formulation including high performance liquid chromatography (HPLC),[8–10] non-aqueous capillary electrophoresis,[11,12] gas chromatography,[13] potentiometry,[14] gas chromatography-mass spectrometry,[15] polarography,[16] single sweep voltammetry[17] and spectrophotometry.[18] Electrochemical methods have been widely applied for the determination of pharmaceuticals and biomolecules.[19–41] Electrochemical techniques have led to the advancement in the field of analysis because of their sensitivity, low cost and relatively short analysis time, compared with other techniques.[42–44]

Many drugs developed by the pharmaceutical industry suffer from poor water solubility which may substantially limit bioavailability.[45,46] The development of meaningful dissolution procedure for drug products with limited water solubility has been a great challenge for analysts.[47] It has been seen that surfactants play a very important role in electrode reactions, not only in solubilizing[48–50] organic compounds but also by providing specific orientation to the molecules at the electrode interface. Surfactants[51] are included as excipients in many drug formulations, with the objective of improving the dissolution rate, increasing drug solubility, reducing interfacial tension and contact angle between solid particles and aqueous media, thus improving drug wettability and increasing surface availability for the drug dissolution.

No comprehensive electroanalytical study of tamoxifen of using cyclic voltammetry, differential pulse voltammetry or square-wave voltammetry at gold electrode and in solubilized systems is available in the literature. The gold electrode has been widely used in electrochemical studies and electro analysis for various substrates for a long time because of its stability, wide potential window and fast electron transfer rate.[52,53]

The present communication reports a validated, rapid and selective voltammetric method for the simple and direct determination of tamoxifen in bulk form, pharmaceutical formulation in the presence of surfactant without any time-consuming extraction or separation steps prior to drug assay.

Experimental

Reagents and materials

Tamoxifen was obtained from different pharmaceutical manufactures and was used as received. Tablets containing tamoxifen citrate labelled 20.0 mg tamoxifen citrate were obtained from commercial sources. For the preparation of standard tamoxifen citrate stock solution 2.0 mgmL^{-1}, 100 mg tamoxifen citrate was accurately weighed, dissolved in 1.0% Triton X-100 and then adjusted to 50 mL with the same surfactant to give the appropriate concentration. Standard working solutions were prepared by appropriate dilutions of the stock solution. Britton Robinson buffer in the pH range 2.0–12.0 was prepared in distilled water by adding suitable amounts of 0.4 M NaOH solution to a stock solution composed of a mixture of 2.14 mL phosphoric acid, 2.472 g boric acid and 2.3 mL of glacial acetic acid.

The pH metric studies were carried out on a Decibel DB-1011 digital pH meter with combined glass calomel and saturated calomel electrode. All reagents used were AR grade and the

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solutions were protected from light. High purity water was obtained from Millipore (Milford, MA, USA) Milli-Q Plus system.

Instrumentation

Electrochemical measurements were performed with Metrohm Computrace Voltammetric Analyzer μ-AUTOLAB TYPE III Potentiostat Ecochemie (Utrecht, the Netherlands) Model 757 VA computrace software. A conventional three-electrode system was used consisting of an Ag/AgCl (3.0 M KCl) as a reference electrode, gold electrode as a working electrode and a graphite rod as auxillary electrode. The whole measurements were automated and controlled through the programming of the apparatus. The data were obtained through a PC connected to the Electrochemical Analyzer version-757 VA computrace. The controlled potential coulometric experiments were performed using μ-Autolab Potentiostat/Galvanostat PGSTAT Metrohm 663 VA stand as electrochemical cell, fitted with the appropriate GPES 4.2 Software.

Controlled potential electrolysis and coulometric experiments were performed in the potentiostatic mode using Pt foil with large surface area as working electrode and Pt wire, counter electrode. Working electrode was polished with 0.5-µm alumina powder on a polishing cloth before each electrochemical measurement. All the solutions examined by electrochemical technique were purged for 5 min with purified nitrogen gas. All measurements were carried out at room temperature.

Tablets assay procedure

Tamoxifen citrate determination was performed on commercially available tablets from tamoxifen citrate. The amount of tamoxifen citrate present in each tablet was 20.0 mg. A sufficient amount of powder for preparing a stock solution of 10.0 mgmL^{-1} was weighed and transferred into a 25-mL volumetric flask and completed to volume with 1.0% Triton X-100 surfactant. The content of the flask was sonicated for 30 min to provide complete dissolution and then completed to volume with the same solvent and centrifuged. A suitable amount of the liquid was diluted to 10 mL with appropriate B.R. buffer solution of pH 2.5–12.0, 1.0% Triton X-100 and mixed 1.0 M KCl as supporting electrolyte. The sample solution was transferred to a voltammetric cell. The content of the drug in the tablet was determined referring to the calibration graph or regression equation.

Recovery studies

To study the accuracy and repeatability of the applied methods, recovery experiments were carried out using the standard addition method. In order to know whether the excipients show any interference in the analysis, known amounts of the pure tamoxifen was added to the pre-analyzed tablet vial formulation and the mixtures were analyzed by differential pulse voltammetry (DPV) and squarewave voltammetry (SWV) techniques. After three repeated experiments, the recovery results were calculated using the related calibration equations.

Results and discussion

The electrochemical behaviour of tamoxifen citrate on gold electrode was studied by using cyclic voltammetry (CV), DPV, SWV.

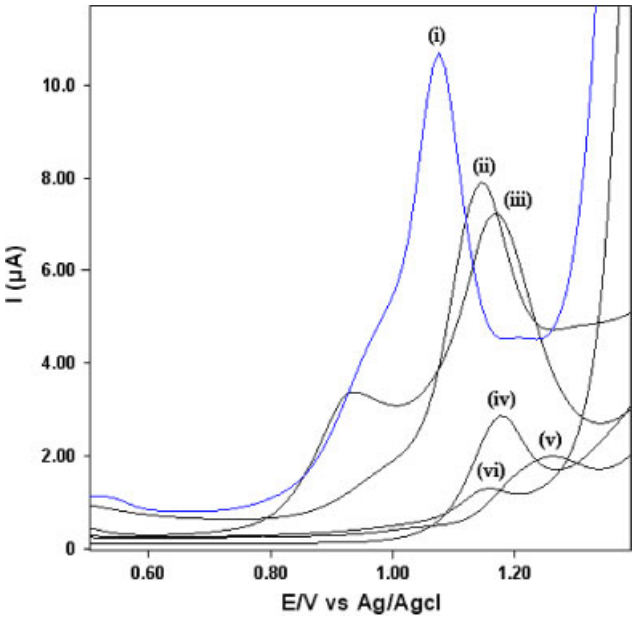


Figure 1. Square wave voltammogram of 2.0 µgmL^{-1} tamoxifen citrate (i) TX-100 (ii) Methanol (iii) CTAB (iv) SLS (v) Tween-20 (vi) Water.

In all electrochemical methods tamoxifen citrate gave one well-defined oxidation peak in different media viz. water, methanol, SLS, CTAB, Tween-20 and Triton X-100, which is attributed to the formation of new bond at gold electrode (Figure 1).

Effect of surfactants

The squarewave voltammetric response of tamoxifen citrate was compared in water, methanol and in presence of surfactants. The influence of different kinds of surfactants including cetyltrimethyl ammonium Bromide (CTAB), sodium lauryl sulfate (SLS), Tween-20 and Triton X-100 were investigated. Maximum peak current is observed when tamoxifen citrate solution was solubilizied in Triton X-100 (Figure 1).

The reason for the increase in peak current may arise from the evidence given by Fuerstenau *et al*. due to the occurrence of lateral interaction in the adsorbing species. They concluded that once the adsorbed ions reach a certain critical concentration at the interface, they begin to associate into two dimensional patches of ions, which Fuerstenau *et al*. termed as 'hemi micelles'.[54–56] The tamoxifen citrate molecules which are essentially non-polar, as is observed by its low solubility in water, are attracted to the non-polar region of these hemi micelles, which are oriented towards the electrode surface. Thus more tamoxifen citrate molecules reach to the electrode surface as a consequence of which there is a rise in peak height.

The effect of surfactants on the peak height of poorly soluble drugs can also be explained by the fact that the amphiphilic structure of surfactants and their assembly in aqueous solution provides a multifunctional environment for the solubilization and partitioning of aqueous soluble and insoluble compounds.[57] Micellar assemblies have the ability to dissolve significant amounts of different types of water insoluble redox active probes that can be electrochemically studied at suitable electrodes. Aqueous micellar solutions are surfactant-based organized systems that can be used as less hazardous and versatile substitutes for organic solvent in voltammetry.

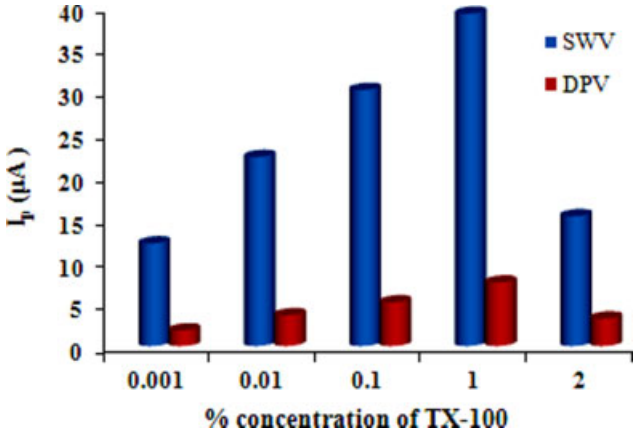


Figure 2. Plot of (SWV and DPV) i_p (μA) vs concentration of TX-100 (1) 2.0% (2) 1.0% (3) 0.1% (4) 0.01% (5) 0.001% in B.R.buffer, pH 2.51.

The voltammetric behaviour of tamoxifen citrate with different concentration of Triton X-100 was examined and it was found that the enhancement in oxidation peak current is closely related to the concentration of Triton X-100. The relationship between the oxidation peak current and Triton X-100 concentration is illustrated in Figure 2. Gradually improving the concentration of Triton X-100 from 0.001%–1.0%, the oxidation peak current increases gradually; when further increasing Triton X-100 concentration to 2.0%, the oxidation peak current changes decrease.

The decrease in peak current with increased concentration of Triton X-100 is due to micelle formation, resulting in partition of the drug between the aqueous phase and micelle, i.e. it gets entrapped in the insulated hydrophobic environment of the micelle and then diffuses along with the micelle, which leads to drop in peak current.[58] Therefore 1.0% concentration of Triton X-100 is chosen as optimum one.

Effect of pH

For controlling pH, various buffers such as Britton Robinson (BR), acetate, borate, citrate and phosphate were used. The best results with respect to sensitivity accompanied with sharper response are obtained with B.R. buffers. Therefore study was made in the pH range 2.5–12.0 in Britton Robinson buffers at a target concentration of 1.0 μgmL^{-1} tamoxifen solution. With the rise in pH, the peak potential shifted towards positive potential, which indicated the existence of a protonation reaction coupled with the tamoxifen oxidation process.

The relation between E_p and pH over the range 2.5–8.0 is expressed by the following equations:

$$\text{SWV, pH 2.5–8.0}: E_p\,(V) = 0.026 + 1.057\ \text{pH}, r^2 = 0.989 \quad (1)$$

$$\text{DPV, pH 2.5–8.0}: E_p\,(V) = 0.028 + 1.005\ \text{pH}, r^2 = 0.996 \quad (2)$$

Linear pH dependence of the peak potential for oxidation wave in the range of 2.5–8.0 shows that protons participate directly in the reduction process. After pH 8.0, no significant displacement in peak potential was observed. The peak potential of the two-electron wave is pH independent because equilibrium is completely shifted to the left-hand side (i.e. pH < 8.0), which indicates that proton-transfer occurs as a step consecutive to irreversible electrode processes. The height of the peak reaches a maximum at pH 2.5 and after that it decreases. Therefore, pH 2.5 was chosen as the optimum value for the determination of tamoxifen.

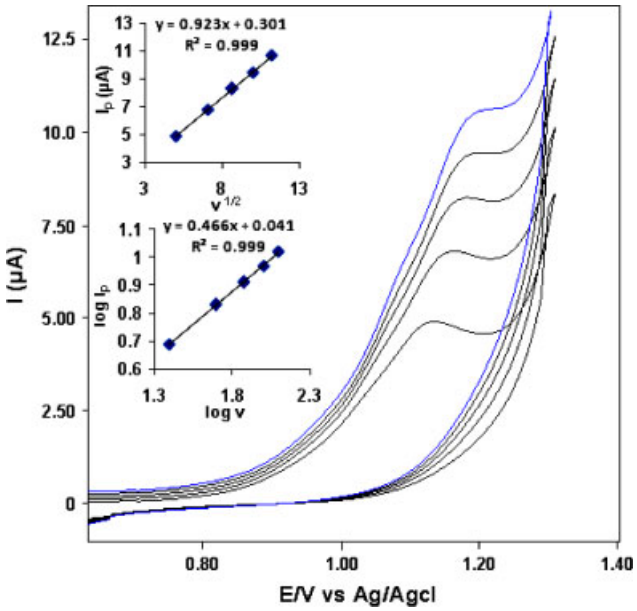


Figure 3. Cyclic voltammograms of 6.0 μgmL^{-1} tamoxifen citrate in 1.0% TX-100 at different scan rates; 25, 50, 75, 100 and 125 mVs^{-1}.

Characterization of the electrode reaction

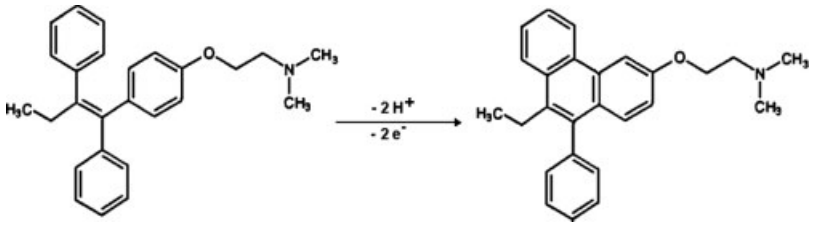
The cyclic voltammogram of 6.0 μgmL^{-1} tamoxifen citrate solution in B.R. buffer of pH 2.5 at gold electrode exhibited a single well-defined anodic peak 1.17 V (Figure 3). No cathodic peak was observed on the reverse scan confirming the irreversible nature of the electrode process. Moreover, the peak potential shifted to a more positive value with increasing scan rate, also pointing towards the irreversible nature of the electrode process.

The effect of scan rate (υ) on the peak current (i_p) was also examined. A linear correlation was obtained between the peak intensity i_p (μA) and the square root of the scan rate $\upsilon^{1/2}$ (mVs^{-1}) expressed by the equation (i_p) (μA) = $0.923\upsilon^{1/2} + 0.301$ (μA), $r^2 = 0.999$.[59,60] This finding is further confirmed by the plot of log i_p vs logυ, log i_p (μA) = 0.466 logυ + 0.041 (μA), $r^2 = 0.999$. A slope of 0.466 is observed which is close to 0.5.[60]

Controlled potential coulometry

Using controlled potential coulometry, the number of electrons transferred, 'n' were calculated from the charge consumed by the desired concentration of tamoxifen. The charge consumed was determined in acidic medium. For this purpose 10.0 $mgmL^{-1}$ solution of the electro active species was placed in the cell and electrolysis was carried out at a potential 1.4 V against Ag/AgCl reference electrode. Number of electrons 'n' was calculated using the equation Q = nFN, where Q is the charge in coulombs, F is the faraday constant and N is the number of moles of the tamoxifen. The number of electrons involved in the oxidation process was found to be two.

On the basis of CV, DPV, SWV and coulometry experimental results, the following mechanism for the oxidation of tamoxifen in Triton X-100 has been postulated (Scheme 1).



Scheme 1.

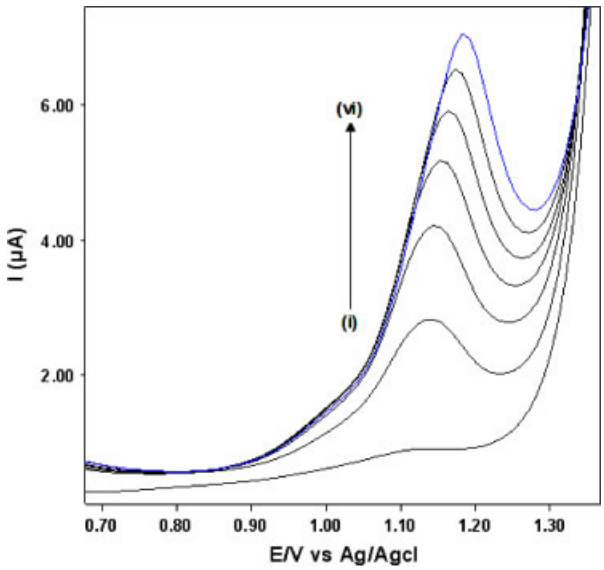


Figure 4. The dependence of the DPV current for tamoxifen citrate at different concentrations; B.R. buffer pH 2.5, (i) Blank (ii) 1.0 µgmL^{-1} (iii) 2.0 µgmL^{-1} (iv) 3.0 µgmL^{-1} (v) 4.0 µgmL^{-1} (vi) 5.0 µgmL^{-1} (vii) 6.0 µgmL^{-1}.

The oxidation peak obtained was attributed due to the cyclization reaction to form the corresponding phenanthrene derivative.

Analytical application

Validation of the analytical procedure

The linearity of the proposed SWV and DPV procedures as an analytical tool for the determination of tamoxifen citrate was examined by measuring the peak current as a function of concentration of the bulk drug for at least three times under the optimized operational parameters. The calibration plot of the peak current versus the concentration are linear over the range 1.0 to 5.0 and 1.0 to 6.0 µgmL^{-1} in the square wave and differential pulse (Figure 4) voltammetric methods and the linear regression equations are expressed as:

$$\text{SWV} : [I_p(\mu A) = (2.902)\, C\ (\mu g mL^{-1}) + 4.130],\ r^2 = 0.984 \quad (3)$$

$$\text{DPV} : [I_p(\mu A) = (0.957)\, C\ (\mu g mL^{-1}) + 1.086],\ r^2 = 0.987 \quad (4)$$

The regression plots show that there is a linear dependence of the current intensity on the concentration in both SWV and DPV modes over the range as given in Table 1.

The sensitivity of the optimized procedure for quantitative assay of tamoxifen was examined via evaluation of the limit of detection (LOD), limit of quantification (LOQ), accuracy, precision and recovery. Results are compiled in Table 1.

Table 1. Analytical parameters for voltammetric determination of tamoxifen citrate

Operational Parameter	SWV	DPV
Measured potential (V)	1.18	1.17
Linear range (µgmL^{-1})	1.0–5.0	1.0–6.0
Slope (µA/(µgmL^{-1})	2.902	0.957
Intercept (µA)	4.130	1.086
Correlation coefficient (r^2)	0.984	0.987
S_a	0.0025	0.0030
Number of data points	5	6
LOD (ngmL^{-1})	2.59	9.40
LOQ (ngmL^{-1})	8.94	31.3
Repeatability (RSD %)	0.68	0.76
Reproducibility (RSD %)	0.72	0.84
Application	Tablet	Tablet

The precision and reproducibility of these developed methods (SWV, DPV) for tamoxifen were determined in five replicates analyses of 2.0, 4.0 and 6.0 µgmL^{-1} (Table 1). The precision of the proposed procedure was estimated by analyzing tamoxifen in tablets assay solutions five times in three successive days using SWV and DPV. These yielded the average RSD value of 0.68% and 0.76% for SWV and DPV respectively. Further the average RSD value for intraday assay reproducibility of 2.0, 4.0 and 6.0 µgmL^{-1} solutions are 0.72% and 0.84% for SWV and DPV. The corresponding results are shown in Table 1.

Determination of tamoxifen in pharmaceutical dosages

The developed DPV method was applied successfully for the assay of tamoxifen in tablets. The results of analysis of tamoxifen in tablets are recorded in Table 2. In order to validate and to obtain the precision and accuracy of the developed method, recovery studies were carried out at different concentrations of the drug. These studies were carried out by standard addition method. For this, known quantities of pure tamoxifen were mixed with definite amounts of pre-analyzed formulations of the drug and the mixtures analyzed as before. The total amount of the added drug was calculated by difference. The average percent recoveries obtained was 99.98% indicating good recovery of the drug.

Conclusion

Electrochemical study of tamoxifen was carried out at a gold electrode in solubilized system. Based on the study of the influence of several physicochemical parameters (buffers, scan rate, pH,

Table 2. Assay results of tamoxifen citrate tablets by DPV from pharmaceutical bulk forms and mean recoveries

Tablets	Tamoxifen citrate[a]	Tamoxifen citrate[b]	Tamoxifen citrate[c]
Label claim (mg)	20	20	20
Amount found (mg)[#]	19.99	20.00	19.91
RSD (%)	0.88	0.64	0.74
Amount of pure drug added to tablet solution (µg)	10.0	10.0	10.0
Amount found (µg)[#]	9.99	10.08	9.98
Recovered (%)*	99.98	100.8	99.80
RSD (%)	0.92	0.68	0.79

[#] Average of three replicate measurements.
[a] Marketed by Dabur India Ltd, India.
[b] Marketed by Hetero Healthcare Ltd, India.
[c] Marketed by Samarth Pharma Pvt. Ltd, India.
* Recovery (%) = (Found/Added × 100).

nature of the surfactant, concentration of dug and different surfactant concentration) were investigated. The SWV and DPV procedure provides a convenient and efficient method for the assay of tamoxifen in tablets. The proposed method is rapid, requiring less than 3 min to run a sample and does not include time-consuming steps. The simplicity, sensitivity, selectivity and low cost of analysis are the main advantages of developed method.

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