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Effect of surfactants on the voltammetric response and determination of an antihypertensive drug

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Abstract

The effect of adding surface-active agents to electrolytes containing terazosin, an antihypertensive drug, on the voltammetric response of glassy carbon electrode was studied. The current signal due to the oxidation process was a function of the amount of terazosin, pH of the medium, type of surfactant, and accumulation time at the electrode surface. Two surfactants were used, an anionic type, sodium dodecyl sulfate (SDS) and a cationic type, cetyl trimethyl ammonium bromide (CTAB). Addition of SDS to the terazosin-containing electrolyte was found to enhance the oxidation current signal while CTAB showed an opposite effect. Beside the interfacial interaction of the surfactant with the electrode surface in reference to the bias applied potential and the charge of surfactant, terazosin-surfactant interaction in the electrolytic solution was found to be critical to the magnitude of current signal. Addition of SDS to terazosin-containing buffer solution resulted in a decrease in the drug absorption spectrum both in the ultra-violet and visible (UV–vis) regions. Moreover, NMR measurements showed considerable chemical shifts for the aromatic protons of the quinazolinyl moiety of the terazosin in presence of SDS. The affected aromatic protons are positioned next to the interacting protonated amino-group of the terazosin with the charged sulfonate-group of SDS. On the other hand, addition of CTAB did not cause noticeable changes both to the UV–vis and NMR spectra of the drug. The use of SDS in the electrochemical determination of terazosin using linear sweep voltammetry and differential pulse voltammetry at solid glassy carbon electrode enhanced the detection limit from 6.00×10^{-7} mol L^{-1} in absence of surfactant to 4.58×10^{-9} mol L^{-1} when present. The validity of using this method in the determination of drug active ingredient in urine samples and tablet formulations was also demonstrated.

Keywords: Surfactants; Modified electrodes; Voltammetry; UV–vis; NMR; Drug interaction; Terazosin

1. Introduction

Surfactants have been widely used in chemistry and in particular affecting several electrochemical processes [1]. Several applications of surfactants in electrochemistry are in electroplating [2], corrosion [3], fuel cells [4], electrocatalysis [5], and electroanalysis [6]. The area of surface modified electrodes is of particular interest because of its application in sensors. Rusling [7] indicated the influence of surfactant aggregates at the electrode/electrolyte interface in micelle solutions. In his study [7], it was shown that the entry of an electrochemical reactant into this dynamic surface film is a key preceding electron transfer step.

On the other hand, surfactants have proven effective in the electroanalysis of biological compounds and drugs. For example, it was recently shown that surfactants are highly effective in stabilizing the voltammetric response of serotonin by protecting the electrode surface from fouling [8]. In another study [9], it was shown that anionic surfactants could also be used to improve the accumulation of some electroactive organic molecules such as ethopropazine at gold electrodes. Recently, the influence of micelles in the simultaneous determination of two components was also demonstrated, as in the case of ascorbic acid and dopamine [10] and catechol and hydroquinone [11]. It was not clear whether the micelle interaction with the analyte in the solution phase contributes to the selective response. It is well established that interaction between aggregates and solutes in the solution phase is controlled by diffusion and takes place in the microsecond time scale [12]. Electrode surfaces with hydrophobic characters such as carbon paste electrodes interact

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with surfactants, namely through surface adsorption. Thus, carbon paste electrode modified with surfactants proved to be useful for the determination of both inorganic species [13] and biological compounds [14].

Terazosin hydrochloride is an α_1-adrenoceptor blocker with a long lasting action. It is used in the management of hypertension [14], and in benign prostate hyperplasia to relieve symptoms of urinary obstruction [15]. Terazosin is rapidly and almost completely absorbed from the gastrointestinal tract after oral administration; the bioavailability is reported to be about 90%. Peak plasma concentrations are achieved in about 1 h. It is metabolized in the liver; one of the metabolites is reported to possess antihypertensive activity and the half-life in plasma is approximately 12 h. It is excreted in phases via the bile, and in the urine, as unchanged drug and metabolites. Terazosin is 90–94% protein bound when administered orally as the hydrochloride, but doses are usually expressed in terms of the base. Following oral administration its hypotensive effects are seen within 15 min and may last for up to 24 h, permitting once daily dose.

It is therefore essential to study the effect of changing the charge of the surfactant used, namely SDS and CTAB, its connection with the solution pH, and concentration of analyte on the voltammetric response of this drug. The electrochemical behavior of this drug in aqueous solutions at solid electrodes was not studied. Moreover, in this work we relate the observed UV–vis and NMR measurements of terazosin in the absence and presence of each surfactant type to the electrochemical data obtained.

2. Experimental

2.1. Materials and reagents

2.1.1. Metal substrates and electrochemical cell

A glassy carbon (GC) electrode (3.0 mm diameter) from BAS (USA) was used as the working electrode, a platinum wire (2.0 mm diameter, 10 cm long) as auxiliary electrode, and an Ag/AgCl (3 mol L^{-1} NaCl) as the reference electrode. A one-compartment glass cell (30 mL) fitted with gas bubbler was used for electrochemical measurements. Solutions were degassed using pure nitrogen prior to and throughout the electrochemical measurements.

2.1.2. Reagents and solution preparations

Terazosin hydrochloride (TH) and Itrin® tablets (5.0 mg TH per tablet) were supplied by Kahira Pharmaceutical and Chemical Industries Co. (Egypt). A stock solution of TH (1.0×10^{-3} mol L^{-1}) was prepared with deionized water. Diluted working standard solutions were then prepared daily with deionized water freshly just prior to use. Britton–Robinson (B–R) (4.0×10^{-2} mol L^{-1}) buffer of pH 2–11 was used as the supporting electrolyte. All solutions were prepared from analytical grade chemicals and sterilized Milli-Q deionized water. The surfactants, SDS from Aldrich (USA), and CTAB from Prolabo (France) were prepared as a stock solution of 1.0×10^{-2} mol L^{-1}/deionized water.

2.2. Electrochemical and spectroscopy instrumentation

The voltammetric measurements were performed using a PC-controlled AEW2 electrochemistry workstation and data were analyzed with EC_{prog3} electrochemistry software (Sycopel, UK). The one-compartment cell with the three electrodes was connected to the electrochemical workstation through a C_3-stand from BAS (USA). A JENWAY 3510 pH meter (England) with a glass combination electrode was used for pH measurements. All UV measurements were performed using a Shimadzu 1601 spectrophotometer (Kyoto, Japan). NMR measurements were performed using a 300 MHz Varian NMR instrument in D_2O and with TEMAC as internal standard.

3. Results and discussion

3.1. Cyclic voltammetry of terazosin in presence and absence of surfactant

The drug under investigation, terazosin ((RS)-1-(4-amino-6,7-dimethoxy-2-quinazolinyl)-4-((tetrahydro-2-furanyl) carbonyl) piperazine monohydochloride dihydrate), has a structure in which the central element is a piperazine ring and contains a quinazoline moiety. The mechanism of anodic oxidation of terazosin is expected to be complicated at the glassy carbon electrode in aqueous media [16]. The first step is the removal of an electron to form a radical–cation. However, in this particular structure with the presence of an amino-group, the electron will also be removed from the heteroatom and oxidation takes place around 1.0 V or less [17]. The ease of oxidation at this relatively lower positive potential is attributed to the resonance stabilization of the radical–cation. Fig. 1 shows the cyclic voltammograms (CVs) of 4.76×10^{-5} mol L^{-1} terazosin (in B–R buffer, pH 2) at GC electrode (curve I), in presence of 1.1×10^{-4} mol L^{-1} SDS anionic surfactant without stirring (curve II), and after stirring for 5 min (curve III). The

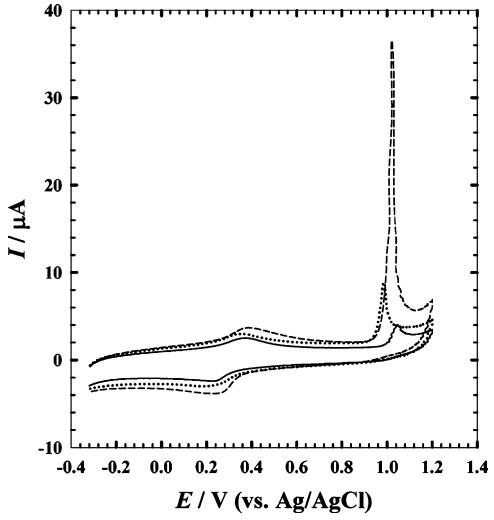

Fig. 1. CVs of 4.76×10^{-5} mol L^{-1} terazosin (in B–R buffer, pH 2) at GC electrode (—), in presence of 2.5×10^{-5} mol L^{-1} SDS without stirring (●●●●), and after stirring for 5 min (—-). Scan rate 100 mV s^{-1}.

CVs are characterized by the appearance of distinct anodic peaks at +1.05 V, +0.98 V, and +1.02 V for the three curves, respectively. The reverse scan in the negative direction did not show any indication of a reduction peak in the potential window studied. It was indicated that a reduction peak would be expected at relatively lower potentials, ca. −1.60 V at mercury surfaces [18]. It is interesting to notice the large difference in the oxidation peak current, i_{pa}, in the three cases: 0.9 μA, 1.9 μA, and 25 μA, respectively. A pair of ill-defined peaks can be distinguished in the potential range +0.2 V to +0.4 V that could be related to the redox behavior of C=O group in tetrahydro-2-furanyl piperazine moiety. The reversibility and current signal of this pair of peaks is a function of the pH and type of buffer used.

The suggested mechanisms for the aggregation of surfactants on the electrode surface in the form of bilayers, cylinders, or surface micelles (in the case of relatively higher concentrations added of SDS) could explain the increase in current in the presence of surfactants [7]. The electron transfer process will take place when the electroactive species approaches the vicinity of the electrode surface. Two main possibilities allow the transfer of charge; first is the displacement of the adsorbed surfactant by the analyte, and second is the approach of the analyte to the surface of the electrode within the space of one to two head groups of adsorbed surfactant moieties. We believe that the second mechanism is more plausible, as will be indicated later from the data obtained when using the cationic surfactant CTAB. Furthermore, a possible mechanism suggests the formation of ion-pair that anchor onto the surface of the electrode that should posses some hydrophobic character [19]. Thus, the resulting ion-pair of the charged surfactant and drug tend to adhere to the surface through the lipophilic parts in both moieties.

3.2. Effect of pH on the electrochemical response of terazosin

The reported pK_a value of terazosin is 7.1 [20]. The effect of changing the pH on the electrochemical response of terazosin was examined in the absence and presence of the surfactant. Fig. 2a and b shows the effect of changing pH of B–R buffer on the voltammetric response of 4.76×10^{-5} mol L^{-1} terazosin in the absence and presence of 2.5×10^{-5} mol L^{-1} SDS, respectively. In general, the oxidation peak potential shifts to more positive values as the pH decreases in the absence and presence of SDS. Maximum oxidation current signal was obtained in pH 5.0 and the minimum in pH 9.0 in the SDS-containing and free solution. Therefore, all subsequent electrochemical measurements will be conducted in either pH 2.0 or 5.0. The pH dependency of the oxidation peak potential indicates that protonation/deprotonation is taking part in the charge transfer process. The pair of peaks appearing in the potential range of +0.2 V to +0.4 V was greatly affected by the pH change that proves the involvement of carbonyl group in the charge exchange.

3.3. Comparison of the cyclic voltammetry of terazosin in presence of anionic and cationic surfactants

The use of different surfactants with varying charges and lengths of hydrocarbon chain affects the redox behavior of electroactive species and complicates the corresponding voltammetric response [21]. Terazosin could be considered lipophilic in nature with amphiphilic molecules that are capable of adsorbing on the surface of the electrode. This leads to the formation of self-micelle aggregates and mixed aggregates with the surfactant. The adsorption of amphiphilic species on electrode surface may result in changing the overpotential of the electrochemical

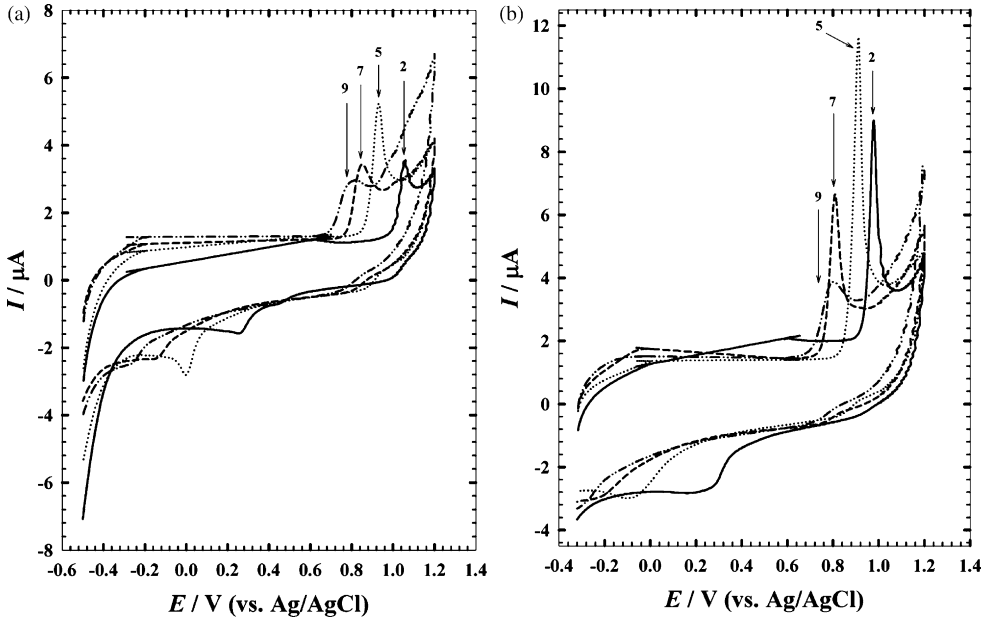

Fig. 2. (a) Effect of pH on the response of 4.76×10^{-5} mol L^{-1} terazosin at GC electrode. pH 2(—), pH 5(●●●●), pH 7(—·—), pH 9(●●-●●-). Scan rate 100 mV s^{-1}. (b) Effect of pH on the response of 4.76×10^{-5} mol L^{-1} terazosin at GC electrode in presence of 2.5×10^{-5} mol L^{-1} SDS. Scan rate 100 mV s^{-1}. pH 2(—), pH 5(●●●●), pH 7(—·—), pH 9(●●-●●-). Scan rate 100 mV s^{-1}.

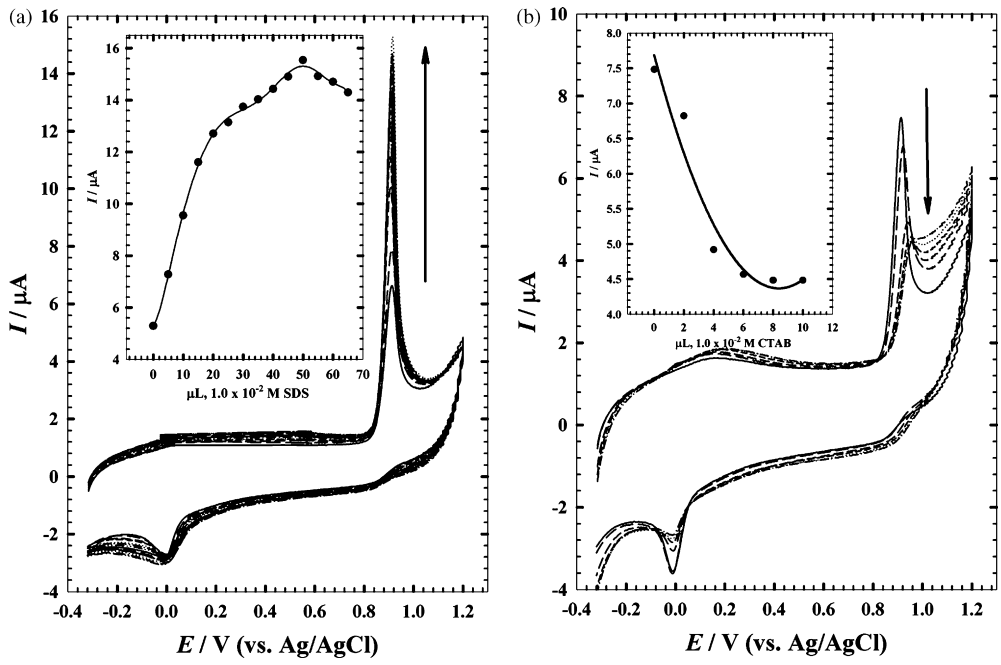

Fig. 3. (a) Effect of successive addition of SDS (increments add 1.0×10^{-5} mol L^{-1} SDS of each addition) on the voltammetric response of terazosin in universal buffer, pH at GC electrode. Scan rate 100 mV s^{-1}. (b) Effect of successive addition of CTAB (increments add 4.0×10^{-6} mol L^{-1} CTAB of each addition) on the voltammetric response of terazosin in universal buffer, pH 5 at GC electrode. Scan rate 100 mV s^{-1}.

process and the rate of its corresponding charge transfer [22]. Alternatively, in the solution phase the premicellar aggregate formation will affect the mass transport of the electroactive species [23]. The data in Fig. 3a and b show the cyclic voltammetry response of a GC electrode for 4.76×10^{-5} mol L^{-1} terazosin in B–R buffer (pH 5.0) upon incremental addition of 5 μL 0.01 mol L^{-1} SDS and 2 μL 0.01 M CTAB, respectively.

Upon closer examination of the data in Fig. 3a and b, one observes the anodic oxidation peak potential, E_{pa}, and current, i_{pa}, of terazosin are concentration-dependent upon the addition of CTAB. On the other hand, only the oxidation peak current, i_{pa}, showed the concentration-dependent behavior upon the addition of SDS. The value of i_{pa} plateaus as the concentration of surfactant reaches a definite concentration, namely 1.1×10^{-4} mol L^{-1} SDS and 2.0×10^{-5} mol L^{-1} CTAB, respectively. This is attributed to the adsorption of the surfactant molecules on the electrode surface that could be followed by the formation of micelle aggregates as the distance from the electrode surface increases [7,21]. The presence of positive charge on the amino-group of terazosin, at this pH, and its hydrophobic character enhances the aggregation of the latter with SDS, which possesses negatively charged polar groups. The possibility of aggregation of terazosin with CTAB can only be attributed to hydrophobic interactions and lead to reduced aggregation as compared to the SDS case. The strength of interaction and binding between the drug and the surfactant should result in the observed distinct behavior and should also partially affect the transport of their corresponding aggregates in solution [24]. It was previously mentioned that the saturation adsorption over the electrode surface is reached with the critical micelle concentration of the surfactant (CMC) [25] and should coincide with the concentration of added surfactant that resulted in the plateau indicated in Fig. 3a and b. However, the values we obtained are different from those reported earlier for the CMC of SDS and CTAB [21,25]. One might suggest that other factors such as the type of buffer used (supporting electrolyte) and the nature of analyte studied should affect greatly the estimate of CMC from the cyclic voltammetric results. It is important to mention that no visual turbidity formation was observed in the solution as the final addition of surfactant was reached. Additionally, the oxidation peak potential, E_{pa}, shifted to lower positive values of ca. 100–25 mV in presence of SDS for all pHs studied except for solutions with pH ≥ 5 in which the potential shifted by the relatively small value of 2 mV.

3.4. Effect of scan rate on the voltammetric response of terazosin

The relation between anodic oxidation peak current, i_{pa} (mA), diffusion coefficient of the electroactive species, D_0 (cm^2 s^{-1}), and scan rate, ν (V s^{-1}), is given by [26]:

$$i_{pa} = (2.99 \times 10^5) n\alpha^{1/2} A C_0^* D_0^{1/2} \nu^{1/2} \quad (1)$$

where n is the number of electrons exchanged in oxidation, α is the transfer coefficient, A is the apparent surface area of the electrode (cm^2), C_0^* is the concentration of the electroactive species (mmol dm^{-3}). The transfer coefficientα, for an irreversible process can be calculated from [26]:

$$|E_{pa} - E_{pa/2}| = \frac{47.7}{\alpha} \quad (2)$$

where $E_{pa/2}$ is the potential at which the current equals one half of the peak current. A plot of i_{pa} versus $\nu^{1/2}$ (ranging from 10 to 250 mV s^{-1}) gave a straight line according to Eq. (1). Careful

Table 1
Electrochemical parameters of terazosin determined at GC electrode in different electrolyte solutions

Electrolyte (B–R buffer pH 5)	[a]E_{pa}/mV (vs. Ag/AgCl)	[a]I_{pa}/μA	α	D/cm^2 s^{-1}
4.76×10^{-5} mol L^{-1} terazosin	0.91	1.696	0.3	1.61×10^{-7}
4.76×10^{-5} mol L^{-1} terazosin + 2.5×10^{-5} mol L^{-1} SDS	0.89	3.075	0.2	4.19×10^{-6}
4.76×10^{-5} mol L^{-1} terazosin + 3.0×10^{-6} mol L^{-1} CTAB	0.96	1.384	0.6	9.61×10^{-8}

[a] Oxidation peak potential E_{pa}, and current i_{pa}, were determined at scan rate $\nu = 50$ mV s^{-1}.

inspection of data on the effect of scan rate reveals that the linearity of the relationship is realized up to a scan rate of 150 mV s^{-1} that is followed by a deviation from linearity at higher scan rates. This indicates that the charge transfer is under a partially diffusion control process and that adsorption of aggregates at the electrode surface is also possible. The relation between the oxidation peak potential E_{pa}, and the scan rate ν, shows that deviation also begins at a scan rate of 150 mV s^{-1}. The apparent diffusion coefficients (D_0) can be calculated and are listed in Table 1. D_0 can be considered as an average value of the diffusion process in the bulk, within the surfactant aggregates in solution and the surfactant layer adsorbed at the surface of the electrode.

The size of the diffusion layer at the electrode surface proximity changes with the voltage scan used. At relatively slow voltage scans the diffusion layer grows much further towards the solution side and further from the electrode surface. Therefore, as the scan rate increases the flux to the electrode surface increases considerably. At relatively higher scan rates and in presence of SDS that mainly aggregates at the electrode surface and forms a pair with the drug in electrolyte, the diffusion layer grows less further from the vicinity of the electrode. This results in the observed two slopes in the i_{pa} versus $\nu^{1/2}$ and E_{pa} versus ν relations.

The values indicated in Table 1 for D_0 show that the diffusion is enhanced in presence of SDS compared to GC and that the lowest value was in presence of CTAB. The values reported are relative and cannot be considered as absolute, and therefore, further studies can be conducted using chronoamperometry measurements.

3.5. UV–vis studies

Interaction of anionic surfactant (SDS) or cationic surfactant (CTAB) and terazosin in aqueous B–R buffer solutions were followed by UV–vis spectroscopy. Fig. 4a shows the effect of different concentrations of SDS surfactant on the absorption spectrum of terazosin. Basically, the anionic surfactant SDS showed no absorption background. The anionic character of SDS favors coulombic forces with the drug and should lead to the formation of aggregates in the solution phase. Successive aliquots of 15 μL of 0.01 mol L^{-1} SDS were added to the UV–vis cuvette containing 4.0 mL of 1.96×10^{-5} mol L^{-1} terazosin (pH 2.0). All the bands in the UV and visible regions at ca. 210 nm, 240 nm, and 330–340 nm (broad), decreased with each SDS addition. It was mentioned previously that aggregation in aromatic systems could be also attributed to the formation of larger units (possibly due to the formation of longer repeat unit chains) [27]. This "oligomerization" was due to the London–Margenau attractive forces between the π-electrons that is counterbalanced

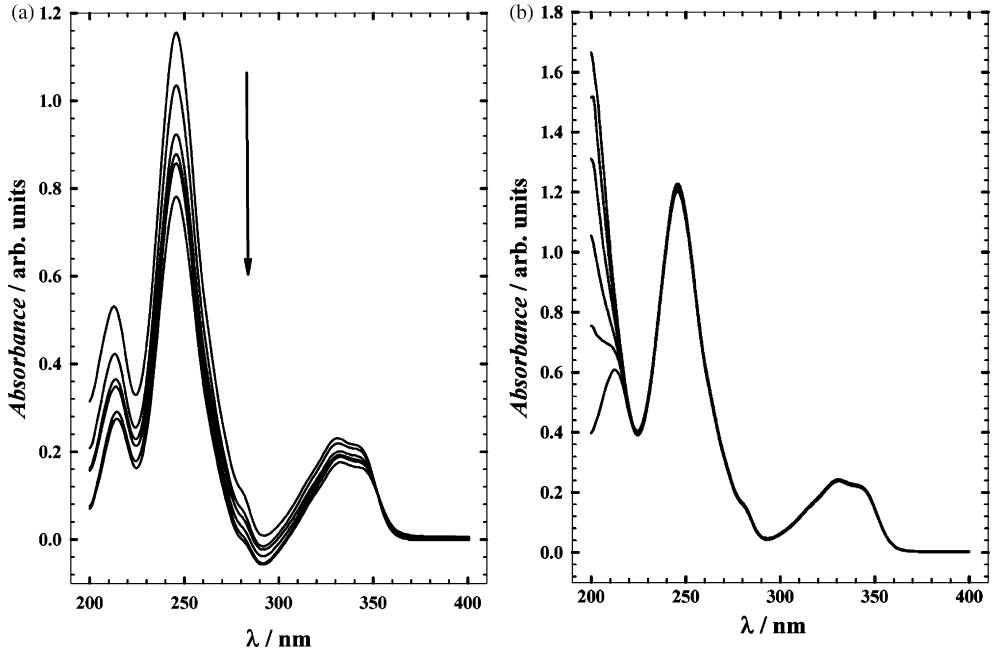

Fig. 4. (a) The effect of different concentrations of SDS surfactant on the absorption spectrum of 4.76×10^{-5} mol L^{-1} terazosin dye in aqueous universal buffer, pH 2.0. (b) The effect of different concentrations of CTAB surfactant on the absorption spectrum of 4.76×10^{-5} M terazosin dye in aqueous universal buffer, pH 2.0.

by the coulombic and Lenard–Jones repulsive forces. This should be accompanied with a blue-shift [27] or a red-shift [28] in the corresponding spectra that was not observed in the present case for terazosin. This indicates that the charge interaction of the drug with SDS is the main contribution to the association that resulted in the decrease in the absorption spectra. It is important to mention that a total of 0.09 mL SDS was added, and therefore no dilution effect is expected to be observed on the absorption spectra. Moreover, as the pH of solution increases the effect of addition of SDS on the change of the terazosin spectra decrease.

CTAB is a cationic surfactant, therefore coulombic repulsion are expected to be significant and should result in the exclusion of terazosin. Thus, as shown in Fig. 4b the successive addition of small aliquots, ca. 15 μL, of 0.01 mol L^{-1} CTAB (pH 2.0) showed no significant effect on the absorption intensity bands at ca. 210 nm, 240 nm, and 330–340 nm (broad). We would expect that the repulsive coulombic forces between the positively charged amino-group of terazosin and the positively charged ammonium group of CTAB prevent the aggregation of the drug molecules in solution. Therefore, the only existing attractive forces competing with the repulsive ones are the hydrophobic interactions.

The foregoing data showed that aggregation in the solution phase takes place between the drug and the surfactant molecules and is mainly based on the type of charge on the drug that is dictated by the pH of the buffer used and the corresponding charge of the polar group of the surfactant. Secondary interactions from the hydrophobic character of these species are also possible; however they are apparently weaker than the coulombic forces. The spectrophotometry data are in good agreement with what we obtained in the voltammetry experiments. One important conclusion is that the aggregation of an electroactive species is still possible at submicellar concentrations depending on the strength of binding with the corresponding surfactant.

3.6. NMR studies

NMR measurements led us to similar conclusions, and ascertain to a great extent the involvement of direct interaction between the drug and the SDS. The proton NMR spectra of terazosin are given in Fig. 5a. As noticed, NMR spectra of terazosin show characteristic signals for the aromatic quinazolinyl moiety at 6.561 ppm and 6.829 ppm, respectively. The multiplets between 2.0 and 2.6 ppm are attributed to the protons of the tetrahydrofuranyl, while those between 3.6 and 4.2 ppm are attributed to the protons of the piperazine moieties, respectively. The proton peaks at approximately 4.8 ppm (of D_2O) are attributed to the dimethoxy protons.

Therefore, the three regions of interest in which the chemical shift and interactions are observed upon the addition of surfactants are for quinazolinyl, tetrahydrofuranyl, and piperazine moieties, respectively. We believe that the most clearly influenced environment of terazosin protons is that of the quinazolinyl portion of the molecule as shown in Fig. 5b. The protons are expected to be in close proximity to the interacting $-NH_3^+$ group with the incoming polar end, in the particular case of

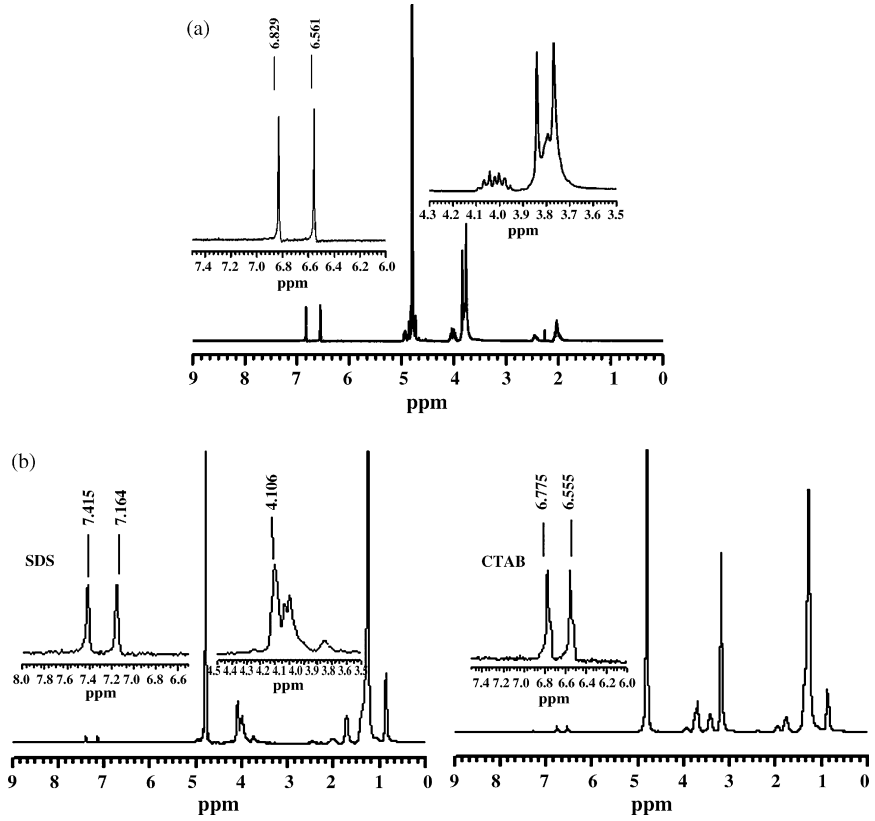

Fig. 5. (a) NMR spectra of terazosin in absence of surfactants. (b) Effect of addition of SDS and CTAB on the NMR spectra of terazosin.

SDS. On the other hand, both protons of the tetrahydrofuranyl and piperazine moieties are equally affected by the hydrophobic interaction of the surfactant's hydrocarbon chains for SDS and CTAB. In this respect, and as depicted in Fig. 5b, the shielding and deshielding effects experienced by the quinazolinyl protons upon the addition of SDS and CTAB show a change in chemical shift of $+\Delta\delta = 0.59, 0.58$ ppm and $-\Delta\delta = 0.10, 0.17$ ppm, respectively. It is important to notice that the change in chemical shift is opposite in direction upon addition of SDS and CTAB and is substantially higher in magnitude in the case of SDS. Moreover, the intensity of the signal decreased relatively in the case of SDS when compared to that of CTAB. As previously mentioned in the electrochemical and UV–vis section, the hydrophobic interaction between the surfactant and drug molecule affects the solution composition as is made clear from the noticeable change in the chemical shifts of protons of the tetrahydrofuranyl and piperazine moieties upon the addition of SDS or CTAB (cf. Fig. 5b).

3.7. Applications on commercial tablets and urine

The effect of changing the concentration of terazosin, in the presence of 1.1×10^{-4} mol L^{-1} SDS in pH 2.0, on the differential pulse voltammograms, DPV, measured with a GC working electrode and an accumulation time of 300 s is given in Fig. 6a. The following are the parameters for the DPV experiments: $E_i = 0.45$ V, $E_f = 1.35$ V, scan rate = 10 mV s^{-1}, pulse width = 25 ms, pulse period = 200 ms, and pulse amplitude = 10 mV. The oxidation peak current for terazosin is linearly proportional to the concentration of the drug in the range of 4.0×10^{-8} mol L^{-1} to 2.4×10^{-6} mol L^{-1}. A linear regression relation results from the fitting with the following equation:

$$I = (4.65 \times 10^6)C + 0.0708 \quad (3)$$

The correlation coefficient, $r = 0.998$, and the detection limit, DL, is 4.58×10^{-9} mol L^{-1} and were calculated from the equation

$$\mathrm{DL} = \frac{3s}{m} \quad (4)$$

where s is the standard deviation ($s = 7.10 \times 10^{-3}$) and m is the slope.

The above procedure was used for the determination of terazosin in commercial tablets both for buffered solutions and urine samples. The commercial tablets containing terazosin, Itrin® (5 mg/tablet terazosin) were analyzed without pre-measurement treatment. Fig. 6b shows the data generated by standard addition method for the analysis of Itrin® in buffered solutions of pH 2. The Itrin® was dissolved in buffer solution with a "start concentration" of 3.78×10^{-7} mol L^{-1}. This was calculated per mass of a 5 mg containing tablet. The standard terazosin provided by the National Organization for Drug Control and Research of Egypt was then injected by a micro-syringe with concentrations of 4.0×10^{-7} mol L^{-1}, 8.0×10^{-7} mol L^{-1}, 12×10^{-7} mol L^{-1}, 16×10^{-7} mol L^{-1}, and 20×10^{-7} mol L^{-1}. Data represented are calculated from five replicates and the assay data are reported in Table 2. A linear relationship was obtained from fitting with the following equation:

$$I = (5.93 \times 10^6)C + 0.234 \quad (5)$$

The same measurements were conducted successfully on urine samples. In this set of experiments, terazosin was dissolved

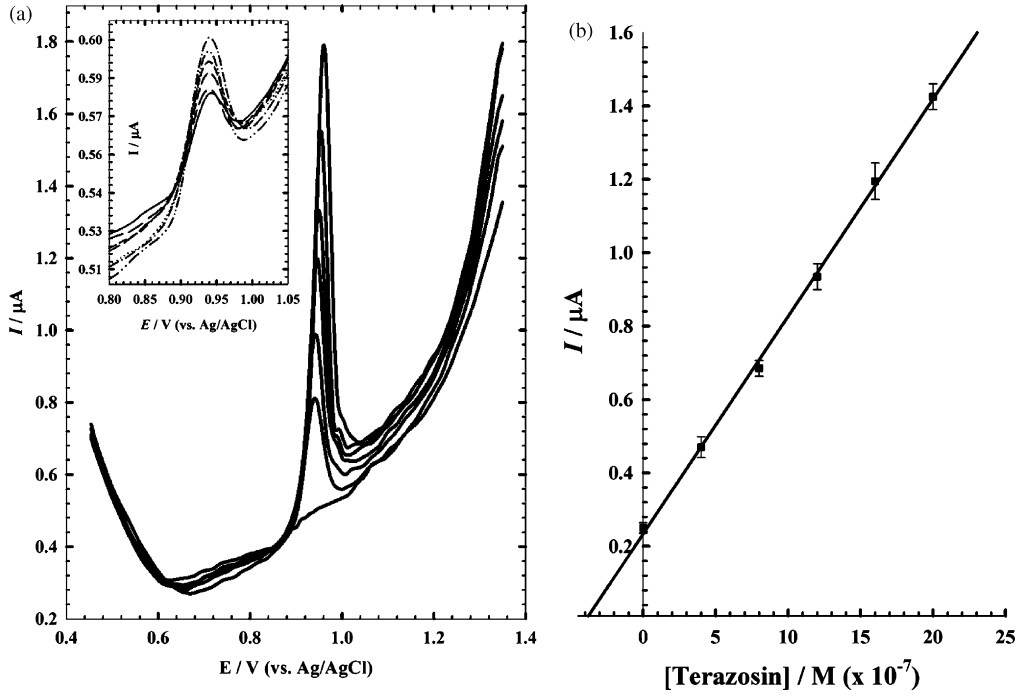

Fig. 6. (a) DPV of different concentrations of terazosin, insert (4.0×10^{-8} mol L^{-1} to 2.4×10^{-7} mol L^{-1}), main (4.0×10^{-7} mol L^{-1} to 2.4×10^{-6} mol L^{-1}) in presence of 2.5×10^{-5} mol L^{-1} SDS, universal buffer (pH 2.0). (b) Standard addition plot of Itrin® in buffer pH = 2.

Table 2
Assay data of terazosin in Itrin® in buffer pH = 2 (data from Fig. 6b)

Analyte concentration in sample solution ($g\,L^{-1}$) $\times 10^{-4}$	Spike solution		Total found ($g\,L^{-1}$) $\times 10^{-4}$	R.S.D. (%)	Recovery (%)
	Volume added (μL)	Concentration ($g\,L^{-1}$)			
1.837	4.0	0.4593	3.673	1.04	100.01
3.672			5.510	0.851	100.19
5.505			7.308	0.730	98.37
7.338			9.122	1.31	97.43
11.01			12.81	1.01	99.94

in urine to make a stock solution with 1.0×10^{-3} mol L^{-1} concentration. A 4 μL of this urine stock containing terazosin was injected in a 10 mL buffer (pH 2). Standard addition of 4 μL of 1.0×10^{-3} mol L^{-1} terazosin (in buffer pH 2) was made and the corresponding DPV was measured. The calibration curve gave a straight line with correlation coefficient, $r^2 = 0.999$, R.S.D. (%) = 1.04, recovery (%) = 100.02.

4. Conclusions

In conclusion, we were able to examine the voltammetric behavior of terazosin in different pH buffer solutions. The oxidation peak potential and current values were function of pH of electrolyte. The use of surfactants affects the oxidation peak current according to the nature of charge of the surfactant's polar group. Spectrophotometric measurements showed that solution aggregate formation affects the surface interaction of the adsorbed species at the electrode surface and consequently the rate of charge transfer. NMR studies showed that predominant interactions between the drug molecule and the surfactant are coulombic in nature and that the secondary forces are less predominant on the electrochemical behavior. The use of surfactants can be applied for the analysis of drug with a direct analytical procedure in aqueous, drug formulations, and urine samples.

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