Electrochemical oxidation of butein at glassy carbon electrodes

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ABSTRACT

The electrochemical oxidation of flavonoid butein is studied at glassy carbon electrodes in phosphate and citrate buffer solutions of different pH values, and 1 M perchloric acid aqueous solutions by cyclic and square wave voltammetries. The oxidation peak corresponds to the $2e^-$, $2H^+$ oxidation of the 3,4-dihydroxy group in B ring of butein, given the corresponding quinone species. The overall electrode process shows a quasi-reversible behavior and an adsorption/diffusion mixed control at high butein bulk concentrations.

At low butein concentrations, the electrode process shows mainly an adsorption control. Butein surface concentration values were obtained from the charge associated with the adsorbed butein oxidation peaks, which are in agreement with those values expected for the formation of a monolayer of adsorbate in the concentration range from 1 to 5 μM.

Square wave voltammetry was used to perform a full thermodynamic and kinetics characterization of the butein surface redox couple. Therefore, from the combination of the "quasi-reversible maximum" and the "splitting of the net square wave voltammetric peak" methods, values of (0.386 ± 0.003) V, (0.46 ± 0.04), and 2.7×10^2 s^{-1} were calculated for the formal potential, the anodic transfer coefficient, and the formal rate constant, respectively, of the butein overall surface redox process in pH 4.00 citrate buffer solutions. These results will be then used to study the interaction of butein, and other flavonoids with the deoxyribonucleic acid, in order to better understand the potential therapeutic applications of these compounds.

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1. Introduction

Butein (BU), whose IUPAC name is (*E*)-1-(2′,4′-dihydroxyphenyl)-3-(3,4-dihydroxyphenyl) prop-2-en-1-one, belongs to a subclass of flavonoids (chalcones). Its molecular formula is shown in Scheme 1.

Flavonoids form a very large group of natural products. They are important components of human and animal diet. Flavonoids are secondary metabolites widely found in many fruits and vegetables. They have important biochemical and physiological properties, such as a high antioxidant activity and inhibition of some enzyme activities [1,2]. Their biological activities have been shown to be dependent on the degree and nature of the substitution of the phenolic hydroxyl groups, which has effects on both the radical scavenging properties and phase II enzyme induction [3–5].

BU has two benzene rings in its structural formula linked by a β-unsaturated carbonyl group and a double bond (Scheme 1). One of the benzene rings (B-ring in Scheme 1) has a catecholic group, which has been shown to be the active site of flavonoids to scavenge free radicals [6–9]. In addition, the double bond between the two benzene rings also favors the antioxidant activity of flavonoids promoting the delocatization of unpaired electrons of phenoxyl radicals [10]. BU has been reported to inhibit xanthine oxidase and shows inhibitory effects

on lipid peroxidation in rat liver microsomes [11]. It has also been verified that BU is a natural antioxidant against lipid peroxidation in rat brain homogenates and inhibits copper-catalyzed oxidation of low-density human lipoprotein [12]. The inhibitory effect of BU on the proliferation of human colon adenocarcinoma cells has also been reported [13]. An investigation about the antioxidant activity of BU and its action mechanism in linoleic acid was studied [14]. Recently, a theoretical study based on the calculation of the bond dissociation energy (BDE) and the ionization potential (IP) showed that BU may be an antioxidant more effective than the α-tocopherol, considering that the BDE for BU is lower than that of the α-tocopherol [15].

As far as we know, only a paper is reported in literature related to the electrochemical oxidation of BU. Therefore, Hodnick et al. [16] studied the electrochemical oxidation of BU at a glassy carbon electrode by cyclic voltammetry in 0.1 M phosphate buffer solutions of pH 7.5 containing a final concentration of 2.5% (v/v) of dimethylsulfoxide. They found a quasi-reversible redox couple in the potential range from -0.100 to 0.400 V vs. SCE, with a separation between the anodic and the cathodic peak potentials (ΔE_p) of 0.024 V at a scan rate (v) of 0.100 V/s when the BU bulk concentration [BU] was 0.5 mM, which would indicate that the BU electrochemical oxidation appears to be a $2e^-$ process.

On the other hand, we have started to study the electrochemical properties of some flavonoids in recent years in order to develop electroanalytical techniques for their determination in real matrices, and

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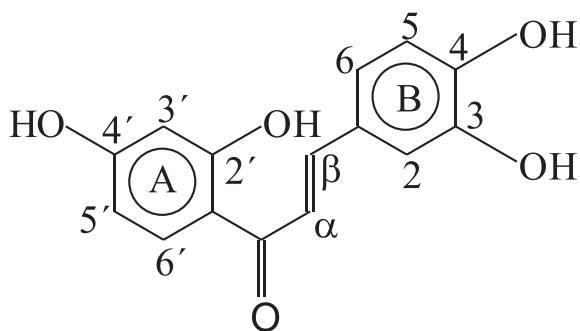
Scheme 1. Structural formula of butein.

compare their antioxidant activity. Thus, we have studied the electrochemical oxidation of rutin [17] and morin [18] at glassy carbon electrodes in 10% ethanol + 90% 1 M HClO$_4$ aqueous solution, and 0.2 M phosphate buffer solutions, respectively. We have found that these flavonoids and their oxidation products are strongly adsorbed on the electrode surface. In addition, it is known that adsorption of these compounds may play an important role in their antioxidant properties [19], hence the importance of being able to discriminate between the contribution to the current of adsorbed species and the same species which arrives to the electrode surface by diffusion.

In this study, we report the BU electrochemical oxidation at glassy carbon (GC) electrodes in phosphate (PBS), and citrate (CBS) buffer solutions of different pH values, and 1 M HClO$_4$ aqueous solutions. Cyclic (CV) and square wave (SWV) voltammetries were the electrochemical techniques used. The combination of the "quasi-reversible maximum" and the "splitting of the net SW voltammetric peak" methods [20,21] was used to perform a full thermodynamic and kinetics characterization of the BU overall surface redox couple. These results will be then used to study the interaction of butein, and other flavonoids with the deoxyribonucleic acid, in order to better understand the potential therapeutic applications of these compounds.

2. Material and methods

2.1. Reagents

BU was purchased from Sigma-Aldrich. Stock solutions of BU (1.47 mM) were prepared in ethanol (Merck p.a.), protected from light, and kept in the refrigerator. They were stable for at least two months. Working solutions were prepared daily by adding different aliquots of the stock solution to the corresponding reaction medium. The percentage of ethanol in all solutions was 10%. HClO$_4$, HCl and KOH were Merck, p.a. Water was Sintorgan (HPLC grade). PBS were prepared using 0.1 M Na$_2$PO$_4$H (Merck p.a.) and 0.1 M KPO$_4$H$_2$ (Merck p.a.). CBS were prepared from pH 4.00 ± 0.01 commercial citrate buffer, Merck p.a. (20 °C; citric acid + NaOH + HCl, reference number 109435). The final pH value was achieved by adding small aliquots of 1 M HCl or KOH aqueous solutions as appropriate.

2.2. Apparatus and experimental measurements

Cyclic and square wave voltammograms were recorded with an AutoLab PGSTAT 12 potentiostat, controlled by GPES 4.9 electrochemical software from EcoChemie, Utrecht, The Netherlands. The scan rate in cyclic voltammograms was varied from 0.010 to 0.500 V/s. For square wave voltammograms, amplitude (ΔE_{SW}) of 0.025 V and a staircase step height (ΔE_s) of 0.005 V were mainly used. The frequency (f) was varied from 10 to 500 Hz. In some experiments, ΔE_{SW} was varied from 0.025 to 0.150 V.

Electrochemical measurements were performed in a home-made two-compartment Pyrex cell [22]. The working electrode was a GC disk (from Bioanalytical System, Inc., USA, 3 mm diameter). It was polished with 0.3 and 0.05 μm wet alumina powder (from Fischer), copiously rinsed with water, and sonicated in a water bath for 5 min. Finally, the electrode was transferred to the corresponding supporting electrolyte solution and cycled 10 times between 0 and 1 V (vs. SCE). This pre-treatment of the working electrode produced an electrochemical activation of its surface and allowed to obtain very reproducible voltammetric responses with higher currents. After applying the physical and electrochemical pre-treatment previously described, the working electrode electrochemical area (A) was determined by chronoamperometry measurements using 1.1 mM ferrocene (Fc) + acetonitrile + 0.1 M tetrabutyl ammonium perchlorate through Cottrell plots [23], using a value of 2.26×10^{-5} cm^2/s for Fc diffusion coefficient [24]. An average value of A = (0.083 ± 0.002) cm^2 was determined from replicated measurements performed with three new pretreated electrodes. The counter electrode was a large-area platinum foil (area ≈ 2 cm^2). The reference electrode was an aqueous saturated calomel electrode (SCE) fitted with a fine glass Luggin capillary containing a bridge solution identical to that containing the same sample which is measured. Although it is well known that potassium ions of the reference electrode can form with perchlorate ions a precipitate of potassium perchlorate, we did not notice this problem, at least in the experiments lasting time. Thus, the SCE was used in all media studied.

Studies related to find the best accumulation potential (E_{acc}) were performed recording cyclic voltammograms of BU in pH 4.00 CBS at v = 0.050 V/s using a [BU] = 2.02 μM, where the E_{acc} was varied from −0.500 to 0.200 V (vs. SCE) at intervals of 0.100 V. No significant change was observed in the current values as the E_{acc} was varied (results no shown). Therefore, the experiments were carried out using a $E_{acc} = 0$ V (vs. SCE, potential at which the sweep was started, see below). Voltammetric signals showed a good repeatability and reproducibility. Thus, a percent relative standard deviation (RSD%) of (7 ± 1) % was determined for anodic peak currents ($I_{p,a}$) of four cyclic voltammograms obtained at v = 0.050 V/s with four new GC electrodes pretreated as described previously. On the other hand, consecutive cyclic voltammograms recorded on the same GC electrode at a given v showed a very good reproducibility (4.2%).

Pure nitrogen was bubbled in the solutions for at least 10 min prior to measurements. The temperature was varied from 10 to 35 °C. The temperature was controlled using a thermostat ColeParmer, coupled to the electrochemical cell.

The pH values were determined using an Orion Model 720A pH-meter, which was calibrated daily with three commercial buffers.

Experimental data were fitted using a non-linear least square procedure in order to find the best adsorption isotherm that describes the specific interaction of BU with GC electrodes. The best fit between the experimental and theoretical data was chosen as that which gave the minimum value of the Chi-square function (χ^2).

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1a shows cyclic voltammograms of BU in 1 M HClO$_4$ and PBS of different pH values at a given scan rate, and a BU bulk concentration, [BU] = 0.15 mM.

These cyclic voltammograms show a quasi-reversible behavior, since a well-defined cathodic peak is observed when reversing the direction of the potential sweep. Under these experimental conditions, it was observed that the intensity of the current increased in all reaction media when cyclic voltammograms were recorded at different accumulation times (t$_{acc}$) and at $E_{acc} = 0$ V (vs. SCE). Constant current-potential responses were obtained at t$_{acc} = 1$ min. In addition, after recording cyclic voltammograms in solutions in the presence of BU, the working electrode was copiously rinsed with the corresponding blank solution, and transferred to another electrochemical cell containing the supporting
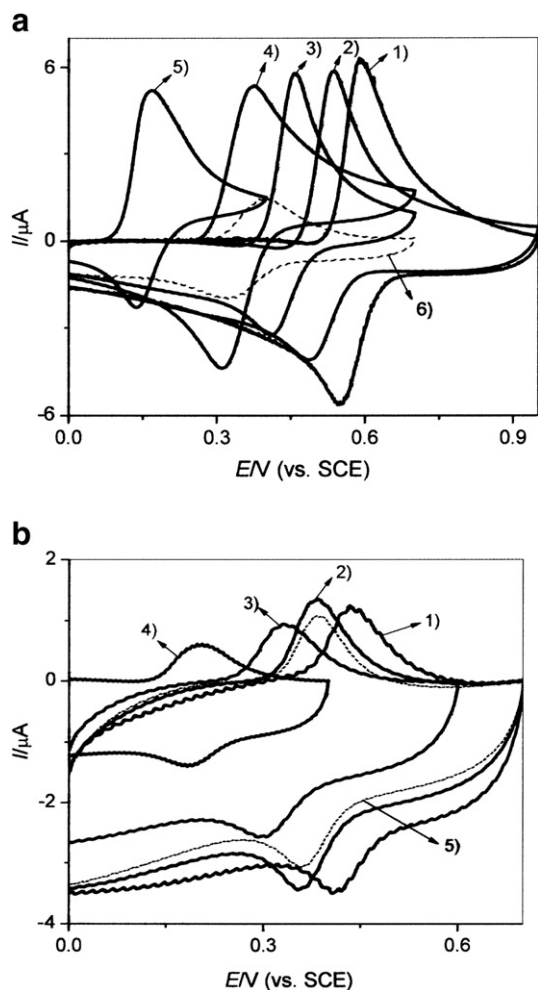
Fig. 1. a) Cyclic voltammograms of BU in 1 M HClO$_4$ (1) and PBS of different pH values: 2) 0.92, 3) 2.26, 4) 4.12, 5) 7.00, and 6) after transferring the electrode to another electrochemical cell containing only pH 4.12 PBS. [BU] = 0.15 mM. v = 0.050 V/s. t$_{acc}$ = 1 min; b) cyclic voltammograms of BU in CBS of different pH values: 1) 3.00, 2) 4.00, 3) 5.00, 4) 7.00, and 5) after transferring the electrode to another electrochemical cell containing only pH 4.00 CBS. [BU] = 0.5 μM. v = 0.050 V/s. t$_{acc}$ = 60 min. t = 25 °C.

electrolyte solution, where quasi-reversible cyclic voltammograms were clearly defined with lower current values than those previously obtained in the presence of BU (line 6 in Fig. 1a). These results put in evidence that, under these experimental conditions, the overall electrode process shows an adsorption/diffusion mixed control. This behavior could also be inferred from the analysis of a plot of the current function ($\Psi = I_{p,a}/Av^{1/2}$) vs. $v^{1/2}$. Thus, at pH 4.12 and [BU] = 0.15 mM, a linear dependence was found between $\Psi = I_{p,a}/Av^{1/2}$ vs. $v^{1/2}$ at 25 °C, with an intercept on the y-axis of (151 ± 3) μA s$^{1/2}$/cm^2 V$^{1/2}$ (r = 9.9986), which suggests an adsorption/diffusion mixed control [25], i.e.:

$$I_{p,a} = \left(2.69 \times 10^5\right) n^{3/2} AD_{BU}^{1/2}[BU]v^{1/2} + n^2F^2A\Gamma_{BU}v/4RT \tag{1}$$

where n is the electron number exchanged in the electrode process, D$_{BU}$ is the BU diffusion coefficient, Γ_{BU} is the surface concentration of BU adsorbed, F and R are the Faraday constant and molar gas constant, respectively, and T is the absolute temperature. A value of D$_{BU}$ = 1.8x10^{-6} cm^2/s was determined from the intercept of the $I_{p,a}/Av^{1/2}$ vs. $v^{1/2}$ plot at 25 °C.

A shift of the voltammetric peak to less positive potentials is observed as the pH of the medium increases, with a variation of the

anodic peak potential ($E_{p,a}$) with the pH of $\partial E_{p,a}/\partial pH = -(0.052 \pm 0.002)$ V (r = 0.9978). From the Nernst equation:

$$E_{p,a} = E_f^o - (0.059/n) \log\left([BU]_{ox}/[BU]_{red}\right) + (0.059 \, a/n) \, pH \tag{2}$$

where E_f^o is the formal potential, [BU]$_{ox}$ and [BU]$_{red}$ are the oxidized and reduced forms of BU, respectively, and a is the number of protons involved in the oxidation reaction. It is possible to infer that the same number of electrons and protons is involved in the electrode process, which is thermodynamically favorable as the pH increases.

It is well known that the first oxidation peak of flavonoids that have a catecholic group in its molecular formula corresponds to the 2e$^-$, 2H$^+$ oxidation of that group (the 3,4-dihydroxy group in the B ring of BU, Scheme 1), given the corresponding quinone species [26–28]. On the other hand, ΔE_p values varied from 0.041 V (vs. SCE, 1 M HClO$_4$ aqueous solution) to 0.062 V (vs. SCE, pH 4.12 PBS), being these values greater than that theoretically expected for a simple bielectronic redox couple, i.e., 0.0295 V at 25 °C [23]. An explanation to this behavior could be based on the fact that these voltammetric responses have a contribution of both species that adsorbed on the electrode surface and that which arrives to the electrode surface by diffusion. Moreover, a value of ΔE_p = 0.032 V was found at pH 7.00 PBS (line 5 in Fig. 1a), which is close to that theoretically expected for a simple bielectronic redox couple. This result could be explained considering that the extent of adsorption is lower at this pH than at lower pH values. A slight decrease in the $I_{p,a}$ is also observed as the pH of the medium increases (Fig. 1a). This behavior could be explained considering that protons are involved in the electrode process and their availability decreases as the pH increases, which would affect the overall reaction rate. A similar behavior to that previously described for 1 M HClO$_4$ and PBS was also found when the BU electrochemical oxidation was studied in CBS of different pH using a [BU] = 0.15 mM (results no shown). However, experiments carried out at very low BU concentrations showed that voltammograms are slightly more reproducible in CBS than in PBS. Therefore, systematic studies at very low BU concentrations were performed in CBS.

Cyclic voltammograms obtained at a [BU] = 0.5 μM in CBS at different pH values are shown in Fig. 1b. A cyclic voltammogram recorded after transferring the electrode to another electrochemical cell containing only pH 4.00 CBS is also shown in Fig. 1b (line 5). As can be observed, the difference in currents from cyclic voltammograms recorded in the presence and in the absence of BU is smaller as the concentration decreases (compare lines 4 and 6 in Fig. 1a with lines 2 and 5 in Fig 1b). These results indicate that for BU concentrations ≤0.5 μM the voltammetric response arises from BU adsorbed, and the diffusion component is negligible. Cyclic voltammograms recorded under these experimental conditions also show dependence with the medium pH, being $\partial E_{p,a}/\partial pH = -(0.048 \pm 0.001)$ V, r = 0.9993 at v = 0.050 V/s. Values of $E_{p,a}$, $I_{p,a}$, the anodic peak charge, Q$_{BU}$, the anodic peak width at half height ($E_{p,a,1/2}$), the difference between the anodic peak potential and the corresponding potential at half height ($E_{p,a}$ - $E_{p,a/2}$), and ΔE_p at different scan rates for the different media are shown in Table 1.

Plots of $I_{p,a}$ vs. v were linear, with r in the range from 0.9876 to 0.9986 for 1 M HClO$_4$, and 3.00–5.00 CBS, indicating that at [BU] ≤ 5.00 μM (see below) the electrode process shows, as expected, an adsorption control [23]. From the shape of cyclic voltammograms, it is possible to infer that both the reagent and the corresponding quinone species are strongly adsorbed at the electrode surface, showing a nearly quasi-reversible redox couple. In addition, the charge Q$_{BU}$ associated with the oxidation of BU adsorbed at the electrode surface, obtained after subtracting background currents, can be expressed as [23]:

$$Q_{BU} = nFA\Gamma_{BU}. \tag{3}$$

From Table 1, average values of Q$_{BU}$ of (1.8 ± 0.1), (2.2 ± 0.3), (2.5 ± 0.5), (2.2 ± 0.2), and 2.01 μC were determined for 1 M HClO$_4$, and pH 3.00, 4.00, 5.00 and 7.00 CBS, respectively. Therefore, values

Table 1
Characteristic parameters of anodic peaks of BU obtained from cyclic voltammograms at different scan rates. [BU] = 0.5 μM; t = 25 °C. Reference electrode: SCE.

Reaction medium	v (V/s)	$E_{p,a}$ (V)	$I_{p,a}$ (μA)	Q_{BU} (μC)	$E_{p,a,1/2}$ (V)	$E_{p,a} - E_{p,a/2}$ (V)	ΔE_p (V)
1 M HClO₄	0.025	0.578	0.57	1.89	0.074	0.033	0.027
	0.050	0.579	1.04	1.62	0.069	0.032	0.028
	0.075	0.579	1.71	1.68	0.066	0.031	0.025
	0.100	0.575	2.51	1.89	0.069	0.028	0.026
pH 3.00 CBS	0.025	0.435	0.49	1.89	0.085	0.035	0.026
	0.050	0.439	1.14	2.52	0.097	0.042	0.021
	0.075	0.439	1.62	2.30	0.094	0.039	0.027
	0.100	0.440	2.18	2.18	0.099	0.040	0.027
pH 4.00 CBS	0.025	0.386	0.60	2.14	0.079	0.036	0.027
	0.050	0.380	1.50	2.62	0.096	0.036	0.023
	0.075	0.389	2.02	2.60	0.095	0.042	0.027
	0.100	0.387	2.56	2.64	0.097	0.038	0.026
pH 5.00 CBS	0.025	0.333	0.48	1.95	0.094	0.041	0.030
	0.050	0.338	0.97	2.30	0.106	0.046	0.034
	0.075	0.339	1.39	2.29	0.107	0.046	0.035
pH 7.00 CBS	0.100	0.343	1.80	2.27	0.108	0.049	0.039
	0.050	0.206	0.62	2.01	0.093	0.042	0.023

Fig. 2. Dependence of $I_{p,a}$ with t_{acc} obtained for the oxidation of BU in pH 4.00 CBS at different [BU]: 1) 0.1; 2) 0.2; 3) 0.4; 4) 0.5, 5) 1 and, 6) 5 μM. v = 0.050 V/s. t = 25 °C. Each point is an average of three experimental measurements.

of Γ_{BU} of 1.1×10^{-10}, 1.4×10^{-10}, 1.5×10^{-10}, 1.4×10^{-10}, and 1.2×10^{-10} mol/cm² were obtained for 1 M HClO₄, and pH 3.00, 4.00, 5.00, and 7.00 CBS, respectively. These values are close to those values expected for the formation of a monolayer of adsorbate [23] (see below). The specific interaction of BU, in particular, and other flavonoids with the surface of GC electrodes can be explained considering that different functional groups containing oxygen such as carbonyls, phenols, carboxyl acids, lactones, quinones, etc. can be present on the GC surface [29]. The interaction between these functional groups and −OH and C=O groups present in the chemical structure of BU would be responsible for the specific adsorption of BU on GC electrodes. The pi-stacking interactions could also explain the specific interaction of BU with GC electrodes considering the presence of aromatic rings in the molecular formula of BU [30].

The BU surface redox couple was well defined at all pH studied. However, slightly larger currents were observed at pH 4.00. Therefore, we chose this pH value to find the optimal t_{acc}, and the adsorption isotherm which best describes the specific interaction of BU with glassy carbon electrodes. Our choice was also based on results found by other authors when studying surface properties of other flavonoids. Therefore, Zoulis and Efstathiou [31] have reported the pre-concentration of rutin and quercetin at GC electrodes, finding that the optimum pH value was 5.00. Volikakis and Efstathiou [32] studied the influence of pH on the analytical signal of several flavonoids, and they found a greater signal in the acid region, with a maximum at pH 5.00. Markovic et al. [28] reported an experimental and theoretical study related to the antioxidant activity of fisetin at pH 4.00. A likely explanation for these results could be related to the fact that protons are involved in the electrochemical reaction. In addition, flavonoids are weak organic acids, and depending on the values of their acid constants, at pH values close to 7 they can exist in solution in equilibrium with some of their phenolate ions. It is further know that oxidation reactions of phenolate ions can be complicated by the presence of dimerization reactions coupled to the initial charge transfer reaction [33]. In acidic conditions, the dimerization reactions are largely suppressed and the o-quinone species is the main oxidation product. However, at very low pH values, the phenol and carboxyl acid groups present on the GC electrode surface would be highly protonated, making more difficult the adsorption of flavonoids at the GC electrode surface. At pH 4.00, the reaction mechanism would be of the eHHe type, as it was previously found for fisetin [28].

Studies were then conducted to find the optimal t_{acc} for obtaining the best signal for the surface redox couple. The dependence of $I_{p,a}$ with t_{acc} for different [BU] at 25 °C is shown in Fig. 2.

In addition, we also studied the dependence of $I_{p,a}$ with t_{acc} at different temperatures, and a given [BU] (Fig. 3).
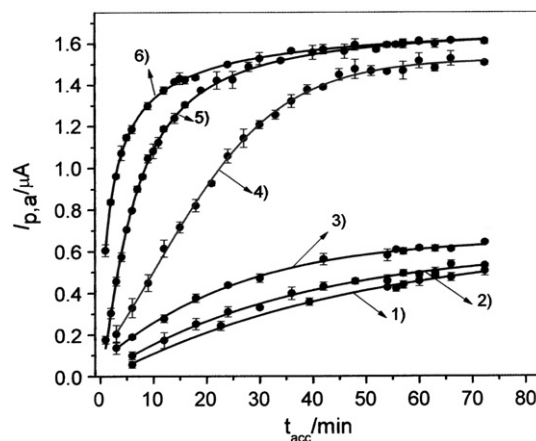
Values of higher peak currents were obtained as the temperature was increased, indicating a positive value for the enthalpy of adsorption of BU from CBS at GC electrodes. A similar behavior was previously found for the electrosorption of ethylene from 1 N sulfuric acid at Pt-plated gold electrodes [34], and the electrosorption of benzene at Pt-plated gold electrodes from solutions of 1 N sulfuric and phosphoric acids [35]. It is known that during the adsorption from solution, several solvent molecules may be released from the electrode surface for each substrate molecule adsorbed, and an increase in entropy may be expected [36]. This behavior is observed in this case as discussed below.

Stationary currents were achieved at about t_{acc} = 60 min from BU solutions in pH 4.00 CBS in all concentrations at 25 °C (Fig. 2), where it is observed that $I_{p,a}$ values are practically indistinguishable for $t_{acc} \geq 50$ min for BU concentrations of 1 and 5 μM. From these results, values of Γ_{BU} of 6.5×10^{-11}, 7.2×10^{-11}, 1.2×10^{-10}, 1.5×10^{-10}, 2×10^{-10}, and 2×10^{-10} mol/cm² were calculated for BU concentrations of 0.1, 0.2, 0.4, 0.5, 1, and 5 μM, respectively. Thus, at lower concentrations, the adsorbate surface concentration would correspond to a sub-monolayer, while Γ_{BU} values obtained in the concentration range from 1 to 5 μM correspond to the coverage of a monolayer of adsorbed substrate, i.e., 1.9×10^{-10} mol/cm² [23]. The following experiments were performed using a t_{acc} = 60 min.

Fig. 4a shows a plot of Q_{BU} vs. [BU]. Practically constant charge values were obtained at [BU] ≥ 2.0 μM. Moreover, the dependence between [BU] and the surface coverage (θ) was studied for the purpose
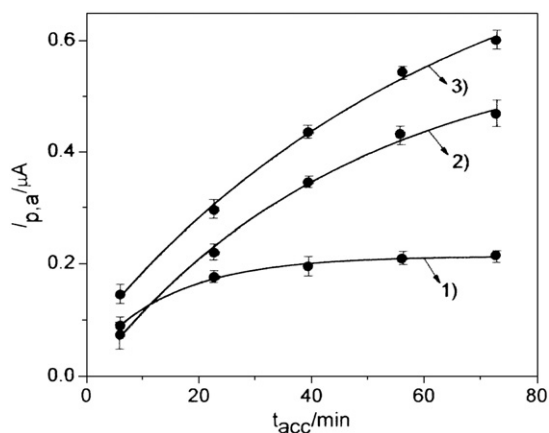

Fig. 3. Dependence of $I_{p,a}$ with t_{acc} obtained for the oxidation of BU in pH 4.00 CBS at different temperatures. [BU] = 0.10 μM. v = 0.050 V/s. t = 1) 10; 2) 25 and 3) 35 °C. Each point is an average of two experimental measurements.
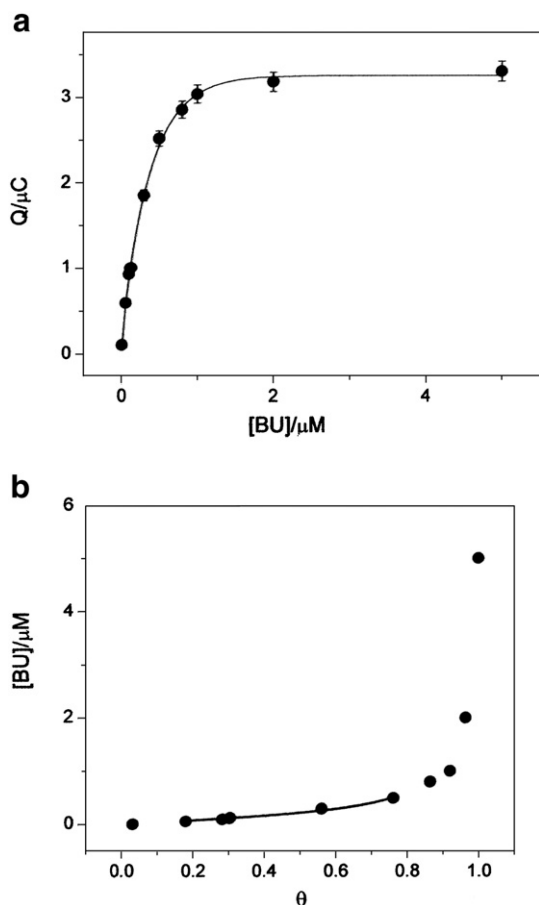
Fig. 4. a) Dependence of Q with [BU] for the adsorption of BU from pH 4.00 CBS. v = 0.050 V/s. Each point is an average of three experimental measurements. b) BU bulk concentration as a function of the surface coverage. Experimental data (●) are compared with the best fit obtained using the Frumkin adsorption isotherm (—). t = 25 °C.

of deriving the adsorption isotherm. The surface coverage was defined as $\theta = Q_{BU}/Q_{BU,max}$, where Q_{BU} is the charge from cyclic voltammograms obtained for different [BU] at a $t_{acc} = 60$ min and $Q_{BU,max}$ is the maximum value of Q_{BU} obtained at the same accumulation time for the greatest BU concentration studied, i.e., [BU] = 5.00 μM. A plot of [BU] vs. θ is shown in Fig. 4b.

Experimental data were fitted to different models of adsorption isotherms (Langmuir, Temkin, Frumkin, Freundlich) with the purpose of finding the best isotherm describing the specific interaction of BU with the surface of GC electrodes. The Langmuir, and the Frumkin isotherms can be expressed as indicate in Eqs. (4), and (5), respectively [23,36,37]:

$$\beta[BU] = \theta/(1-\theta) \qquad (4)$$

and

$$\beta[BU] = [\theta/(1-\theta)] \exp(-g'\theta) \qquad (5)$$

where $g' = 2g\Gamma_{BU,s}/RT$ is the parameter characterizing the interactions among the adsorbed molecules, g expresses the way in which the adsorption energy changes as a function of the coverage surface. If g is positive, the interactions among adsorbed species are attractive; and if g is negative, the interactions are repulsive. $\Gamma_{BU,s}$ is the BU saturation coverage, and β the adsorption coefficient, which is defined as β = $\exp(-\Delta G^o_{ads}/RT)$, where ΔG^o_{ads} is the Gibbs standard free energy of adsorption [23,36]. The fit was carried out for values of θ in the range from 0.15 to 0.78. The best fitting was obtained for the Frumkin adsorption isotherm [23,36]. The best fit between experimental and theoretical

data is shown in Fig. 4b (solid line). From the best fit, values of β = $(4.2 \pm 0.2) \times 10^6$, g' = (1.4 ± 0.2) and $\chi^2 = 7.6 \times 10^{-15}$ were obtained. From these results, a value of $\Delta G^o_{ads} = -37.8$ kJ mol^{-1} was calculated for the Gibbs standard free energy of adsorption. These results indicate that the process of BU adsorption at GC electrodes is energetically favorable and that attractive lateral interactions among the adsorbed molecules are present [23]. These results compare reasonably well with those obtained previously in our laboratory for the adsorption of similar compounds, such as rutin adsorbed at GC electrodes from 10% ethanol + 90% 1 M HClO$_4$ aqueous solution ($\Delta G^o_{ads} = -31.9$ kJ mol^{-1}; g' = (0.54 ± 0.02)) [17], and morin at GC electrodes in 0.2 M phosphate buffer solutions ($\Delta G^o_{ads} = -26.1$ kJ mol^{-1}; g' = (1.90 ± 0.08)) [18].

A negative value for ΔG^o_{ads} indicates a higher contribution of the entropy of adsorption than the heat of adsorption. Unlike what happens in the gas phase, during adsorption from solution several solvent molecules are usually released from the electrode surface for each substrate molecule adsorbed, and an increase in entropy is expected [34] as it was previously discussed. For the electrosorption of benzene on Pt-plated gold electrodes from solutions of sulfuric and phosphoric acids, a positive enthalpy of adsorption of $\Delta H^o_{ads} = 41.8$ kJ mol^{-1} was calculated [35]. The negative values of ΔG^o_{ads} found for these systems were explained considering the large positive entropy value, as a result of desorption of approximately nine water molecules permolecule of benzene adsorbed [35].

3.2. Square wave voltammetry

The square wave voltammograms of surface redox couples are highly sensitive to the kinetics of charge transfer [20,21]. The SW surface voltammetric responses are characterized by the so called "quasi-reversible maximum" [20,21]. The voltammetric profile of surface reactions depends on the dimensionless kinetic parameter, ω, the electron transfer coefficient and the amplitude of the potential modulation. The reversibility of surface redox couples depends on the dimensionless kinetic parameter, defined as $\omega = k_s/f$, where k_s is the formal rate constant and f the frequency. If both the reactant and the product of a surface redox couple are strongly adsorbed on the electrode surface, a plot of $I_{p,n} f^{-1}$ vs. f shows a maximum, which appears at a frequency which is approximately equal to k_s of the surface redox couple, where $I_{p,n}$ is the net peak current. It was shown that the maximum frequency is $f_{max} = k_s/\omega_{max}$. Then, k_s can be calculated through the following equation [21]:

$$k_s = \omega_{max} f_{max}. \qquad (6)$$

Values of the critical kinetic parameter, ω_{max}, depend on the electron transfer coefficient and the amplitude of the square wave. Values of ω_{max} were theoretically calculated under different experimental condition by Lovric et al. They are given in Table 2.3 of reference [21] for no interactions among adsorbed molecules. The error in the estimation of k_s using ω_{max} is close to 10%. In the presence of lateral interactions among adsorbed molecules and following the nomenclature given by Lovric et al., an apparent formal rate constant ($k_{s,app}$) is defined as [20,21]:

$$k_{s,app} = k_s \exp(-2a\theta) \qquad (7)$$

which depends of the surface coverage θ and the Frumkin interaction parameter a. Thus, a parameter in Eq. (7) is equivalent to g' parameter in Eq. (5). The following equation is satisfied when the quasi-reversible maximum is reached:

$$k_{s,app}/f_{max} = (\omega_{int})_{max} \qquad (8)$$

where $(\omega_{int})_{max}$ values are equals to ω_{max} values for a surface redox couple without lateral interactions among adsorbed molecules. From Eq. (7), it is possible to infer that the formal rate constant of the surface

redox process decreases if the lateral interactions among the adsorbed molecules are attractive (a > 0).

The forward (I_f), reverse (I_r) and net (I_n) currents obtained from SW voltammograms recorded for BU in pH 4.00 CBS are shown in Fig. 5. The shape of the three current responses obtained at $\Delta E_{SW} = 0.025$ V is characteristic of those expected for a quasi-reversible surface redox couple (Fig. 5a) [20,21]. In addition, any change was observed in the SW voltammetric signal (i.e., peak splitting or shifts) with the surface coverage, in concordance with monolayer coverage [38].

Plots of $I_{p,n}/f$ vs. f at three [BU] are shown in Fig. 6. The critical frequency, f_{max}, decreases as the coverage surface increases as it is theoretically expected for a surface redox couple with attractive interactions among the adsorbed molecules [20,21].

Another characteristic of a quasi-reversible surface redox couple is the splitting of the net peak as the amplitude of the square wave is increased [21,39]. The splitting of the square wave net peak allows to calculate the E_f^o of the surface redox couple from $E_f^o = \frac{1}{2}(E_{p,f} - E_{p,r})$, where $E_{p,f}$ and $E_{p,r}$ are the peak potentials for the forward (anodic) and reverse (cathodic) scans, respectively. An average value for the formal potential ($\overline{E_f^o}$) of the BU surface redox couple of (0.386 ± 0.003) V was calculated in pH 4.00 CBS. Therefore, for $\Delta E_{SW} = 0.025$ V a single net peak was observed (Fig. 5a). However, the net peak started to split as the amplitude of the square wave was increased (Fig. 5b and c).

In addition, for $(1 - \alpha) > 0.2$, it has also demonstrated theoretically that the ratio between the forward (anodic) and reverse (cathodic) currents ($I_{p,f}/I_{p,r}$) can be approximated by the following simple exponential equation [40]:

$$I_{p,f}/I_{p,r} = 5.6414 \exp[-3.4606(1-\alpha)]. \qquad (9)$$

Therefore, from Eq. (9), we can calculate $(1 - \alpha)$. An average value for the anodic transfer coefficient $(\overline{1-\alpha})$ of (0.46 ± 0.04) was calculated for BU surface redox couple in CBS of pH 4.00.

Experimental values $E_{p,f}$, $I_{p,f}$, $E_{p,r}$, $I_{p,r}$, E_f^o and $(1 - \alpha)$ obtained for the BU overall two-electron oxidation in CBS of pH 4.00 at two frequencies are shown in Table 2.

Values of $k_{s,app}$ were calculated from Eq. (7) at different θ, using a value of $\omega_{max} = 0.885$, which was extracted from Table 2.3 of reference 21 (for $n\Delta E_{SW} = 0.050$ V and $(1 - \alpha) = 0.46$).

A plot of ln $k_{s,app}$ vs. θ (Eq. (7)) was linear in the range from $\theta = 0.29$ to $\theta = 0.84$ (four points were taking into account in the regression, r = 0.9870), with an intercept of 5.6 ± 0.2 and a slope of 3.1 ± 0.4. From the intercept, a value of $k_s = 2.7 \times 10^2$ s^{-1} was calculated, and from the slope a value of a = 1.55 was determined. This value for the interaction parameter is in good agreement with that value obtained from the fitting of the best adsorption isotherm (g' = 1.4).

Similar studies to those previously described for the BU surface redox couple at GC electrodes in pH 4.00 CBS were also carried out in 1 M HClO$_4$, and pH 3.00, 5.00, and 7.00 CBS. Average values of E_f^o and $(1 - \alpha)$ and values of k_s obtained in different reaction media studied are gathered in Table 3.

As seen in Table 3, values of $(1 - \alpha)$ are practically independent of pH, the formal rate constant increases as the acidity of the medium increases, which can be explained considering that the BU overall electrode process involves 2e$^-$, 2H$^+$. In addition, the formal potential decreases as the acidity of the medium decreases, as expected for charge transfer reactions that also involve proton transfer. The value of k_s obtained for the BU surface redox couple at GC electrodes in 1 M HClO$_4$ ($k_s = 4.6 \times 10^2$ s^{-1}, Table 3) compares reasonably well with the value of k_s obtained for the rutin surface redox couple at GC electrodes ($k_s = 6.1 \times 10^2$ s^{-1}) in 10% ethanol + 90% 1 M HClO$_4$ aqueous solutions [17].

4. Conclusions

To our knowledge, this is the first comprehensive study related to the electrochemical oxidation of butein on glassy carbon electrodes in
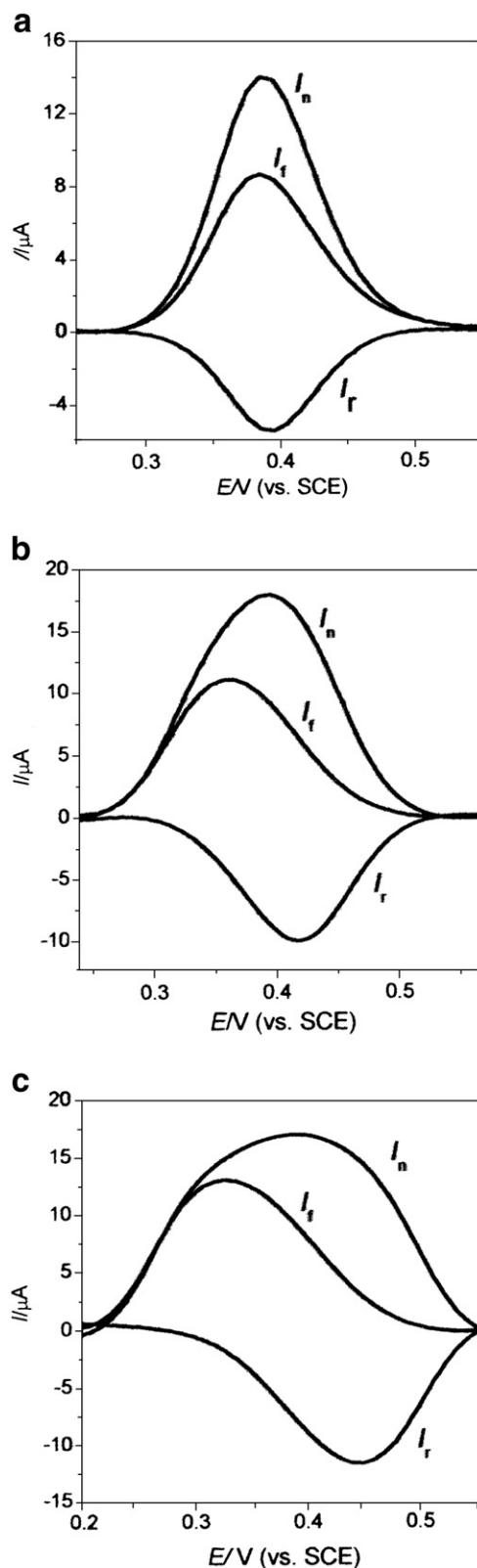

Fig. 5. Forward (I_f), reverse (I_r) and net (I_n) currents obtained from SW voltammograms of BU in pH 4.00 CBS. [BU] = 2.02 μM. $\Delta E_s = 0.005$ V; f = 20 Hz; $t_{acc} = 60$ min. $\Delta E_{SW} =$ a) 0.025, b) 0.075 and c) 0.125 V. t = 25 °C.

different reaction media. Depending on the experimental conditions, the electrode process showed a mixed control diffusion/adsorption or mainly an adsorption control. The Frumkin adsorption isotherm was found the best to describe the specific interaction of butein
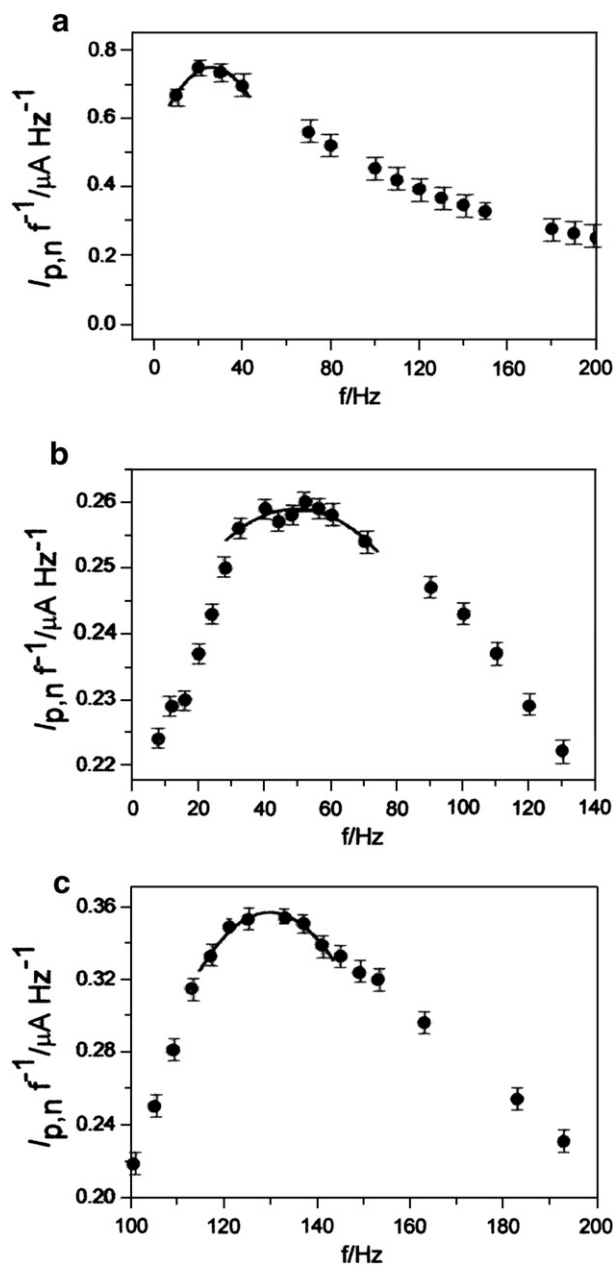
Fig. 6. Variation of the ratio of the net peak current and frequency ($I_{p,n}$ f^{-1}) on the frequency obtained for BU in pH 4.00 CBS at different coverage surfaces. [BU] = a) 2.02 μM ($\theta = 0.84$), $f_{max} = 24$ Hz; b) [BU] = 1.00 μM (($\theta = 0.56$), $f_{max} = 51$ Hz; c) [BU] = 0.10 μM ($\theta = 0.29$), $f_{max} = 130$ Hz. $\Delta E_{SW} = 0.025$ V. $\Delta E_s = 0.005$ V. The maximum frequency was calculated from the first derivative of the mathematical expression for the parabola resulting from the best fit of experimental $I_{p,n}$ f^{-1} values vs. f. t = 25 °C.

with glassy carbon electrodes. Under adsorption controlled conditions, square wave voltammetry allowed to perform a full thermodynamic and kinetics characterization of the butein surface redox couple. A dependence of formal potentials, and formal rate constants with the pH of the reaction medium was found, as expected for heterogeneous charge transfer reactions of catecholic groups.

Acknowledgments

Table 2

Forward ($E_{p,f}$) and reverse ($E_{p,r}$) peak potentials (vs. SCE), forward ($I_{p,f}$) and reverse ($I_{p,r}$) peak currents for the split SW peaks, formal potential (E_f^o) and ($1 - \alpha$) for the BU overall two-electron redox couple adsorbed at GC electrodes in pH 4.00 CBS at two frequencies. $\Delta E_s = 0.005$ V. [BU] = 2.02 μM. t = 25 °C.

f (Hz)	ΔE_{SW} (V)	$E_{p,f}$ (V)	$I_{p,f}$ (μA)	$E_{p,r}$ (V)	$-I_{p,r}$ (μA)	E_f^o (V)	($1 - \alpha$)
20	0.025	0.378	9.1	0.387	6.0	0.382	0.38
	0.050	0.372	14.4	0.401	12.1	0.386	0.45
	0.075	0.360	17.3	0.412	16.0	0.386	0.48
	0.100	0.345	18.6	0.425	17.9	0.385	0.49
	0.125	0.328	19.9	0.441	18.9	0.384	0.48
	0.150	0.305	20.9	0.459	19.5	0.382	0.48
40	0.025	0.387	16.2	0.391	9.9	0.389	0.36
	0.050	0.381	26.0	0.399	20.7	0.390	0.43
	0.075	0.372	33.3	0.407	29.2	0.389	0.46
	0.100	0.361	37.5	0.418	36.0	0.389	0.49
	0.125	0.348	41.1	0.428	40.6	0.388	0.50
	0.150	0.334	43.5	0.440	42.8	0.387	0.49

$\overline{E_f^o} = (0.386 \pm 0.003)$ V; $(\overline{1 - \alpha}) = (0.46 \pm 0.04)$.

Table 3

Average values of the formal potential ($\overline{E_f^o}$) (vs. SCE) and anodic transfer coefficient ($\overline{1 - \alpha}$) with the corresponding standard deviations and values of k_s obtained for BU surface redox couple at GC electrodes in different reaction media by square wave voltammetry. [BU] = 2.02 μM. t = 25 °C.

Reaction media	$\overline{E_f^o}$ /V	($\overline{1 - \alpha}$)	10^2 k_s/s^{-1}
1 M HClO$_4$	0.570 ± 0.04	0.45 ± 0.03	4.6
pH 3.00 CBS	0.439 ± 0.005	0.45 ± 0.04	3.7
pH 4.00 CBS	0.386 ± 0.003	0.46 ± 0.04	2.7
pH 5.00 CBS	0.335 ± 0.05	0.44 ± 0.05	2.5
pH 7.00 CBS	0.213 ± 0.06	0.47 ± 0.03	2.1

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