



Theoretical and experimental study of the surface redox reaction involving interactions between the adsorbed particles under conditions of square-wave voltammetry

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Abstract

A surface redox reaction of a strongly adsorbed redox couple involving interactions between the adsorbed particles was analyzed theoretically under conditions of square-wave voltammetry (SWV). If uniform interactions act between the adsorbed particles, the effect of interaction forces is represented through the product of the relative surface coverage and Frumkin interaction parameter Θa . The kinetics of the redox reaction in the presence of uniform interactions are a function of the apparent rate constant defined as $k_{s,app} = k_s \exp(-2a\Theta)$, where k_s is a real standard rate constant. The apparent reversibility of the redox reaction is determined solely by a dimensionless kinetic parameter defined as the ratio of the apparent rate constant and the signal frequency, $\omega = k_{s,app}/f$. This dimensionless kinetic parameter unifies the effects of both the interaction forces and the charge transfer rate. The height of the dimensionless response depends parabolically on the kinetic parameter ω , as a consequence of the phenomenon known as a 'quasireversible maximum'. Based on this peculiarity, a method for estimating the real standard rate constant k_s and Frumkin interaction parameter a is proposed. The theoretical results are compared qualitatively with the experimental SW voltammograms of probucol. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Square-wave voltammetry; Surface reaction; Interactions; Simulations

1. Introduction

The surface redox processes are an important class of redox reactions observed frequently with conducting and redox polymer films, 'self-assembled' structures populated with the redox sites and simple adsorbates. Characterization of these structures with respect to their thermodynamic and kinetic properties is of keen interest for surface science. Being one of the most advanced electroanalytical techniques, square-wave voltammetry (SWV) appears to be a powerful tool for both thermodynamic and kinetic study of these processes [1–7].

Moreover, in the last few years, the general interest in SWV [8–19] and related techniques [20–22] has

increased consistently. Recently, a number of studies of merit, describing theoretically the application of SWV to the study of different electrode mechanisms at channel [8–10], spherical [11,12], and mercury-plated electrodes [13] have been published. Furthermore, an alternative means of simulation of miscellaneous electrode mechanisms under conditions of SWV, based on the backward implicit method, has been also presented [14,15]. A few interesting experimental studies have been recently published, in which the applicability of SWV for the study of bioelectrochemical systems [17,18], as well as the determination of stability constants [19], was demonstrated. Finally it is worth noting, that interest in alternating current voltammetry, as a related technique to SWV, has recently been revived [20–22], and a novel approach in the study of electrode kinetics and trace analysis, based on fast Fourier transform method has been presented [20,21].

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In our previous publications, we have treated theoretically a surface redox reaction under conditions of SWV addressing particular attention to the phenomena of ‘split SW peaks’ [7,23] as well as the ‘quasireversible maximum’ [3–5]. It was demonstrated that these unique features of the SW voltammetric responses of the adsorbates enable assessment of the kinetic parameters of the system by a simple and fast experimental procedure. This approach differs by that of O’Dea and Osteryoung, who suggested studying the surface electrode reaction by a non-linear least-square analysis of the experimental SW voltammograms applying the well known COOL algorithm [1].

In all the theoretical work presented so far regarding this subject, an absence of lateral interactions between immobilized particles of the adsorbate was postulated, which is frequently not the case in the experimental reality. For these reasons, in this paper we extend our theoretical consideration to the case of a kinetically controlled surface redox process accompanied by interactions between the adsorbed species. The aim of the work is to comprehend the influence of the interactions upon the SWV response. An attempt was made to establish criteria for both qualitative and kinetic characterization of these systems when uniform interactions between immobilized particles exist.

Theoretical studies of the redox process in diffusionless conditions involving interactions, were initiated by Laviron applying linear scan voltammetry [24]. In this theoretical paper, the existence of distinct interactions between the Ox–Ox, Red–Red and Ox–Red couples were postulated for a reversible redox reaction. For this complex case, Laviron stressed clearly that it is impossible to resolve the discrete interactions and only a common interaction parameter may be estimated by comparing the experimental and theoretical voltammograms. Recently, Fang et al. [25] processed the surface cyclic voltammogram with an integration analysis method. These authors analyzed a quasireversible redox reaction including four different interaction parameters, suggesting a statistical approach for the estimation of all these parameters. However, the authors did not elucidate the physical meanings of the interaction parameters, avoiding the fact that similar results could be obtained with a few different sets of the interaction parameters.

The theoretical results presented in this paper are illustrated experimentally with SW voltammograms of probucole. The basic electrochemical properties of this drug have already been described in our previous communications [23,26]. In an aqueous medium, its voltammetric behavior could be successfully described with a theoretical model involving uniform interactions between adsorbed molecules.

2. Mathematical model

A redox reaction of two chemically stable compounds, which are strongly adsorbed to the working electrode surface, is investigated:



It is assumed that the reaction is controlled by the charge transfer kinetics, the adsorption of both the reactant and product is totally irreversible, and there are interactions between the adsorbed molecules in the case of a submonolayer surface coverage. Moreover, the additional adsorption and the redox reaction of the dissolved species could be neglected. Under these conditions, the system (1) is represented mathematically by the following set of differential equations and boundary conditions:

$$d\Gamma_{\text{Ox}}/dt = -I/(nFS) \quad (1)$$

$$d\Gamma_{\text{Red}}/dt = I/(nFS) \quad (2)$$

where $t = 0$: $\Gamma_{\text{Ox}} = \Gamma_0$, $\Gamma_{\text{Red}} = 0$ and $t > 0$: $\Gamma_{\text{Ox}} + \Gamma_{\text{Red}} = \Gamma_0$

If uniform interactions between deposited particles exist on the electrode surface, the following condition is valid [27]:

$$\frac{I}{nFS} = k_s e^{-\alpha\phi} e^{-2a\Theta} (\Gamma_{\text{Ox}} - e^{\phi} \Gamma_{\text{Red}}) \quad (3)$$

where $\phi = nF(E - E^\circ)/RT$ is a dimensionless potential, Γ_{Ox} and Γ_{Red} are surface concentrations of Ox and Red, respectively, Γ_0 is the initial surface concentration of the reactant Ox, k_s is the standard redox reaction rate constant expressed in units of s^{-1} , α is the cathodic transfer coefficient, a is an interaction parameter, $\Theta = \Gamma_0/\Gamma_{\text{max}}$ is the fraction of the electrode covered by the adsorbed material, Γ_{max} is the maximal surface concentration, I is the current, E is the working electrode potential, E° is the standard potential, S is the electrode surface area, while n , F , R , T and t have their usual meanings. According to Frumkin’s isotherm law, a is positive for attractive and negative for repulsive interactions between the adsorbed species.

Considering a complex case that involves different interactions between the adsorbed species, the following form of the kinetic equation should be used [27]:

$$\frac{I}{nFS} = k_s e^{-\alpha\phi} (\Gamma_{\text{Ox}} e^{-2a_{\text{O}}\Theta_{\text{O}}} - 2a_{\text{OR}}\Theta_{\text{R}} - e^{\phi} \Gamma_{\text{Red}} e^{-2a_{\text{R}}\Theta_{\text{R}} - 2a_{\text{OR}}\Theta_{\text{O}}}) \quad (4)$$

Here, a_{O} , a_{OR} , and a_{R} , are the interaction parameters between the Ox–Ox, Ox–Red and Red–Red couples, respectively. If, $a_{\text{O}} = a_{\text{OR}} = a_{\text{R}} = a$, then Eq. (4) reduces to Eq. (3).

The solutions of the differential Eqs. (1) and (2) are:

$$\Gamma_{\text{Ox}} = \Gamma_0 - \int_0^t \frac{I(\tau)}{nFS} d\tau \quad (5)$$

$$\Gamma_{\text{Red}} = \int_0^t \frac{I(\tau)}{nFS} d\tau \quad (6)$$

Substituting Eqs. (5) and (6) into kinetic Eq. (3), an integral equation is obtained which can be regarded as a mathematical representation of the electrode mechanism (I) under voltammetric conditions in the case of uniform interactions:

$$\frac{I}{nFS} = k_s e^{-\alpha\phi} e^{-2a\theta} \left[\Gamma_0 - (1 + e^\phi) \int_0^t \frac{I(\tau)}{nFS} d\tau \right] \quad (7)$$

For the system involving distinct interaction parameters, Eqs. (5) and (6) are substituted in Eq. (4) and the following integral equation is obtained:

$$\frac{I}{nFS} = k_s e^{-\alpha\phi} \left[\left(\Gamma_0 - \int_0^t \frac{I(\tau)}{nFS} d\tau \right) e^{-2a_{\text{O}}\theta_{\text{O}} - 2a_{\text{OR}}\theta_{\text{R}}} - e^\phi e^{-2a_{\text{R}}\theta_{\text{R}} - 2a_{\text{OR}}\theta_{\text{O}}} \int_0^t \frac{I(\tau)}{nFS} d\tau \right] \quad (8)$$

The integral Eqs. (7) and (8) were solved numerically under conditions of the SWV exciting signal according to the method previously described by Nicholson and Olmstead [28]. The dimensionless current is represented in the form $\Psi = I/(nFSf\Gamma_0)$ where f is the SW frequency.

3. Experimental

Probucole (4,4'-[(1-methylethylidene) bis (thio)] bis-[2,6-bis(1,1-dimethyl) phenol.]] propionamide ('Henkel KGaA'), KNO_3 and CH_3CN (Merck, analytical grade) were used as received. Water was doubly distilled. A

stock solution of probucole was prepared by dissolving in acetonitrile. KNO_3 (1 mol dm^{-3}) was used as the supporting electrolyte.

All the measurements were performed at room temperature. Extra pure nitrogen was purged through the solutions for 8 min prior to each measurement and a nitrogen blanket was maintained thereafter.

All voltammograms were recorded using an Autolab multimode polarograph (ECO Chemie, Utrecht, Netherlands) which was connected to the static mercury drop electrode (SMDE), Model 303A from Princeton Applied Research. A platinum wire was used as an auxiliary electrode and $\text{Ag} | \text{AgCl} | 3 \text{ mol dm}^{-3} \text{ KCl}$ as the reference electrode.

4. Theoretical results

4.1. Case of uniform interactions

The shape of any dimensionless response of the surface redox reaction involving uniform lateral interactions between the adsorbed species is a function of the interaction product $a\theta$, kinetic parameter k_s/f , the electron transfer coefficient α , as well as the properties of the excitement signal. The degree of interactions depends on both the relative coverage of the electrode θ and Frumkin interaction parameter a . The effect of the charge transfer rate is reflected through the ratio of the standard rate constant k_s and the signal frequency f .

The interaction product $a\theta$ affects simultaneously the shape, position and height of the SW peak. As shown in Fig. 1, the dimensionless peak current depends parabolically on the interaction product $a\theta$, passing through a maximum for a certain critical value

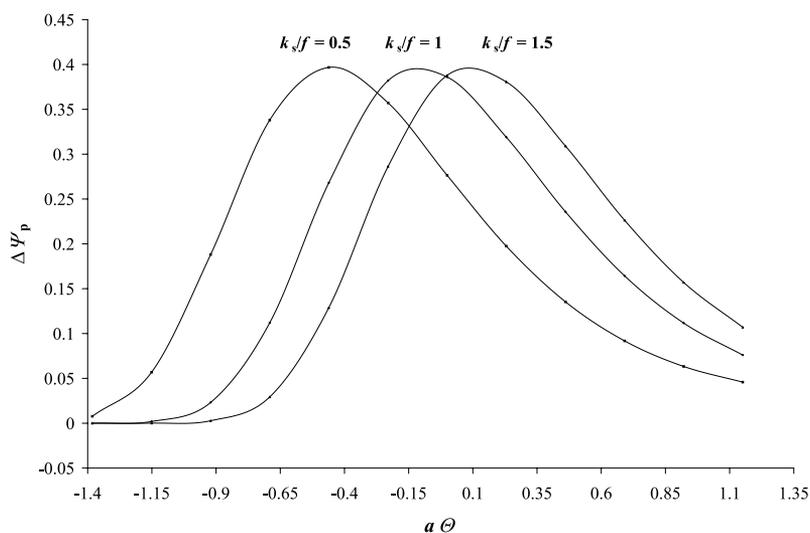


Fig. 1. The dependence of the dimensionless peak currents $\Delta\Psi_p$ on the interaction product $a\theta$ for three values of the kinetic parameter k_s/f . The conditions of the simulations were: electron transfer coefficient $\alpha = 0.5$, signal amplitude $E_{\text{sw}} = 20 \text{ mV}$, potential scan increment $dE = 10 \text{ mV}$, number of exchanged electrons $n = 1$.

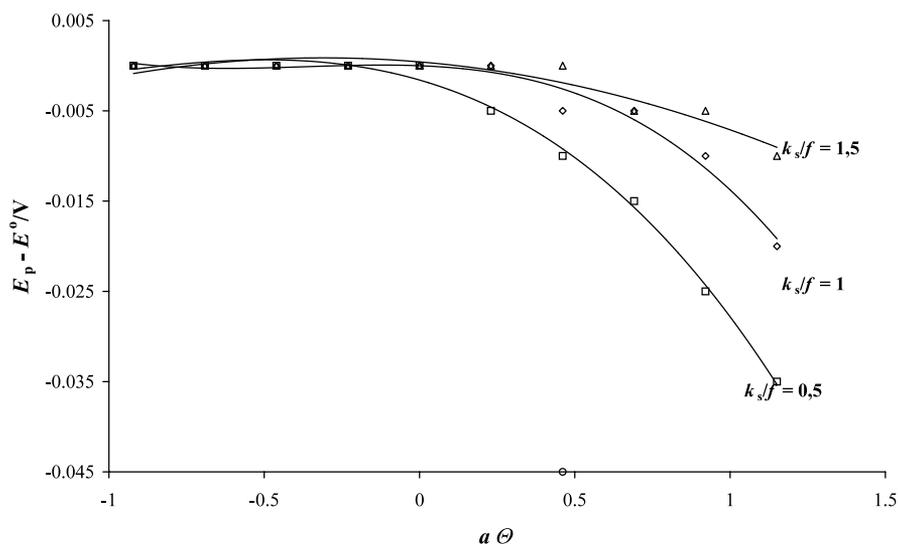


Fig. 2. The dependence of the peak potentials E_p on the interaction product $a\theta$ for three values of the kinetic parameter k_s/f . All other conditions were the same as in Fig. 1.

of the interaction product $(a\theta)_{\max}$. For $k_s/f=1$, the maximum of the parabola is located at about $(a\theta)_{\max}=0$. Under these conditions, the increase of either the attractive or repulsive interactions will cause almost an identical decrease of the dimensionless peak current. However, the exact position of the maximum depends markedly on the kinetic parameter k_s/f , and to some extent on the transfer coefficient α and the signal amplitude E_{sw} . As Fig. 1 shows clearly, the position of the maximum is displaced in the region of the attractive or repulsive interactions for $k_s/f > 1$, and $k_s/f < 1$, respectively. Therefore, one cannot generalize the exact influence of attractive or repulsion interactions to the peak current. If the standard rate constant of the surface redox reaction is known, then the critical values of the product $(a\theta)_{\max}$ associated with the maximum peak current may be estimated through the relation $(a\theta)_{\max} = 0.4277 (k_s/f) - 0.576$ which is valid for $\alpha = 0.5$ and $nE_{sw} = 20$ mV.

In the real experiment, when a single surface redox reaction is analyzed, the foregoing theoretical analysis could be demonstrated by inspecting the SW peak current as a function of the accumulation time. The accumulation time will affect the interaction product $a\theta$ through the relative coverage θ . Note that under particular experimental conditions, each redox reaction is characterized by a single and unique value of the Frumkin interaction parameter a . The last parameter could be affected only by varying the structure of the electric double layer. In the experimental reality, it is reasonable to expect that only a part of the theoretical curve $\Delta\Psi_p - (a\theta)$ will be reconstructed, since the values of the relative coverage are restricted within the limits of the interval $0 < \theta < 1$. Which part of the theoretical curves presented in Fig. 1 will be reconstructed, de-

pends on the particular value of the kinetic parameter k_s/f , the transfer coefficient α , and the signal amplitude E_{sw} . Fortunately, by varying the signal frequency f and amplitude E_{sw} , one can match conditions which are appropriate to reconstruct the region around the maximum of the parabolic dependence $\Delta\Psi_p - (a\theta)$. Therefore, the parabolic dependence of the peak current on the accumulation time can serve as a qualitative indicator for the presence of interactions between the adsorbed species of the surface redox reaction studied by SWV.

Fig. 2 shows the variation of the peak potential with the interaction product $a\theta$, studied for a variety of values of the kinetic parameter k_s/f . Within the region of repulsive interactions, the position of the SWV response remains virtually unaffected by the interaction product. In the presence of attractive forces, the reduction of the adsorbate becomes thermodynamically unfavorable, and consequently the SWV peak shifts linearly in the negative direction, with the slope being dependent mainly on the kinetic parameter k_s/f . For $k_s/f < 0.1$, the slope of the $E_p - a\theta$ line is $\Delta E_p/a\theta = 2RT/(\alpha nF)$.

Relating the latest theoretical analysis to the real experiment, one can conclude that the type of interaction is easily recognizable in the experimental reality. Whereas the analysis of the peak current on the accumulation time indicates the presence of interactions, the inspection of the peak position as a function of the accumulation time reveals whether repulsive or attractive forces are involved. If the signal frequency is adjusted to fulfil the condition $k_s/f < 0.1$, then the experimental line $E_p - t_{acc}$ is associated with a constant slope of $\Delta E_p/\Delta t_{acc} = 2aRT/(\alpha nF)$. Thus, knowing the number of electrons exchanged in the redox reaction, as

well as the electron transfer coefficient, the interaction parameter a may be estimated with the aid of the last relation.

The influence of the interaction product $a\theta$ upon the half-peak width $\Delta E_{p/2}$ is represented in Fig. 3. Around the region where the height of the SWV response has a maximal value, the response becomes narrowest. Thus, the ratio of the peak current and the half-peak width $\Delta\Psi_p/\Delta E_{p/2}$ passes through a maximum value at the same critical value of the interaction product $(a\theta)_{\max}$, as in the case of the $\Delta\Psi_p - a\theta$ relationship (see Fig. 1).

Further theoretical analysis is undertaken in order to examine the influence of the charge transfer rate, represented through the kinetic parameter k_s/f . Interestingly, the effect of the kinetic parameter k_s/f is completely the same as the effect of the interaction product, although these parameters illustrate two phenomena of different nature. For instance, the peak current again depends parabolically on the kinetic parameter k_s/f , with the maximum being dependent on the interaction product $a\theta$.

In seeking an explanation for this behavior, one should reconsider the integral Eq. (7) that is the mathematical representation of the present mechanism. The product of the real standard rate constant k_s and the exponential term $\exp(-2a\theta)$ defines a new apparent rate constant of the surface redox reaction in the presence of lateral interactions, $k_{s,\text{app.}} = k_s \exp(-2a\theta)$. The apparent rate constant unifies the effect of the charge transfer rate, represented through the real standard rate constant k_s , and the effect of the interactions, represented through the interaction product $a\theta$. The kinetics of the redox process are determined solely by the apparent rate constant $k_{s,\text{app.}}$, which could itself be affected by varying either the real standard rate constant k_s , or the interaction product $a\theta$. For these

reasons, it becomes clear why both the charge transfer rate and the interactions between adsorbed species exhibit the same influence on the voltammetric response of the electrode reaction under study.

Moreover, the effect of the interaction product upon the position of the SWV response, which was illustrated in Fig. 2, may be explained using the concept of the apparent rate constant. As $k_{s,\text{app.}} = k_s \exp(-2a\theta)$, it follows that the attractive forces ($a > 0$) decrease the rate of the redox process. Under these conditions, the irreversibility of the redox process increases, causing the response to shift towards potentials which are more negative (see Fig. 2). Since the repulsive interactions ($a < 0$) transpose the reaction in the reversible region, the peak potential of the response shifts in the positive direction or remains at a constant value.

Introducing the concept of an apparent rate constant, the numerical solution of the current electrode mechanism is associated with a single kinetic parameter $\omega = k_{s,\text{app.}}/f$. With such a definition of the kinetic parameter ω , the mathematical solution of the current electrode mechanism is equivalent to the solution representing the simple surface redox reaction without interactions between adsorbed species [7].

The influence of the kinetic argument ω on the voltammetric response of a simple surface redox reaction is well understood and documented in the literature [3,5,7,23]. Being defined as a ratio of the standard rate constant and the signal frequency, the dimensionless kinetic argument ω determines solely the apparent reversibility of the simple surface redox reaction. Within the quasireversible region ($-1.5 < \log(\omega) < 1.5$) the peak current increases dramatically forming a well defined maximum. This is the most intriguing property of this mechanism known as a 'quasireversible maximum'. This phenomenon is a consequence of the

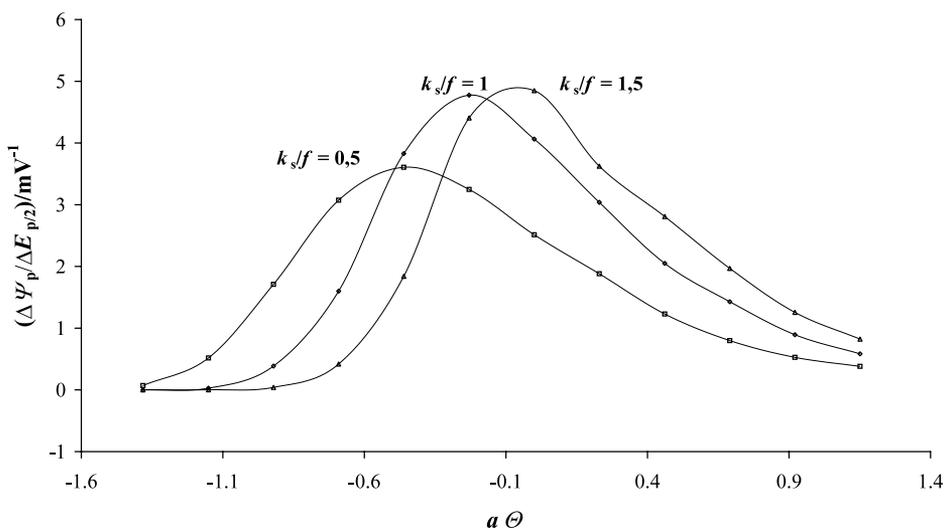


Fig. 3. The dependence of the ratio between the dimensionless peak current and the half-peak width $\Delta\Psi_p/\Delta E_{p/2}$ on the interaction product $a\theta$ for three values of the kinetic parameter k_s/f . All other conditions were the same as in Fig. 1.

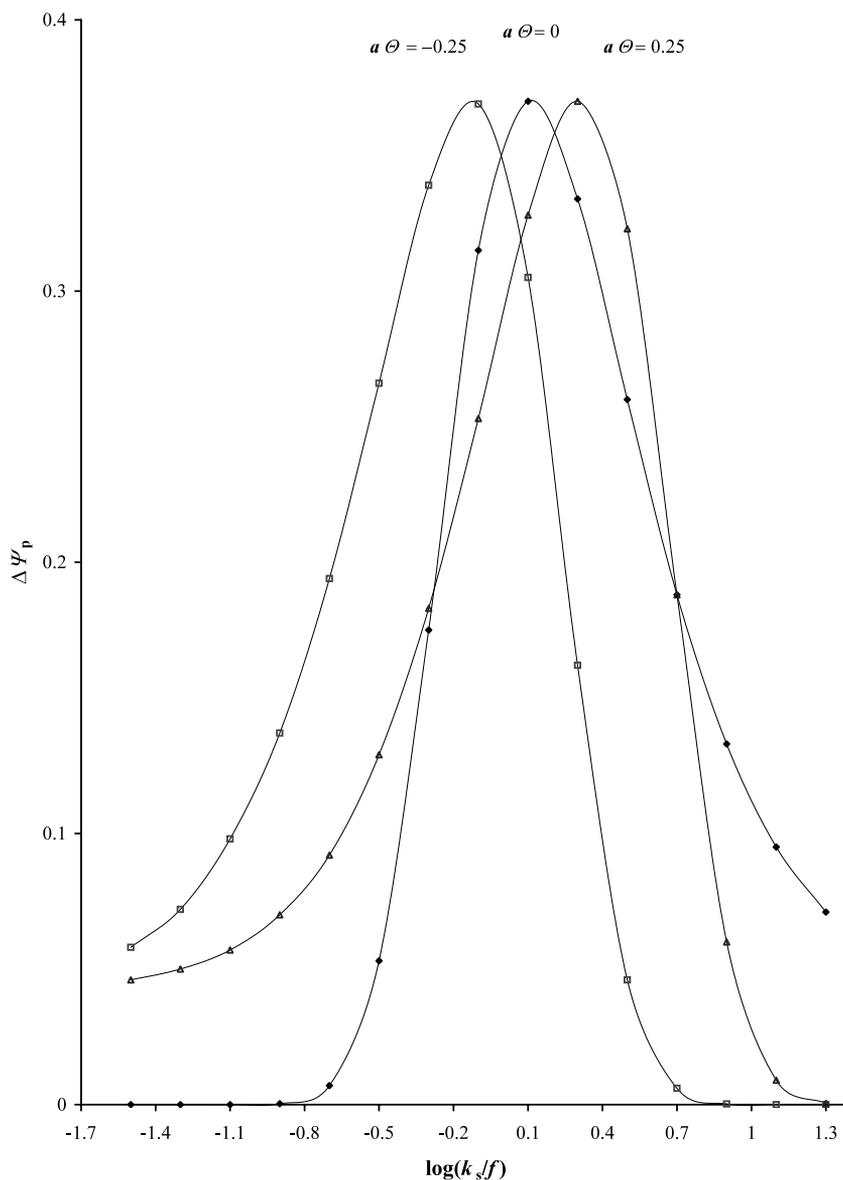


Fig. 4. The dependence of the dimensionless peak current $\Delta\Psi_p$ on the logarithm of the kinetic parameter k_s/f for three different values of the interaction product $a\Theta$. All conditions were the same as in Fig. 1.

current sampling procedure applied in SWV. When the redox reaction rate is synchronized to the duration of the SW pulses, the highest peak current is obtained. The critical values of the kinetic argument ω_{\max} , associated with the position of the quasireversible maximum, have been calculated for a variety of values for both the transfer coefficient α and the signal amplitude E_{sw} . In the real experiment, when a single surface redox reaction is investigated, the quasireversible maximum may be demonstrated by varying the signal frequency. The position of the experimentally reconstructed quasireversible maximum defines the critical frequency f_{\max} . Thus, the standard rate constant may be estimated through the simple relation $k_s = \omega_{\max} f_{\max}$ [5,7].

In the current mechanism, the kinetic parameter ω is defined as $\omega = k_{s,\text{app}}/f$, or in relation to the real parameters of the system as $\omega = (k_s/f) \exp(-2a\Theta)$. Changing either the kinetic parameter k_s/f or the interaction product $a\Theta$, the phenomenon of a quasireversible maximum can be demonstrated. In the light of this discussion it becomes obvious that all the curves in Fig. 1 represent the quasireversible maxima calculated by altering the interaction product $a\Theta$.

Fig. 4 shows the quasireversible maxima calculated by varying the kinetic parameter k_s/f . According to the definition of the kinetic argument $\omega = (k_s/f) \exp(-2a\Theta)$, it follows that the critical values of the parameter $(k_s/f)_{\max}$, associated with the positions of the maxima, are related to the interaction product $a\Theta$ through the

linear equation: $\log(k_s/f) = \log(\omega_{\max}) + (2/2.303)a\Theta$. This equation describes the influence of the interaction forces upon the position of the quasireversible maximum. Moreover, the application of this equation is of particular importance. The intercept of the line is $(k_s/f)_{\max} = \omega_{\max}$ and the slope $\Delta\log(k_s/f)_{\max}/\Delta\Theta = (2/2.303)a$, enabling estimation of both the real standard rate constant k_s in the presence of interactions and the Frumkin interaction parameter a , respectively.

In the real experiment, the quasireversible maximum could be reconstructed either by changing the accumulation time, which corresponds to the theoretical analysis presented in Fig. 1, or by varying the signal frequency, corresponding to the theoretical data in Fig. 4. Adjusting the SW frequency, the quasireversible maximum can be measured at several accumulation times. For each accumulation time, the position of quasireversible maximum will be located at different critical frequencies f_{\max} . Plotting the logarithm of the inverse critical frequencies $\log(1/f_{\max})$ versus the accumulation time t_{acc} , a linear dependence is obtained, which corresponds to the theoretical equation $\log(k_s/f) = \log(\omega_{\max}) + (2/2.303)a\Theta$. From the intercept of the experimental line, a critical frequency to assess the real standard rate constant is obtained, whereas the slope of the line enables estimation of the interaction parameter a .

It should be stressed finally that the kinetic parameters of the surface redox reaction may be estimated by analyzing the system with large signal SW amplitudes. This approach, which yields the interesting phenomenon, known as a 'split SW peak', was elaborated in detail in our previous publications [7,23]. However, the present theoretical work has shown that the analysis of the surface reaction with large signal SW amplitudes provides useful kinetic information only in the absence of interactions between immobilized species. A combination of interactions and large SW amplitudes yields unpredictable voltammetric behavior and complex shapes of the voltammetric response, which implies that this approach is unfavorable for the study of the present electrode mechanism.

4.2. Case of different interactions

The complexity of the system increases enormously when the redox reaction is characterized by three adsorption parameters: a_O , a_R and a_{OR} , related to the interactions between the oxidized, reduced and oxidized-reduced species, respectively.

Although the parameter a_O reflects the interactions between the oxidized species only, it affects all the components of the SWV response simultaneously. This is a consequence of the specific nature of the technique used [29]. One cannot select a component of the SWV response, which is selectively sensitive to the a_O

parameter. This conclusion is valid correspondingly for both a_R and a_{OR} parameters.

From analysis of the vast number of theoretical voltammograms, it was concluded that the influences of the interactions between Ox–Ox and Red–Red species are rather similar, whereas the influence of Ox–Red interactions is notably opposite. The similarity of the effects of the parameters a_O and a_R implies that their influence could be unified in a single parameter. It was found that at a constant value of the parameter a_{OR} , the response depends on the sum $(a_O + a_R)\Theta$, regardless of the particular values of both a_O and a_R parameters. Therefore, with these findings, the system studied is simplified to some extent, since its properties may be described through two parameters defined as $(a_O + a_R)\Theta$ and $a_{OR}\Theta$.

However, it should be emphasized that it was not possible to define a single parameter to combine the influence of all three parameters.

5. Experimental results

Probucole is both an electrochemically and surface active compound. In an aqueous medium it undergoes chemically reversible and electrochemically quasireversible reduction at a potential of about -0.9 V versus $\text{Ag}|\text{AgCl}|1 \text{ mol l}^{-1} \text{ KCl}$. The electrode reaction involves the exchange of one electron to form a chemically stable anion radical, which may be reoxidized back to the initial reactant [23,26]. Due to the low solubility of probucole in water, both components of the redox couple are strongly adsorbed on the mercury electrode surface.

The SW voltammetric response of probucole consists of a single well-defined sharp net-SW peak (Fig. 5). The cathodic and anodic components of the SWV response are located symmetrically with respect to the potential axes. An increase of the accumulation time caused both the components of the response to increase proportionally, which is typical behavior for a surface redox reaction.

The variation of the SWV response under the influence of increasing accumulation time is illustrated in Fig. 6. The enhancement of the accumulation time from 15 to 200 s caused the response to increase in height, while its position was shifted slightly towards more positive potentials. However, a further increase of the accumulation time resulted in a substantial decrease of the peak current as well as a pronounced shift of the response in the positive direction. For an accumulation period of 400 s or longer, a new SW peak at more positive potential was observed. The origin of the second peak could be attributed to the formation of a multilayer film deposited onto the electrode surface, or by reorientation of the adsorbed molecules within the deposited film.

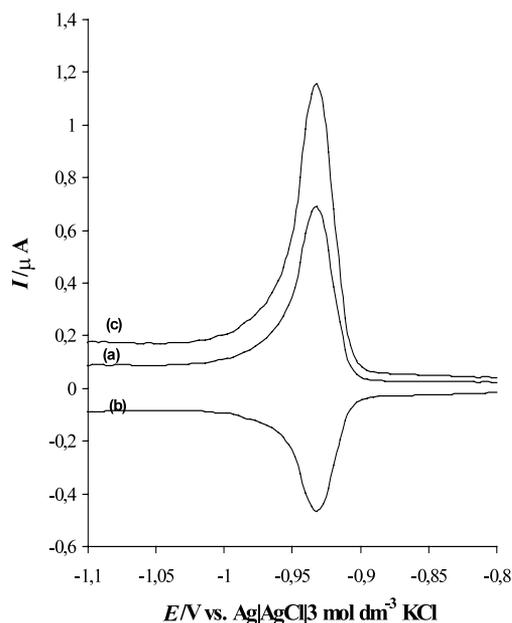


Fig. 5. Cathodic (a), anodic (b), and net (c) components of the square-wave voltammetric response of $4 \times 10^{-6} \text{ mol l}^{-1}$ probucole solution recorded in $1 \text{ mol l}^{-1} \text{ KNO}_3$ solution. The experimental conditions were: accumulation time $t_{\text{acc.}} = 20 \text{ s}$, accumulation potential $E_{\text{acc.}} = -0.7 \text{ V}$ signal frequency $f = 150 \text{ Hz}$, signal amplitude $E_{\text{sw}} = 25 \text{ mV}$ and scan increment $dE = 4 \text{ mV}$.

The dependence of the SW peak current of probucole on the accumulation time is depicted in Fig. 7 (curve 1). The parabolic relationship clearly indicates the presence of significant interactions between the adsorbed molecules. The shift of the peak potential in the positive direction with an increase in the accumulation time implies the existence of repulsive forces. These experi-

mental findings clearly illustrate the theoretical results presented in Figs. 1 and 2.

With the enhancement of the accumulation time from 15 to 300 s, the half-peak width of the SWV response was increased slightly from 27 to 41 mV. The ratio $\Delta I_p / \Delta E_{p/2}$ reached the maximum value at the same accumulation time as the maximum of the $\Delta I_p - t_{\text{acc.}}$ dependence, which is in agreement with the theoretical predictions of the effect of the interactions on the half-peak width (see Fig. 3).

Note that the accumulation time affects the interaction product $a\theta$ through the surface coverage θ . Of course, the interaction product $a\theta$, as a quantity representing the influence of the degree of interaction, may also be varied by changing the Frumkin interaction parameter a . For these purposes, the experiments have been carried out in the presence of a certain amount of acetonitrile. This organic solvent could itself be adsorbed onto the mercury electrode surface, affecting the structure of the electric double layer. As a consequence, the adsorption of probucole decreases, causing variation of the Frumkin interaction parameter. For these reasons, in the presence of 3% (v/v) acetonitrile, the peak currents of probucole are considerably suppressed (see curve 2 in Fig. 7). The shape of the $\Delta I_p - t_{\text{acc.}}$ relationship is still parabolic, but the maximum of the parabola is displaced slightly towards the longer accumulation times. In the presence of 6% (v/v) acetonitrile, the interactions between probucole molecules disappear completely and consequently the $\Delta I_p - t_{\text{acc.}}$ relationship obeys a Langmuir adsorption isotherm type law (see curve 3 in Fig. 7).

Finally, the effect of the signal frequency is discussed. Fig. 8 represents the variation of the $\Delta I_p / f$ ratio with the inverse signal frequency $1/f$. Note, that the ratio

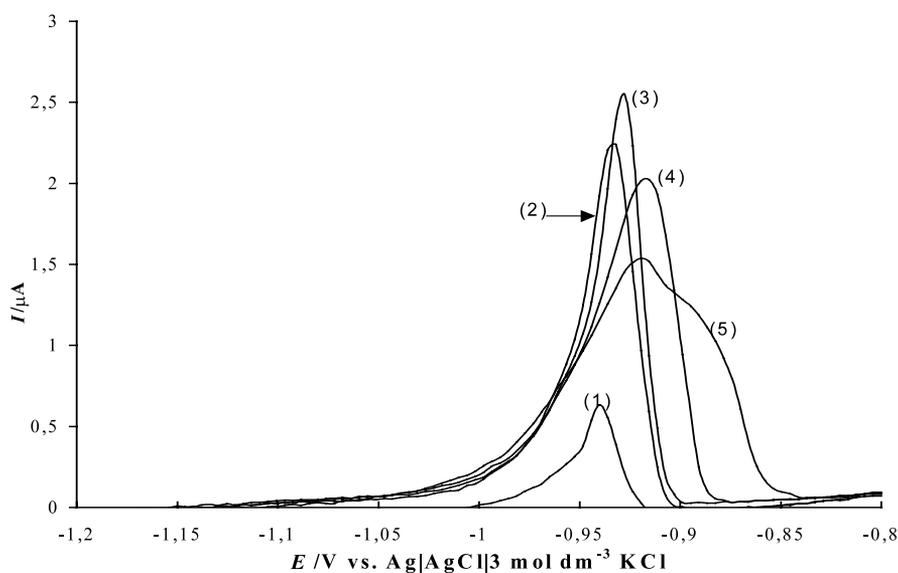


Fig. 6. The effect of increasing accumulation time on the net SWV response of probucole. The experimental conditions were $t_{\text{acc.}} = 15$ (1), 100 (2), 200 (3), 300 (4) and 400 s (5). The other experimental conditions were the same as in Fig. 6.

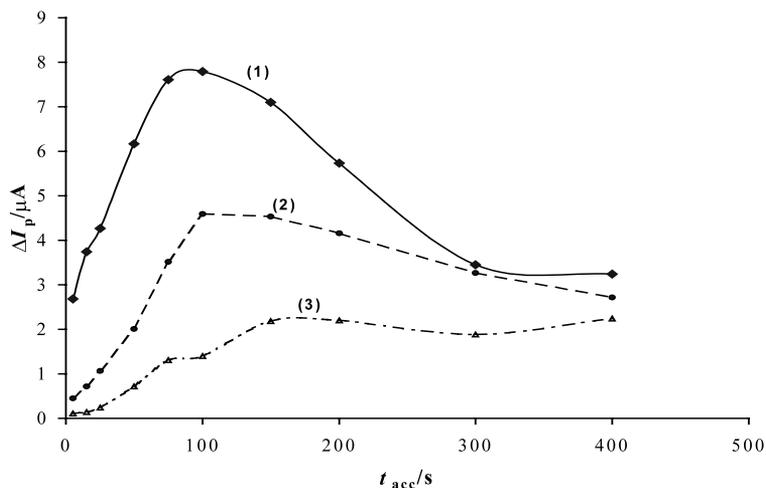


Fig. 7. The dependence of the peak current of probucole on the accumulation time. The amount of acetonitrile in the supporting electrolyte was: 0 (1), 3 (2) and 6% (v/v) (3). The other experimental conditions were the same as in the caption of Fig. 6.

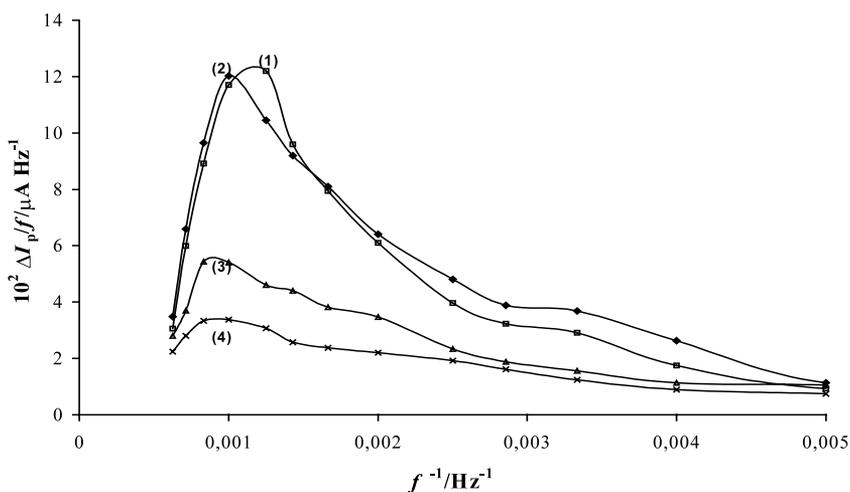


Fig. 8. The dependence of the ratio of the real peak current and the corresponding signal frequency $\Delta I_p/f$ on the inverse signal frequency $1/f$, in the presence of 0.4 (1), 5 (2), 9 (3) and 10% (v/v) (4) acetonitrile in the supporting electrolyte. The other experimental conditions were the same as in the caption of Fig. 7.

$\Delta I_p/f$ corresponds to the dimensionless peak current $\Delta \Psi_p = \Delta I_p / (nS\Gamma_0 f)$, whereas the inverse signal frequency $1/f$ corresponds to the ratio of the standard rate constant and the signal frequency k_s/f . In accordance with the theoretical predictions, the phenomenon of a quasireversible maximum was demonstrated experimentally (compare Figs. 8 and 4). Increasing the frequency over the interval from 100 to 1600 Hz, the apparent reversibility of the redox reaction of probucole was modified. When the frequency of the SW signal was synchronized to the apparent rate of the redox reaction, the highest current was obtained. Since the presence of acetonitrile affects the Frumkin interaction parameter a , the position of the experimental quasireversible maximum depends on the amount of acetonitrile which was predicted theoretically (see Fig. 4). All these experimen-

tal results confirm the validity of the theoretical model presented.

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