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Adsorptive Stripping Voltammetric Behavior of Probucole. Experimental and Theoretical Treatment

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Abstract. Adsorptive stripping voltammetric behavior of probucole has been studied by means of cyclic staircase and square-wave voltammetry. It was found that the redox reaction of probucole in an aqueous medium exhibits properties of a surface process involving significant repulsion interactions between adsorbed molecules. A theoretical model was developed to explain the experimentally observed phenomena. Analytical application of the adsorptive stripping square-wave voltammetry for quantitative determination of probucole has been discussed.

Key words: Probucole; square-wave voltammetry; cyclic voltammetry; surface redox reaction.

The demands for the detection of traces of substances with environmental, clinical and forensic significance increase continuously. The electroanalytical techniques such as differential pulse voltammetry (DPP), cyclic staircase voltammetry (CV) and particularly square-wave voltammetry (SWV) have become indispensable tools in modern analytical chemistry [1, 2].

The unique advantages of square-wave voltammetry such as fast scan rate, large frequency and amplitude, as well as the specific approach in the current sampling procedure ranks SWV as one of the most advanced methods among the family of pulse voltammetric techniques. This voltammetric method is particularly appealing for studying the processes in which the reactant and/or the product of the redox reaction adsorbs to the electrode surface [3–11].

The compound studied in this paper is known in the pharmacy as probucole [4,4′-[(1-methylethylidene)-bisthio)] bis[2,6-bis(1,1-dimethyl]phenole] propionamide (Fig. 1). Probucole is an important drug extensively used as a cholesterol lowering agent [12]. We have recently observed that the redox reaction of probucole at the hanging mercury drop electrode (HMDE) in an aqueous solution exhibits properties of an electrode process coupled by adsorption of the redox couple [11]. It was demonstrated that under suitable experimental conditions the SWV response of probucole splits in two peaks. Utilizing the properties of "split SW peaks" [10] together with the "quasireversible maximum" [3, 5–7], the kinetic parameters of the redox reaction of probucole such as the standard rate constant ($k_s = 1400\,s^{-1}$), the electron transfer coefficient ($\alpha = 0.55$) as well as the number of electrons exchanged ($n = 1$) were estimated [11]. In addition it should be noted that the redox properties of probucole under oxidation mode in a non-aqueous medium have been also recently studied [13].

This paper is concerned with further study of the adsorptive voltammetric behavior of probucole in aqueous medium in order to elucidate some specific properties of its electrode reaction. The objective of this work is also to develop an adsorptive stripping voltammetric method for quantitative determination of probucole.

Experimental

All experiments were performed with a multimode polarographic analyzer PAR 384B connected with static mercury drop electrode PAR 303A from Princeton Applied Research. The reference electrode was Ag/AgCl (saturated KCl) and a Pt-wire was used as a counter electrode.

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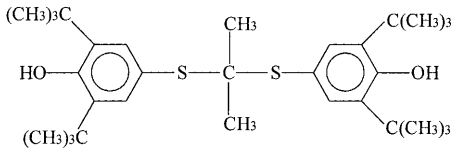

Fig. 1. Structural formula of probucole

The stock solution of probucole was prepared by dissolving of an appropriate amount in 98% methanol. All chemicals used such as methanol, KNO_3, H_2SO_4, $NaClO_4$, KCl, KI, and $NaCH_3COO$ (all Merck) were of analytical reagent grade and were used as received. Probucole was a product of Henkel Germany. Nitrogen of a high purity was used for deoxigenation of each sample solution for 8 min prior the first measurement and nitrogen blanked was maintained thereafter. All measurements were carried out at room temperature.

Results and Discussion

Electrochemical Properties of Probucole

Probucole is both electroactive and surface active compound. A few typical cyclic voltammograms of probucole solution recorded in 0.1 mol/L KNO_3 are presented in Fig. 2. The cyclic voltammetric response is consisted of a single pair of sharp cathodic and anodic peaks with a potential separation of about 30 mV. If the HMD electrode was held polarized at the initial potential for a certain period, the cathodic peak of the CV voltammogram increases in proportion to the accumulation time, upon the accumulation times of approximately 150 s, owing to the adsorptive accumulation of the probucole molecules onto the mercury electrode surface. Besides, it is important to note that the anodic peak also increases proportionally to the duration of the accumulation period in the same interval as cathodic one (see Fig. 2). It implies that both probucole and its electrochemically-generated product remain immobilized on the mercury electrode. Furthermore, at certain experimental conditions (i.e. concentration of probucole of 1×10^{-5} mol/L and accumulation time of $t_{acc.} = 30$ s) the subsequent cycling of the potential exhibits no significant influence upon the peak currents of both CV peaks. This finding indicates that there are no significant desorption of the adsorbed material during the subsequent potential cyclization. All these results indicate that the redox reaction of probucole occurs predominantly as a surface redox process in which both reactant and product of the redox reaction are significantly confined to the electrode surface.

Additional information regarding the properties of the studied redox reaction were collected studying the cyclic voltammograms at different scan rates. As shown in Table 1, on the scan rate over the interval $50 \leq v/\mathrm{mV\,s^{-1}} \leq 1000$ the cathodic peak potential remained virtually unchanged. The anodic peak potential was shifted only for 12 mV in positive direction with increasing the scan rate from 50 to 1000 mV s^{-1}. The constancy of the peak potentials

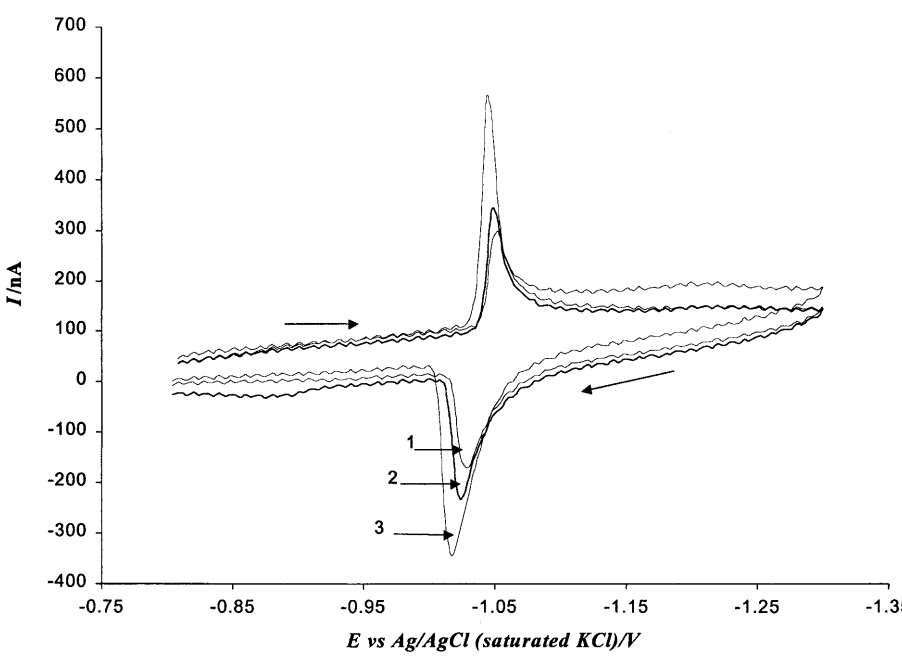

Fig. 2. The effect of accumulation time to the cyclic voltammograms of 1×10^{-5} mol/L probucole solution recorded in 0.1 mol/L KNO_3. The experimental conditions were: accumulation potential $E_{acc.} = -0.8$ V, scan rate $v = 500$ mV/s and accumulation time $t_{acc.} = 5$ (*1*), 10 (*2*) and 20 s (*3*)

Table 1. The effect of the scan rate to the parameters of the cyclic voltammetric response of 1×10^{-5} mol/L probucole solution recorded in 0.1 mol/L KNO_3. The experimental conditions were: accumulation potential $E_{acc.} = -0.8$ V, and accumulation time $t_{acc.} = 60$ s

v/mV s^{-1}	$I_{p,c}$/μA	$I_{p,a}$/μA	$E_{p,c}$/V	$E_{p,a}$/V	$E_{p,c}-E_{p,a}$/mV
1000	1.220	−0.608	−1.052	−1.016	36
666	0.692	−0.376	−1.052	−1.020	32
500	0.732	−0.390	−1.048	−1.020	28
400	0.361	−0.223	−1.052	−1.024	28
200	0.174	−0.094	−1.052	−1.028	24
100	0.106	−0.033	−1.052	−1.028	24
80	0.096	−0.025	−1.052	−1.028	24
50	0.079	−0.010	−1.052	−1.028	24

under the influence on the scan rate suggests that the redox reaction of probucole show some degree of apparent reversibility.

According to the theory of the electrode reactions occurring immobilized on the electrode surface [14] the peak current depends linearly on the scan rate. This properties appears to be one of the most important discrepancies compared to the diffusion controlled processes, in which the peak current increases in proportion to the square root of the scan rate. The variations of both cathodic and anodic CV peak currents of probucole with the scan rate are represented in Fig. 3. These experimental results are in quite good agreement with the theoretical expectations indicating that the redox reaction of probucole could be regarded as a redox process of immobilized redox couple.

A corresponding analysis in square-wave voltammetry (SWV) has been undertaken by varying the frequency of the signal. The SW peak potential of $E_p = -1.056$ V remains totally unaffected by the signal frequency over the range from 30 to 120 Hz, which is consistent with the assumption that the redox reaction is reversible. As shown in Fig. 4, within the same frequency interval, the relationship between peak currents and the SW frequency deviates significantly from linearity which is a consequence of the specific properties of the SWV response of surface processes. According to the theoretical predictions [3, 8], the SW peak current depends parabolically on the signal frequency over the large frequency interval. Within the quasireversible region, the peak current gains a maximum value, and this property of the surface redox reactions is known as a "quasireversible maximum". Therefore, the curve in Fig. 4 represents only the ascending part of the entire parabolic dependency of the peak current on the SW frequency.

Aiming to inspect the influence of the chemical composition and pH of the medium, the voltammetric response of probucole was recorded in diverse supporting electrolytes (see Table 2). On the base of these results one could conclude that probucole is an electrochemically active compound over a wide pH interval (from pH ≅ 1 in 0.1 mol/L H_2SO_4 to pH ≅ 12 in 0.25 mol/L KOH). Moreover the peak potential of the SW response is almost unaffected by the particular pH of the supporting electrolyte, strongly suggesting that the redox mechanism involves formation of a chemically stable anion radical which is not followed by a succeeding protonation. Therefore, the redox reaction of probucole in an aqueous medium proceeds according to general mechanism typical for numerous aromatic compounds [15–18].

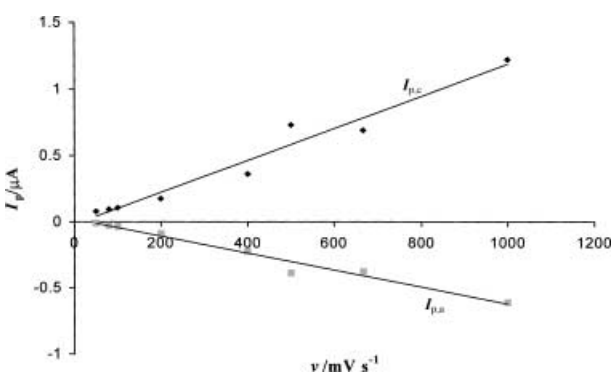

Fig. 3. The dependence of the cathodic and anodic CV peak currents on the scan rate. All experimental conditions are the same as in the caption of the Table 1

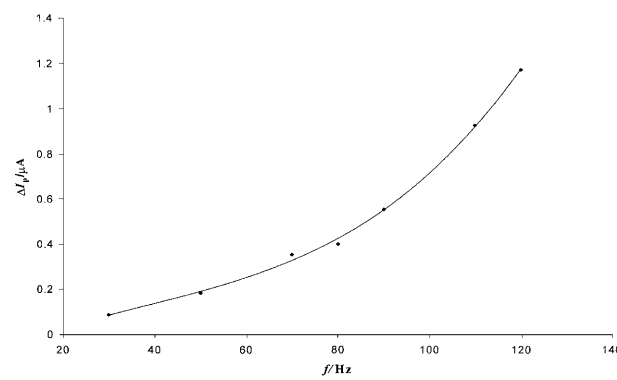

Fig. 4. The variation of the SW peak currents with the signal frequency. The experimental conditions were amplitude $E_{sw} = 20$ mV, scan increment $dE = 4$ mV and accumulation time $t_{acc.} = 45$ s. All other conditions as in the caption of the Fig. 2

Table 2. The parameters of the SWV responses of 1×10^{-5} mol/L probucole solution recorded in diverse supporting electrolytes. The experimental conditions were: frequency $f = 120$ Hz, amplitude $E_{sw} = 20$ mV, scan increment $dE = 4$ mV

Supporting electrolyte	Concentration/mol L^{-1}	E_p/V	ΔI_p/μA	$\Delta E_{p/2}$/mV	$\Delta I_p/\Delta E_{p/2}$ (nA mV^{-1})
$NaClO_4$	0.10	−1.020	1.060	70	15.14
H_2SO_4	0.10	−1.060	2.035	65	31.30
KCl	0.10	−1.104	0.740	75	9.86
KI	0.10	−1.092	0.401	80	5.01
KOH	0.25	−1.04	1.111	80	13.88
CH_3COONa	0.10	−1.064	0.915	75	12.20
KNO_3	0.10	−1.048	2.426	65	37.32
KNO_3	0.30	−1.044	1.179	70	16.84
KNO_3	1.00	−1.028	0.726	75	9.68

In spite of the fact that the peak potential is virtually insensitive to the pH and composition of the medium, the SW peak currents depend markedly on the type of the supporting electrolyte. For electrode reactions accompanied by adsorption of the redox couple, these results could be expected reasonable. The adsorption mechanism, generally strongly depends on the chemical composition and concentration of the supporting electrolyte. For instance, the lowest current was observed in 0.1 mol/L KI (see Table 2) due to the concurrent adsorption of probucole molecules and iodide ions to the mercury electrode surface. A similar result has been obtained in 0.1 mol/L KCl. Nevertheless, the peak current is higher in this medium, which is consistent with the fact that the chloride ions are less adsorbed that the iodide ones. Furthermore, the rate of the surface redox reaction could vary significantly in various supporting electrolytes. For all these reasons, the peak current is a strong function of the type of the supporting electrolyte.

Further study of the voltammetric behavior of probucole produced by the surface redox reaction of probucole has revealed that the adsorption process occurs through a rather complex mechanism. Although the redox reaction appears reversible, the peak currents do not increase in proportion to the accumulation time and concentration of probucole, when accumulation time was increased approximately over 200 s, and concentration of probucole was higher than 5×10^{-5} mol/L. The variation of the SW peak currents with the accumulation time is depicted in Fig. 5. The parabolic relationship between the peak currents and accumulation time indicates that the adsorption of probucole occurs through a complex mechanism, involving most probably significant interactions between the adsorbed molecules. It is interesting fact that both the peak potential and

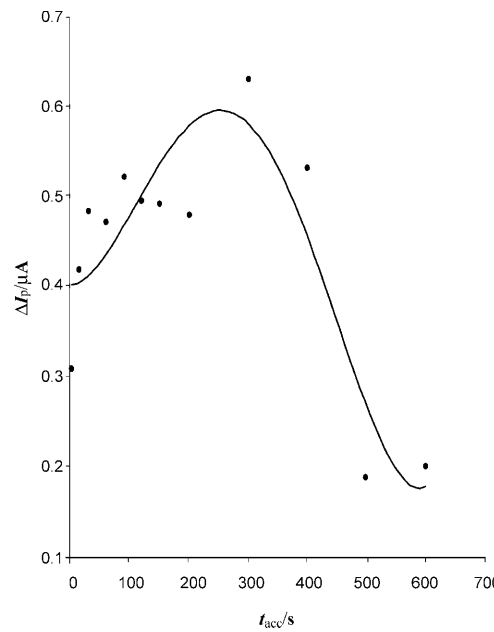

Fig. 5. The dependence of the SW peak currents of probucole on the accumulation time. The experimental conditions are frequency $f = 120$ Hz, amplitude $E_{sw} = 20$ mV, and scan increment $dE = 4$ mV. All other conditions as in the caption of the Fig. 2

half-peak width has remained nearly unchanged upon the influence of the accumulation time. Nevertheless, the most impressive phenomena appear after long accumulation time. As shown in Fig. 6, the cyclic voltammetric response of probucole increases gradually up to accumulation time of 300 s. However, at longer accumulation time, the response diminishes severely such that at accumulation time of 400 s, it disappears totally. Such a complex voltammetric behavior strongly deviates from the theoretical predictions and can not be explained by the theory for a simple surface redox reaction [8].

In order to explain the observed phenomena, a theoretical model was developed for a surface redox

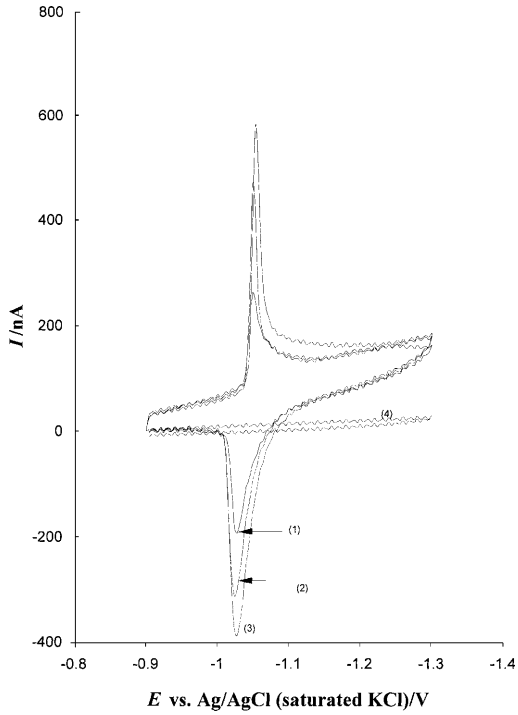

Fig. 6. The effect of the accumulation time on the cyclic voltammetric responses of probucole. The accumulation time was $t_{acc.} = 20$ (*1*), 120 (*2*), 300 (*3*) and 400 s (*4*). All other conditions as in the caption of the Fig. 2

reaction with uniform interactions between the adsorbed species [19]. The mathematical procedure is given in the Appendix to the paper.

According to the Eq. (7) in the mathematical model the dimensionless SW response is mainly controlled by the kinetic parameter $\omega = k_s/f$ (k_s is a surface standard rate constant and f is a frequency), interaction parameter β and the relative surface coverage of the electrode Θ. The apparent reversibility of the redox reaction is determined predominantly by the kinetic parameter ω as in the case of a simple surface redox reaction [8]. Within the interval $-1.5 \leq \log(\omega) \leq 0.5$, the redox reaction is quasireversible. For $\log(\omega) > 0.5$ and $\log(\omega) < -1.5$, the redox reaction is reversible and totally irreversible, respectively. These intervals are meaningful since the influence of the interaction parameter β depends on the apparent reversibility of the redox reaction.

Figure 7 shows the variations of the normalized real peak current $\Delta I_p/(nFS\Gamma_{max}f)$ on the surface coverage Θ when attraction forces exist between the adsorbed molecules ($\beta = 0.5$). This kind of theoretical study corresponds to the experimental analysis in which the peak current is inspected as a function of

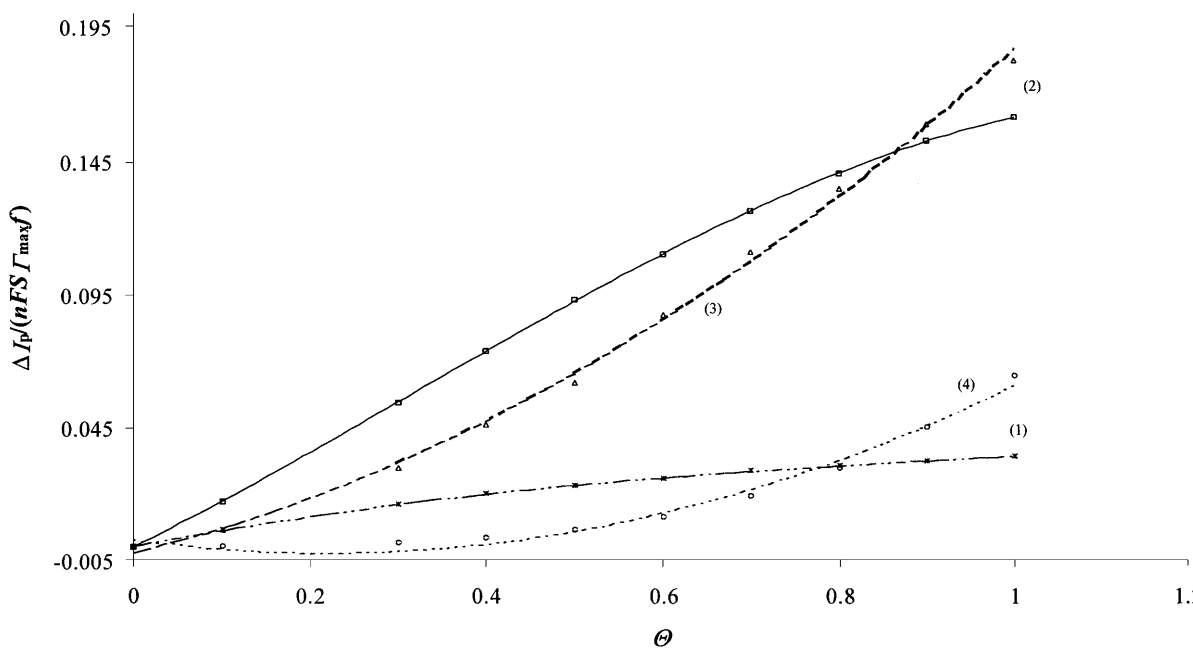

Fig. 7. The effect of the relative surface coverage upon the normalized real peak currents for different reversibility of the surface redox reaction in the presence of attraction interactions between adsorbed species. The conditions of the simulation were: interaction parameter $\beta = 0.5$, transfer coefficient $\alpha = 0.5$, signal amplitude $E_{sw} = 20$ mV, scan increment $dE = 10$ mV, and kinetic parameter $\omega = 0.1$ (*1*); 1 (*2*); 2 (*3*) and 5 (*4*)

the accumulation time. As shown in Fig. 7, the peak current increases with the surface coverage for a various reversibility of the redox reaction. Interestingly, the peak current enhances more rapidly for quasireversible (curves 2 and 3 in Fig. 7) than for irreversible (curve 1) and reversible (curve 4) redox reaction. It is important to note that regardless of the reversibility of the redox reaction, all theoretical dependencies are not linear. In the absence of attraction interactions (for moderate surface coverage), the corresponding dependency should be strictly linear. Therefore, the non-linear dependency of the real peak current on the accumulation time could serve as a criterion to recognize the presence of significant interaction forces between the adsorbed molecules of a surface redox reaction.

The complexity of the redox system increases markedly if repulsion interactions are present between the adsorbed molecules ($\beta < 0$). Figure 8 shows how the peak currents vary with surface coverage for $\beta = -0.5$ and different reversibility of the redox reaction. For irreversible redox reaction only, the peak currents increase non-linearly with surface coverage (curve 1 in Fig. 8). For quasireversible (curves 2 and 3) as well as reversible (curve 4) reaction, the peak currents depend parabolically on the surface coverage. As can be seen, the wideness of this parabola depends on the apparent reversibility of the redox reaction. The effect of the repulsion interactions is obviously most pronounced for reversible redox reaction (curve 4). The curve is characterized with a sharp maximum located at about $\Theta = 0.1$. Increasing the surface coverage over $\Theta = 0.1$ causes the peak currents to diminish severely. At the same time, the other properties of the response, such as the peak potential and the half-peak width are not affected significantly by the surface coverage.

The presented theoretical results clearly show that the type of interactions between the adsorbed species could be readily distinguished, if the surface redox reaction is reversible or quasireversible. It is not the case for irreversible redox reaction only, since both attraction and repulsion interactions produce rather similar effects upon the voltammetric response.

Comparing the experimental results of probucole and the theoretical data presented, one can unequivocally conclude that the redox reaction of probucole is complicated by repulsion interactions between the adsorbed molecules. Considering the number of bulky methyl radicals in the molecular structure of probucole (see Fig. 1), this explanation for observed phenomena sounds reasonably. The SW peak current is a parabolic function of the accumulation time (see Fig. 5), which is in quite good agreement with the corresponding dependencies predicted theoretically (see Fig. 8).

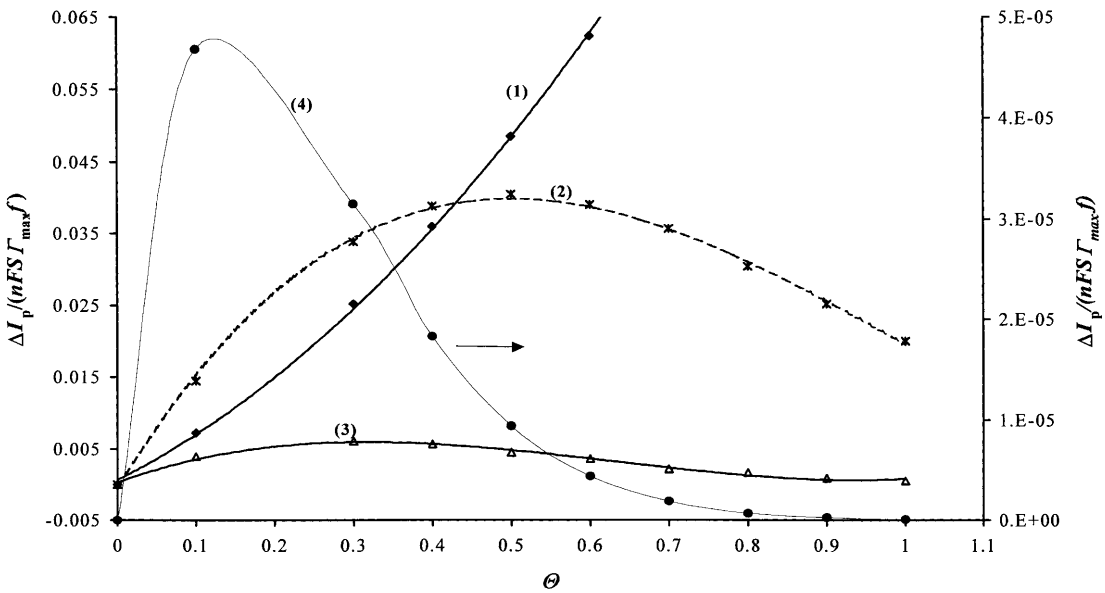

Fig. 8. The effect of the relative surface coverage upon the normalized real peak currents for different reversibility of the surface redox reaction in the presence of repulsion interactions between adsorbed species. All other conditions of the simulation were the same as in Fig. 7

Aiming to confirm the experimentally observed phenomenon after long accumulation time (see Fig. 6), a corresponding theoretical analysis was undertaken under conditions of cyclic staircase voltammetry. For this purpose, a series of cyclic voltammograms were simulated for a reversible surface redox reaction including repulsion interactions between the immobilized species. Figure 9 shows that increasing the surface coverage for a constant value of the interaction parameter $\beta = -0.5$, caused the degree of interactions to become so strong such that the response is virtually completely vanished. This theoretical analysis clarifies the reasons causing disappearances of the voltammetric response of probucole after long accumulation time (curve 4 in Fig. 6).

At the end of this section, it can be concluded that the presented simple theoretical model successfully explains the complex voltammetric behavior of probucole in aqueous solutions. Moreover, it could serve as a useful tool to clarify the properties of the electrode reactions of similar compounds. For instance, rather resembling voltammetric properties were recently observed with the experiments of anti-depressant fluoxetine [20].

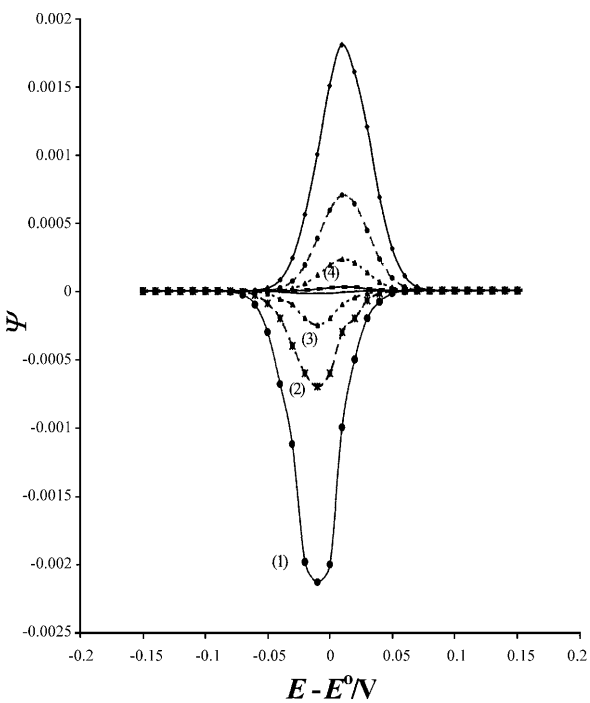

Fig. 9. The theoretical cyclic staircase voltammograms simulated for a surface reversible redox reaction in the presence of repulsion interactions between adsorbed species. The conditions of the simulation were: interaction parameter $\beta = -0.5$, scan rate $v = 100\,\mathrm{mV\,s^{-1}}$ and relative surface coverage $\Theta = 0.1$ (*1*), 0.3 (*2*), 0.5 (*3*) and 0.8 (*4*)

Analytical Application

Aiming to develop an electroanalytical method for quantitative determination of probucole one should first cope with the presence of significant interactions between adsorbed probucole molecules that complicate the electrode mechanism to appreciable extend. To this purpose, a mixture of water and different amounts of methanol was used as solvent for preparing the supporting electrolyte. According to the data listed in Table 2, 0.1 mol/L KNO_3 solution was selected as an optimal medium for analytical application. In this medium, the concurrent adsorption of supporting electrolyte ions does not occur, as well as the reversibility of the redox reaction is such that it produces the highest voltammetric response. Moreover, in this medium the ratio between the peak current and the half-peak width $\Delta I_p/\Delta E_{p/2}$ shows a maximal value, which appears to be the main criterion for selecting particular experimental condition for analytical application.

The effect of methanol upon the SW peak current of probucole recorded in 0.1 mol/L KNO_3 is depicted in Fig. 10. As can be seen, a parabolic dependency between ΔI_p vs. amount of methanol present in the

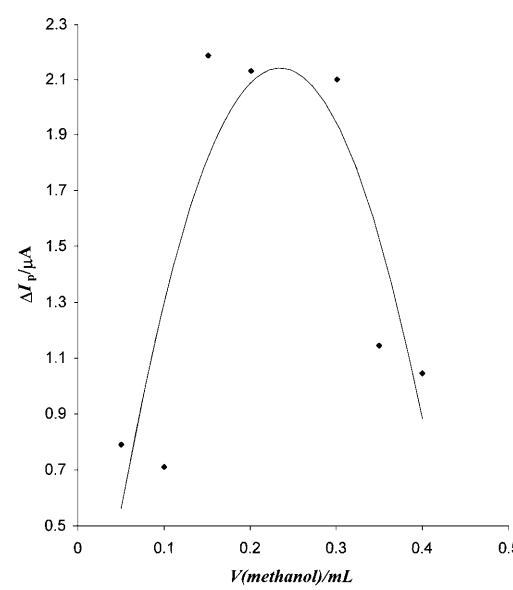

Fig. 10. The effect of methanol on the SW peak current of probucole. Accumulation time was 45 s. All other conditions were the same as in the Fig. 5

supporting electrolyte was found with a maximum located at about 2.5% (v/v) methanol. Keeping in mind that methanol is adsorbed to the electrode surface itself, its effect could be understood through the influence to the structure of the electric double layer as well as through the salting out effect of the organic electroactive substance [21]. In addition, the presence of adsorbed methanol on the electrode surface decreases the adsorption strength of probucole thus preventing the presence of significant interactions between adsorbed molecules. All these effects give rise to an enhancement of the response. However, on increasing the amount of methanol over 2.5% an opposite effect was observed. Under such conditions a strong concurrent adsorption between probucole and methanol occurs. The electrode surface is covered with adsorbed methanol molecules blocking the adsorption of the probucole that causes the height of the response to diminish considerably. At these conditions, the electrode mechanism is mainly controlled by diffusion of the electroactive component, preventing accumulation of the analyte by adsorption.

The variation of the peak current with accumulation time in 0.1 mol/L KNO_3 containing 2.5% methanol is represented in Fig. 11. Obviously, the curve has the shape of the Langmuir isotherm indicating an absence of significant interactions between adsorbed molecules. This analysis clearly shows that the presence of small amounts of methanol in the supporting electrolyte suppresses efficiently the interactions between the adsorbed molecules of the analyte. Thus, within the linear part of the isotherm, the surface concentration is proportional to the bulk concentration of the analyte, which is a crucial prerequisite for developing an adsorptive stripping voltammetric method.

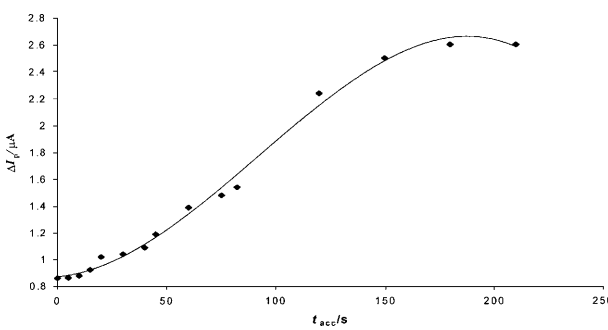

Fig. 11. The effect of the accumulation time on the SW peak currents of probucole in the presence of 2.5% (v/v) methanol in supporting electrolyte. All other conditions were the same as in the Fig. 5

It should be also pointed out that the SWV response of probucole is particularly sensitive to the signal amplitude. If the amplitude was increased over $E_{sw} = 40$ mV, the response splits in two peaks. This phenomenon was thoroughly elaborated in our previous communications [10–11]. The splitting of the SW response is useful property for estimation of redox kinetic parameters, however it is a totally undesirable phenomenon from analytical point of view. Therefore, an amplitude lower than $E_{sw} = 40$ mV is strongly recommended.

Finally, the following set of experimental conditions has been evaluated as optimal for quantitative determination of probucole utilizing adsorptive stripping square-wave voltammetry: 0.1 mol/L KNO_3 containing 2.5% (v/v) methanol as a supporting electrolyte, accumulation potential $E_{acc.} = -0.7$ V, accumulation time $t_{acc.} = 90$ s, SW frequency $f = 120$ Hz, SW amplitude $E_{sw} = 20$ mV, and scan increment $dE = 4$ mV. Under these conditions the SW peak current of probucole is a linear function of the probucole concentration at concentration levels of 10^{-7} and 10^{-6} mol/L associated with the following equations: $\Delta I_p/\text{nA} = 0.01232\,\text{nA L}/\mu\text{mol} + 2.141$ with $R^2 = 0.996$ and $\Delta I_p/\mu\text{A} = 0.526\,\mu\text{A L}/\mu\text{mol} + 0.229$ with $R^2 = 0.999$. A value of 8×10^{-8} mol/L was estimated for the detection limit which was defined as three times to noise.

Precision was calculated by 8 successive measurements of 1.5×10^{-7} mol/L, 5×10^{-7} mol/L and 1×10^{-6} mol/L probucole solutions with a relative standard deviations ranged from 0.8 to 4.5%.

Conclusion

Probucole is surface active and electrochemically active compound that undergoes a reversible reduction at a HMDE surface under potential of about −1.0 V. The redox reaction exhibits properties of a complex surface process in which both reactant and product of the redox reaction are immobilized on the electrode surface. The experimentally observed phenomena by varying accumulation time are successfully explained by a theoretical model for a surface redox reaction involving interactions between adsorbed species. Comparing the experimental and the theoretical results it was found that the repulsion interactions occur between adsorbed probucole molecules. For analytical purposes, it was found that the presence of 2.5% (v/v) methanol in supporting electrolyte

suppresses efficiently the interactions enabling application of adsorptive stripping square-wave voltammetry for quantitative determination of probucole. The proposed electroanalytical method is sensitive, rapid, and precise. The adsorptive stripping voltammetry in general is an attractive method due to the relatively low cost of the instrumentation and short time required for the analysis. The disadvantages of this approach are linked to the problems presented by complex sample types. In principle, the problem of interferences can be solved by means of separation techniques. These problems will need to be addressed case by case, as the specific nature of the problem depends on the type of the sample. Generally speaking, one should expect appreciable interferences if some surface active compounds are present in the sample and the supporting electrolyte.

Appendix

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

$$(\mathrm{Ox})_{\mathrm{ads}} + ne^- \rightleftarrows (\mathrm{Red})_{\mathrm{ads}} \qquad \text{(I)}$$

It is assumed that the reaction is controlled by the charge transfer kinetics, that the adsorption of both reactant and product is totally irreversible, that there are uniform interactions between the adsorbed molecules in the case of submonolayer surface coverage and that the additional adsorption and the redox reaction of the dissolved molecules can be neglected. Under these conditions, the system (I) is described by the following differential equations:

$$\mathrm{d}\,\Gamma_{\mathrm{Ox}}/\mathrm{d}t = -I/(nFS), \qquad (1)$$

$$\mathrm{d}\,\Gamma_{\mathrm{Red}}/\mathrm{d}t = I/(nFS), \qquad (2)$$

which should be solved under the following initial and boundary conditions:

$$t = 0 : \Gamma_{\mathrm{Ox}} = \Gamma_0,\ \Gamma_{\mathrm{Red}} = 0, \qquad \text{(a)}$$

$$t > 0 : \Gamma_{\mathrm{Ox}} + \Gamma_{\mathrm{Red}} = \Gamma_0. \qquad \text{(b)}$$

On the electrode surface, the following condition is valid [19]:

$$I/(nFS) = k_{\mathrm{s}}\exp(-\alpha\phi)\exp(-2\beta\Theta)[\Gamma_{\mathrm{Ox}} - \exp(\phi)\Gamma_{\mathrm{Red}}] \qquad (3)$$

were: $\phi = nF(E - E_{\mathrm{Ox/Red}})/RT$ is 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 unit s^{-1}, α is the cathodic transfer coefficient, β is an interaction parameter, $\Theta = \Gamma_0/\Gamma_{\max}$ is fraction of the electrode covered by an adsorbed material, $\Gamma_{\max}$ is a maximal surface concentration, I is the current, E is the working electrode potential, $E_{\mathrm{Ox/Red}}$ is the standard potential, S is electrode surface, while n, F, R, T and t have their usual meanings. According to Frumkin isotherm law, β is positive for attraction and negative for repulsion interactions between the adsorbed molecules.

The solutions of the differential Eqs. (1) and (2) were obtained with the aid of Laplace transformations and they read:

$$\Gamma_{\mathrm{Ox}} = \Gamma_0 - \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau, \qquad (4)$$

$$\Gamma_{\mathrm{Red}} = \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau. \qquad (5)$$

Substituting Eqs. (4) and (5) into the kinetic Eq. (3), an integral equation is obtained which can be regarded as a mathematical representation of the electrode mechanism (I) under voltammetric conditions:

$$\frac{I}{n \cdot F \cdot S} = k_{\mathrm{s}} \cdot e^{-\alpha \cdot \phi} \cdot e^{-2 \cdot \beta \cdot \Theta} \cdot \left(\Gamma_0 - \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau - e^{\phi} \cdot \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau\right). \qquad (6)$$

Equation (6) was numerically solved according to the method of Nicholson and Olmstead [22]. The numerical solution under conditions of square-wave voltammetry reads:

$$\Psi_m = \frac{\omega \cdot e^{-\alpha \cdot \phi_m} \cdot e^{-2 \cdot \beta \cdot \theta} - \omega \cdot e^{-\alpha \cdot \phi_m} \cdot e^{-2 \cdot \beta \cdot \theta} \cdot \left(\frac{1 + e^{\phi_m}}{50}\right) \cdot \sum_{j=1}^{m-1} \Psi_j}{1 + \omega \cdot e^{-\alpha \cdot \phi_m} \cdot e^{-2 \cdot \beta \cdot \theta} \cdot \left(\frac{1 + e^{\phi_m}}{50}\right)}, \qquad (7)$$

where: $\Psi = I/nFSf\Gamma_0$ is a dimensionless current, $\omega = k_{\mathrm{s}}/f$ is a dimensionless kinetic parameter, and f is the SW frequency.

The square-wave signal is a train of cathodic and anodic pulses that are superimposed to a staircase potential ramp. The height of each cathodic and anodic pulse are equal and designated as square-wave amplitude E_{sw}. Additionally, the SW signal is

characterized by the staircase potential increment dE and frequency f of the pulses.

References

[1] J. Osteryoung, J. J. O'Dea, A. J. Bard (ed.), *Electroanalytical Chemistry*, Vol. 14, Marcel Dekker, New York, 1986, p. 209.

[2] J. G. Osteryoung, R. A. Osteryoung, *Anal. Chem.* **1985**, *57*, 101A.

[3] M. Lovrić, Š. Komorsky-Lovrić, *J. Electroanal. Chem.* **1988**, *248*, 239.

[4] J. J. O'Dea, A. Ribes, J. G. Osteryoung, *J. Electroanal. Chem.* **1993**, *345*, 287.

[5] Š. Komorsky-Lovrić, M. Lovrić, *Fresenius Z. Anal. Chem.* **1989**, *335*, 289.

[6] M. Lovrić, Š. Komorsky-Lovrić, A. M. Bond, *J. Electroanal. Chem.* **1991**, *319*, 1.

[7] Š. Komorsky-Lovrić, *Fresenius J. Anal. Chem.* **1996**, *356*, 306.

[8] J. J. O'Dea, J. G. Osteryoung, *Anal. Chem.* **1993**, *65*, 3090.

[9] J. H. Reeves, S. Song, E. F. Bowden, *Anal. Chem.* **1993**, *65*, 683.

[10] V. Mirčeski, M. Lovrić, *Electroanalysis* **1997**, *9*, 1283.

[11] V. Mirčeski, M. Lovrić and B. Jordanoski, *Electroanalysis* **1999**, *11*, 660.

[12] E. Mutschler, H. Derendorf, Drug Actions, *Basic Principles and Therapeutic Aspects*, MedPharm Scientific Publishers, Stuttgart, 1995, 425.

[13] K. Nesmerak, I. Nemec, M. Sticha, J. Gabriel, V. Mirčeski, *Collect. Czech. Chem. Commun.* **1999**, *64*, 1100.

[14] E. Laviron, *J. Electroanal. Chem.* **1979**, *101*, 19.

[15] A. Zeig, A. H. Maurer, B. G. Roberts, *J. Org. Chem.* **1967**, *32*, 1322.

[16] J. K. Brown, D. R. Burnhan, N. A. J. Rogers, *J. Chem. Soc. (B)* **1969**, 1149.

[17] A. J. Birch, *Quart. Rev.* **1950**, *4*, 69.

[18] A. J. Birch, H. Smith, *Quart. Rev.* **1958**, *12*, 17.

[19] E. Laviron, *J. Electroanal. Chem.* **1974**, *52*, 395.

[20] A. M. S. Roque da Silva, J. C. Lima, M. T. Oliva Teles, A. M. Oliveira Brett, *Talanta* **1999**, *49*, 611.

[21] N. B. Grigorev, B. B. Damaskin, *Advances in the Electrochemistry of Organic Compounds*, Izd. Nauka, Moscow, 1968, p. 66.

[22] R. S. Nicholson, M. L. Olmstead In: J. S. Matttson, H. B. Mark, H. C. MacDonald (eds.), *Electrochemistry: Calculations, Simulations and Instrumentation, vol. 2*, Marcel Dekker, New York, 1972.

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