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Measuring the Electrode Kinetics of Surface Confined Electrode Reactions at a Constant Scan Rate

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Abstract: The kinetics of surface confined electrode reactions of alizarin, vitamin B12, and vitamin K2 is measured with square-wave voltammetry over a wide pH interval, by applying the recent methodology for kinetic analysis at a constant scan rate [V. Mirceski, D. Guziejewski, K. Lisichkov, *Electrochim. Acta* **2013**, *114*, 667–673]. The reliability and the simplicity of the recent methodology is confirmed. The methodology requires analysis of the peak potential separation of the forward and backward component of the response as a function of the pulse height (SW amplitude), for a given frequency (i.e. constant scan rate) of the potential modulation.

Keywords: Alizarin · Vitamin K2 · Vitamin B12 · Square-wave voltammetry · Electrode kinetics

1 Introduction

The application of square-wave voltammetry (SWV) [1] for mechanistic and kinetic studies [2–8] of electrode processes increases permanently in the last decade, due to the intensive development of the theory of the technique for a variety of electrode mechanisms and electrode geometries [9–17]. A plethora of intriguing studies has been conducted in relation to the kinetics of charge transfer processes at liquid/liquid interfaces [18–23], electrochemistry of immobilized proteins [24,25], and catalytic mechanisms [26–28], revealing that SWV is highly suited for both mechanistic and kinetic characterization of electrode reactions, besides its excellent analytical performances [29–34] and its appropriateness for bioanalytical applications [35–41].

Commonly, in analyzing an electrode reaction, the main instrumental tool is the SW frequency (f), i.e., the inverse value of the duration of two neighbouring potential pulses, which determines the critical time and the scan rate of the voltammetric experiment [1]. On the contrary, we have developed recently a novel electrokinetic methodology [42,43] by utilizing the power of the amplitude of the potential modulation (E_{sw}), i.e., the height of SW pulses, at a constant scan rate (constant frequency). Taking into account that the amplitude determines the exact potential of the current measurements one realizes that the amplitude is an intrinsic electrokinetic parameter. Hence, it has been theoretically predicted that kinetic measurements are possible by alteration of the SW amplitude only, while keeping constant the scan rate of the experiment, which seems to be rather unique approach in voltammetry in general. In this strategy, several experimental approaches are possible, ranging from the analysis of peak potential separation of the split net SW peak in the case of fast surface confined electrode processes [44], through a more general approach in which the peak potential separation between the forward and backward SW components is analyzed [42], up to the analysis of the net SW peak current as a function of the varying amplitude [43].

In the present study an attempt is made to demonstrate the applicability of the recent methodology for kinetic characterization of surface confined electrode processes, exemplified by the electrode reactions of alizarin [45], vitamin K2 [46] and vitamin B12 [47]. As well known, the surface confined electrode processes are important for understanding the electrochemistry of conducting polymers, self-assembled monolayers, hydrophobic proteins, redox active drugs and coenzymes etc. Hence, novel experimental strategies for kinetic characterization of surface confined processes [48–50] at a constant scan rate are of obvious importance, in particular when complex electrode mechanisms are considered, the voltammetric response of which depends on numerous frequency-related parameters. Finally, determination of the rate of the redox transformations of vitamins K2 and B12 has particular biochemical significance.

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2 Experimental

All experiments have been conducted by using μAutolab/GPES (General Purpose Electrochemical System-version 4.9, Eco Chemie) or multiAutolab/Nova (v. 1.10.3, Eco-Chemie) computer-controlled electrochemical systems. A hanging mercury drop electrode (HMDE) (mtm anko instruments, Poland, surface area 0.102 mm^2) (for alizarin and vitamin B12) or BASi glassy carbon electrode (GCE) (for vitamin K2) was used as a working electrode. All potentials are referred to the Ag/AgCl (3 mol/L KCl) reference electrode, while a platinum wire served as a counter electrode.

All chemicals were of analytical reagent grade (Sigma-Aldrich), while the solutions were prepared with double distilled water. Fresh stock solutions of alizarin (1,2-dihydroxyanthraquinone) and vitamin B12 (cyanocobalamin) at a concentration of 1 mmol/L were prepared daily in redistilled water. The stock solution of vitamin K2 (menaquinone) was prepared in a mixture of ethanol and water (2:3, *v*/*v*). Britton–Robinson buffers (BR), prepared from acetic, boric, and phosphoric acids (0.04 mol/L) were used as supporting electrolytes. The required pH values from 3 to 9 have been adjusted by mixing the BR acid with 0.2 mol/L NaOH solution. The buffer contained additionally 0.01 mol/L KNO_3 for the experiments with alizarin.

The general procedure for recording SW voltammograms with a negative ongoing staircase potential ramp with a scan increment of $\Delta E = 1$ mV was as follows: 10 ml of the supporting electrolyte was placed in the voltammetric cell and the solution was purged with argon for 10 min while stirring the solution. Prior to the voltammetry, the accumulation step was applied for a given accumulation time (t_{acc}) and potential (E_{acc}) by stirring the solution, followed by an equilibration for 5 s.

3 Results and Discussion

3.1 General Voltammetric Characteristics

Typical SW voltammograms of the studied compounds, all consisted of well-developed voltammetric curves, are depicted in Figure 1. All electrode reactions undergo as surface confined processes, where both components of the redox couple are immobilized on the electrode surface. Both electrode reaction of alizarin and vitamin K2 proceed as an overall two-electron-two-proton redox transformation, which is typical for anthraquinone and naphthoquinone electrochemistry in an aqueous medium, respectively [51–53]. The planar molecular structure of both anthraquinone and naphthoquinone moiety favours adsorption due to aromatic ring electron interactions with the electrode surface, thereby orienting the adsorbed molecules mainly in a planar position [54,55]. The voltammetric response of vitamin B12 (Figure 1B) is assigned to the turnover of the redox couple Co^{2+}/Co^{1+}, within the chemically stable Co-corrin complex [56]. The

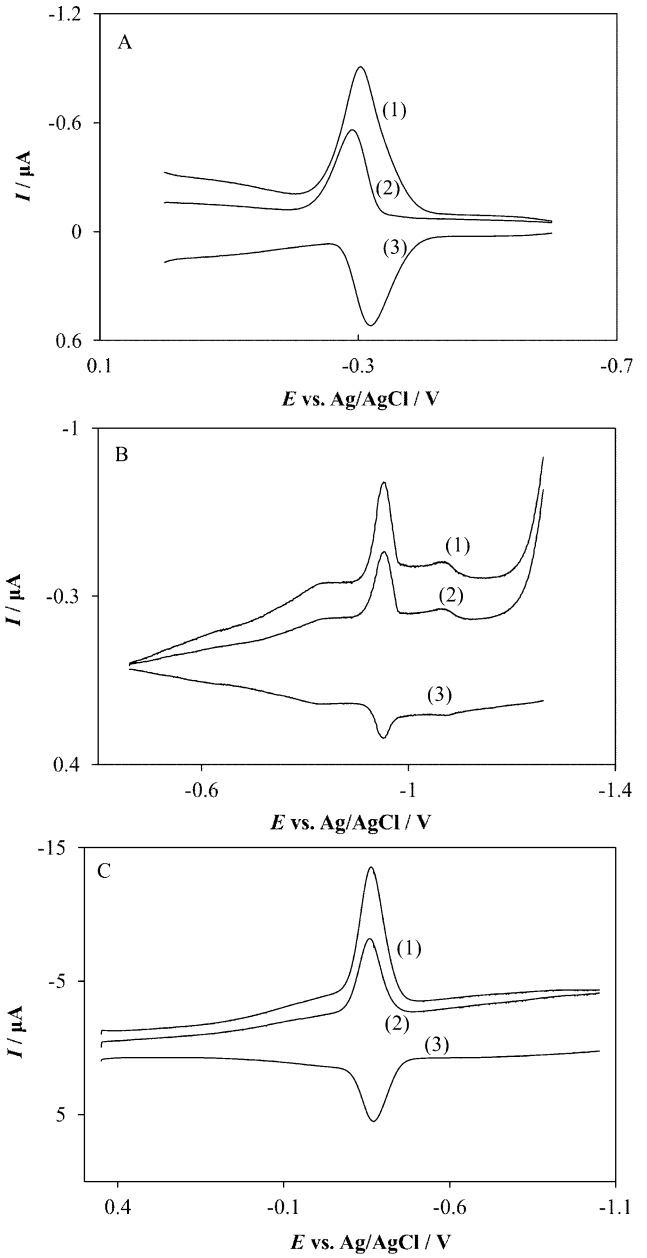

Fig. 1. Typical SW voltammograms recorded in a BR buffer following an adsorptive accumulation of: (A) 2 μmol/L alizarin at pH 9 at HMDE ($t_{acc}=30$ s, $E_{acc}=0.0$ V); (B) 5 μmol/L vitamin B12 at pH 4 at HMDE ($t_{acc}=90$ s, $E_{acc}=-0.4$ V); and (C) 2 μmol/L vitamin K2 at pH 9 at GCE ($t_{acc}=30$ s, $E_{acc}=0.5$ V). The parameters of the potential modulation are: $f=25$ Hz, $E_{sw}=50$ mV and $\Delta E=1$ mV. Numbers 1, 2, and 3 on the plots refer to the net, forward (cathodic) and backward (anodic) components of the SW voltammetric response.

first voltammetric peak (not shown in Figure 1B) at about −0.400 V is attributed to Co^{3+}/Co^{2+} redox couple, while the origin of the weak voltammetric response at potentials more negative than −1.00 V, appearing as a right shoulder of the main voltammetric peak, is not completely clear and might be related either to the presence of impurities or formation of a multilayer adsorbed film on the electrode surface. Additional signal (also not shown in

Figure 1B) at strong negative potential (ca. −1.4 V), overlapped with hydrogen evolution reaction might be related to a complex electrode mechanism of a catalytic nature.

The SW voltammetric response of all compounds consists of a forward (cathodic) and backward (anodic) components, positioned at more positive and more negative potential relative to the formal potential of the corresponding electrode reaction, respectively. The corresponding peak potentials for alizarin, vitamin K2 and vitamin B12 are: $E_{p,c} = -0.291$ V, $E_{p,a} = -0.322$ V; $E_{p,c} = -0.366$ V, $E_{p,a} = -0.377$ V; and $E_{p,c} = -0.954$ V, $E_{p,a} = -0.957$ V, respectively. The relative position of voltammetric curves observed under conditions of SWV is opposite compared to the typical cyclic voltammetric pattern of these compounds; the origin of this peculiarity that is typical for surface electrode processes was explained in our previous study [42]. For the experimental conditions corresponding to Figure 1, the forward-to-backward peak current ratio ($|I_{p,c}/I_{p,a}|$), expressed in absolute current values, is 1.08, 1.35, and 2.08 for alizarin, vitamin K2, and vitamin B12, respectively, reflecting the quasireversible nature of the electrode reactions.

The voltammetric response of all studied compounds is strongly pH dependent (Figure 2), including both the intensity and position of the response. As will be later explained, the strong dependency of the net peak current on pH can be partly related to the pH dependent kinetics of the overall electrode reaction. For alizarin and vitamin K2, the net peak potential variation with pH (Figure 2B) is linear with a slope of −58 and −50 mV, respectively, being close to the ideal Nernstian behaviour for $2e^-/2H^+$ electrode transformation [57]. The pH variation of the vitamin B12 response is even more complex being related to the acid-base properties of the Co-corrin complex.

Figures 3A and 3B summarize the variation of the response with the accumulation time and concentration of the compound, respectively. For alizarin and vitamin B12, the dependency of the net peak current (ΔI_p) on the accumulation time follows the shape of a Langmuir isotherm, revealing that adsorption on the smooth mercury electrode surface proceeds without significant interactions between adsorbed molecules [58]. This is also supported by the constant net peak potential over the accumulation time from 0 to 120 s (E_p(alizarin) = −0.577 ± 0.006 V; E_p(vitamin B12) = −0.886 ± 0.004 V). The same conclu-

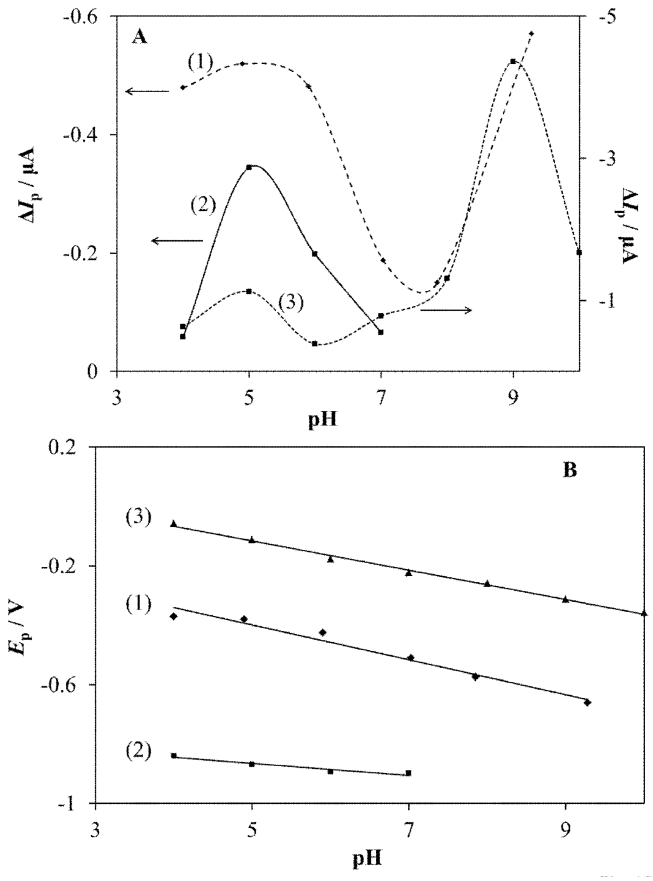

Fig. 2. The dependence of (A) the net peak current (ΔI_p) and (B) the net peak potential (E_p) on pH of alizarin (*1*), vitamin B12 (*2*), and vitamin K2 (*3*). The experimental conditions are the same as for Fig. 1.

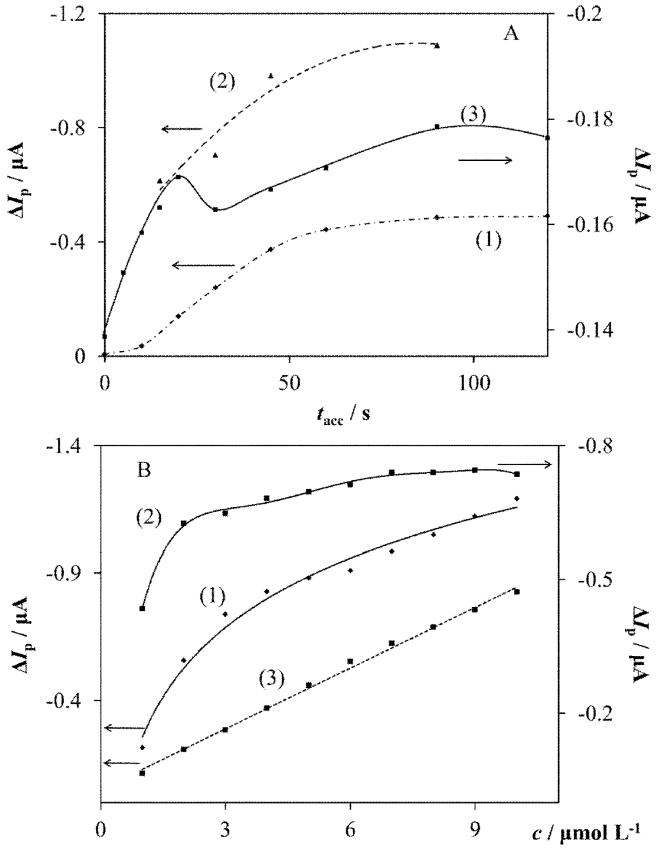

Fig. 3. (A) The dependence of the net peak current on the accumulation time of: (1) 2 μmol/L alizarin (pH 7.8); (2) 1 μmol/L vitamin B12 (pH 5); and (3) 2 μmol/L vitamin K2 (pH 6). All other conditions are the same as for Fig. 1. (B) The dependence of the net peak current on the concentration of: (1) alizarin (pH 9.3, $t_{acc} = 30$ s, $E_{acc} = 0.0$ V); (2) vitamin B12 (pH 5, $t_{acc} = 90$ s, $E_{acc} = -0.4$ V), and (3) vitamin K2 (pH 6, $t_{acc} = 30$ s, $E_{acc} = 0.5$ V). The parameters of the potential modulation are the same as for Fig. 1, except for vitamin B12 ($f = 50$ Hz and $E_{sw} = 75$ mV).

sion stems from the dependency of the net peak current versus the concentration of the compound (Figure 3B, curves 1 and 2). The latter also obeys the shape of a Langmuir-type isotherm, implying that the contribution of the electrode reaction of dissolved species to the voltammetric response is insignificant.

As can be inferred from the data referring to vitamin K2 (curve 3 in Figures 3A and B), the electrode reaction and the adsorption mechanism are more complex. The analysis of the net peak current on the accumulation time reveals interactions between adsorbed species for accumulation time longer than 30 s at a concentration of 2 μmol/L (curves 3 in Figure 3A). Nevertheless, such interactions are not strong, as the peak potential is stable over the whole accumulation time interval ($E_p = -0.192 \pm 0.004$ V). However, the absence of the saturation plateau of the dependence ΔI_p vs. c(vitamin K2) (curve 3 in Figure 3B) implies that the contribution of the electrode reaction from solution resident species cannot be completely excluded. The latter is also confirmed by an independent analysis with cyclic voltammetry, showing that the cathodic peak current is a linear function of the square root of the scan rate, for concentrations of vitamin K2 higher than 2 μmol/L (data not shown). For all these reasons, the electrode reaction of vitamin K2 can be approximated as a simple surface confined electrode process only for accumulation time and concentration approximately lower than 30 s and 2 μmol/L, respectively.

3.2 Amplitude-Based Kinetic Measurements

As previously mentioned, we have recently proposed several strategies for kinetic analysis of electrode processes at a constant scan rate, i.e., at a constant frequency of the potential modulation, by virtue of the amplitude variation only [42]. Here, it is worth recalling that the theory in [42] was developed on the basis of phenomenological Butler–Volmer kinetic model. Recently, Compton et al. analyzed surface electrode mechanism by means of asymmetric Marcus-Hush model, demonstrating that the latter can provide kinetic parameters with more clear physical meaning over the phenomenological Butler–Volmer model [59]. In the current methodology the simplest approach is to measure the peak potential separation between the forward and backward components of the SW voltammogram for different SW amplitudes. Simulations of the voltammetric response conducted for a surface confined electrode reaction predict a linear shift of both voltammetric components with the amplitude [42], which is in agreement with previous studies [44]. The degree of the potential separation depends on the electrode kinetic parameter $\omega = k_{sur}/f$, thus permitting estimation of the standard rate constant k_{sur} (s^{-1}), for a given frequency of the measurements. An important advantage of the proposed methodology is that the potential separation hardly depends on the electron transfer coefficient, which enables independent estimation of the standard rate constant. However, we have to emphasize that the number of electrons (n) involved in the electrode reactions has to be known, as the overall effect of the amplitude depends on the product nE_{sw} indeed [42–44].

In the experimental analysis, one commonly varies the amplitude over the interval from 20 and 250 mV. At smaller values, the SW potential modulation tends to be transformed into a staircase ramp only, whereas higher amplitudes compromise the ability of the technique to discriminate against the charging currents. Figure 4 depicts a typical example of such analysis conducted with alizarin, presenting the variation of the peak potential separation (ΔE_p) with the amplitude, for a given frequency of 25, 50, 100, and 150 Hz. The behaviour of the experimental system is in excellent agreement with theoretical predictions for a simple surface confined electrode reaction [42]. For estimation of the surface standard rate constant, the following working curve has been exploited: $\log|intercept\ (\mathrm{mV})| = -0.7162\ \log(\omega) - 1.3662$, where ω is the electrode kinetic parameter and the *intercept* refers to the regression line of the dependence ΔE_p vs. E_{sw} given in Figure 4. The working curve has been derived with the aid of simulations for a two-electron surface electrode reaction [42]. The estimated values for the standard rate constant are 36, 36, 37, and 40 s^{-1}, for the measurements at 25, 50, 100, and 150 Hz, respectively. Keeping in mind that the electrode mechanism of alizarin is significantly more complex than a simple two-electron charge transfer reaction, the estimated rate constants do not refer to the kinetics of the pure charge transfer step, rather than they reflect the apparent kinetics of the overall electrochemical reaction including protolytic reactions that are generally considered to be at equilibrium in a buffered medium [60]. For these reasons, the estimated rate constants in the current study refer to the apparent rate constant, k_{sur}', in agreement with the terminology used by Laviron [61–

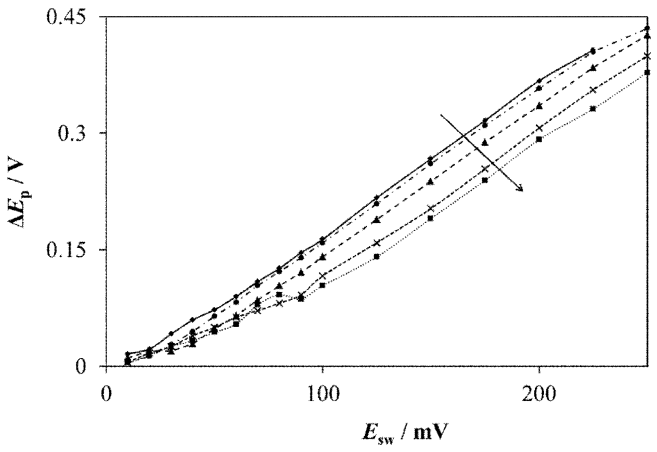

Fig. 4. The dependence of the peak potential difference of the forward and backward SW components (ΔE_p) as a function of the SW amplitude for 2 μmol/L solution of alizarin at pH 8.8. The frequency of the measurements increases in the direction of the arrow from 12, 25, 50, 100 to 150 Hz. All other conditions are the same as for Fig. 1.

66]. This comment is equally valid for all three studied compounds.

Let us note that besides conventional SW voltammograms, the same kinetic analysis can be conducted by using *potential-corrected SW voltammograms* [42]. The latter are constructed by plotting measured currents versus the potential of the SW pulses, i.e., the exact potentials of the current measurement, instead the potentials of the staircase ramp [42]. In corrected voltammograms the potential separation reflects the inherent influence of the electrode kinetics, avoiding the artificial potential separation of the SW components due to the conventional presentation of the voltammetric data. The kinetic analysis based on corrected SW voltammograms is exemplified by the experiments with vitamin B12. The variation of the peak potential separation of corrected voltammograms ($\Delta E_p'$) with the amplitude is summarized in Figure 5, for three series of measurements at the frequency of 12, 25, and 50 Hz. The estimation of the apparent standard rate constant is done with the aid of the following working curve: $\Delta E_p'/(V) = -0.0973 \log(\omega) + 0.0518$, which is valid for one-electron surface electrode reaction. Here, $\Delta E_p'$ is the potential separation measured for the amplitude of 100 mV, and the estimated values are $k_{sur}' = 5.5$, 7.3, and 12 s^{-1}, derived for three sets of measurements at 12, 25, and 50 Hz, respectively. Taking the potential separation measured at $E_{sw} = 200$ mV, the estimation can be done based on the working curve: $\Delta E_p'/(V) = -0.1123 \log(\omega) + 0.0437$, which yields the apparent rate constant of 8.1, 14, and 20 s^{-1}, respectively.

Besides the peak potential separation, the kinetic analysis can be conducted by analyzing the net peak current (ΔI_p) as a function of the amplitude, based on the recently introduced *„amplitude-based quasireversible maximum"* [43]. The latter property is associated with a variety of relatively slow quasireversible electrode mechanisms, both of surface confined and dissolved redox couple, being manifested as a parabolic dependency of the ratio $\Delta I_p/E_{sw}$ versus the logarithm of the amplitude. As explained in [43], the position of the maximum depends on the electrode kinetic parameter ω, shifting toward higher amplitudes by decreasing ω, hence enabling estimation of the standard rate constant.

Figure 6 depicts well-developed amplitude-based quasireversible maxima for vitamin K2, measured for three values of the frequency. As the position of the maximum is determined by the electrode kinetic parameter ω, the quasireversible maximum of vitamin K2 consistently shifts for different frequencies, being in accord with the theoretical predictions [43]. As derived from the simulations, the critical amplitude associated with the position of the maximum $(E_{sw})_{max}$ obeys the following relationship: $(nE_{sw})_{max}/mV = -148.08 \log(\omega) + 0.8$. The critical amplitudes are 100, 125 and 165 mV for the measurements at 12, 25, and 50 Hz, respectively. Hence, the estimated values of the apparent standard rate constants for vitamin K2, assuming $n = 2$, are 0.54, 0.52, and 0.30 s^{-1}, respectively.

Table 1 summarizes the average values of the apparent standard rate constants estimated on the basis of the potential separation of conventional and corrected SW voltammograms for different pH values for the three studied compounds. For vitamin K2, the values estimated by the peak potential separation are in good agreement with those estimated by the amplitude-based quasireversible maximum, mentioned above. Let us note that the latter method works for relatively slow electrode processes characterized with an electrode kinetic parameter within the interval $0.01 \le \omega \le 0.5$, thus it was not possible to be applied in the case of alizarin and vitamin B12, as the maximum was not emerging even for the lowest frequency of 8 Hz.

Finally, taking the rate constants for alizarin from Table 1, a series of simulations has been carried out to es-

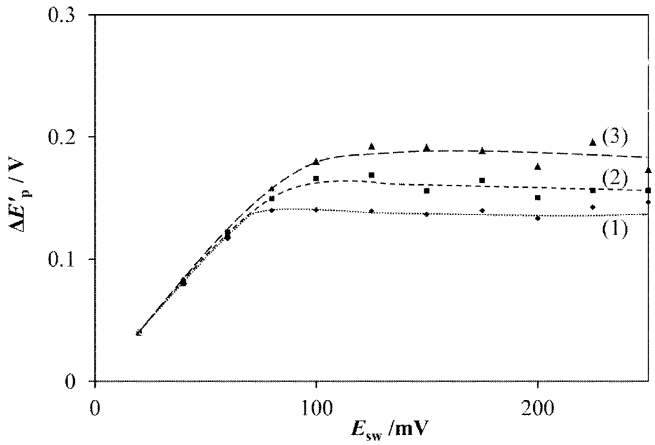

Fig. 5. The dependence of the peak potential difference of the forward and backward SW components of the potential-corrected voltammograms ($\Delta E_p'$) [42] as a function of the SW amplitude for 1 μmol/L solution of vitamin B12 at pH 5. The frequency of the measurements is: $f = 12$ (1); 25 (2) and 50 Hz (3). All other conditions are the same as for Fig. 1.

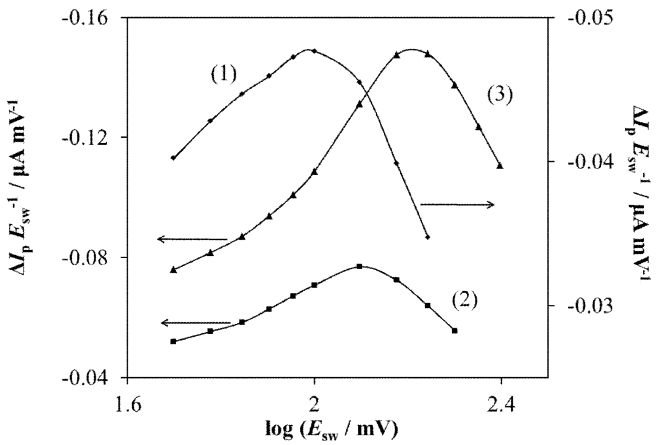

Fig. 6. Amplitude-based quasireversible maximum [43] measured for 5 μmol/L solution of vitamin K2 at pH 6 for the frequency of $f = 12$ (*1*); 25 (*2*); and 50 Hz (*3*). All other conditions are the same as for Fig. 1.

Table 1. An average value for the apparent standard rate constant of studied compounds determined by measuring the potential separation of conventional and corrected SW voltammograms as function of the SW amplitude in a medium with different pH values and at different frequencies (an average ± confidence interval of t-Student test, assuming $\alpha = 0.2$).

Compound	Supporting electrolyte, pH	Estimated apparent standard rate constant k_{sur}' (s^{-1})
Alizarin	3	12.6 ± 1.3
	4	14.4 ± 1.1
	5	10.1 ± 0.9
	6	13.3 ± 1.8
	6.8	7.0 ± 1.3
	7.8	50.5 ± 6.7
	8	50.7 ± 5.3
	8.8	39.0 ± 1.8
	9	42.9 ± 3.5
Vitamin B12	4	14.0 ± 2.1
	5	13.4 ± 1.5
	6	12.0 ± 2.2
Vitamin K2	6	0.47 ± 0.13
	7	0.19 ± 0.06
	9	0.43 ± 0.06

timate the variation of the calculated response over the whole pH interval. Figure 7 compares the variation of the theoretical and experimental net peak current with pH of the medium. The experimental and theoretical data are in very good agreement supporting the correctness of the estimated kinetic data. For consistent comparison of the calculated dimensionless net peak currents with the experimental ones, additional normalization was carried with respect to the net peak current corresponding to the lowest pH value. The physical meaning of the data in Figure 7 can be understood as a comparison of a series of

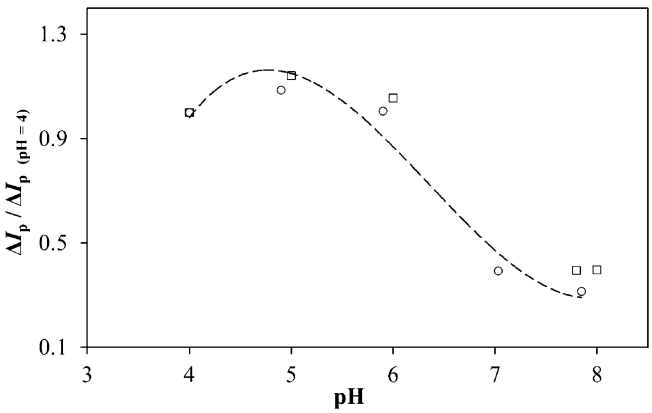

Fig. 7. Comparison of theoretical (□) and experimental (○) net peak currents for alizarin as a function of pH. Simulations have been performed for a simple surface confined electrode reactions assuming electron transfer coefficient $\alpha = 0.5$, $n = 2$, and apparent standard rate constant values listed in Table 1. For consistent comparison, both theoretical and experimental net peak currents (ΔI_p) are normalized with respect to the one corresponding to the lowest pH value ($\Delta I_{p(pH\,4)}$).

surface electrode reactions characterized by different standard rate constants. The latter corresponds to the analysis of the theoretical response by varying the electrode kinetic parameter ω. Obviously, the response decreases by increasing the pH from 3 to 8, although the rate constant increase from 13 to 51 s^{-1}, together with the corresponding enhancement of the electrode kinetic parameter ω from 0.5 to 2 ($\omega = k_{sur}'/f$, $f = 25$ Hz). This is a consequence of the well-known conventional quasireversible maximum of surface electrode processes [1], and non-linear variation of the net peak current with the electrode kinetic parameter.

4. Conclusions

The foregoing simplified analysis of the SW voltammetric response of alizarin, vitamin B12 and vitamin K2 confirms the applicability and reliability of the recently proposed methodology for kinetic characterisation of electrode reactions at a constant scan rate of the voltammetric experiment. Though the kinetic estimation can be conducted by direct fitting between the theory and experiment, it has been demonstrated that reliable data can be derived based on the working curves provided in the previous study [42], thus simulations are not necessary to be carried out in parallel to the experiment. The most recommendable approach would be to measure the peak potential separation between the forward and backward components of the SW response as a function of the amplitude, for a given frequency. If the electrode reaction is very fast at given frequency, one should expect strong potential separation and consequently splitting of the net SW peak. If the electrode reaction is relatively slow, the method of amplitude-base quasireversible maximum can be additionally applied for independent determination of the rate constant. Finally, the application of the current methodology for estimation of kinetic parameters of electrode reactions under conditions of Marcus-Hush kinetic model remains as a challenge for the future work.

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