Kinetika površinske redoks reakcije 2-hidroksi-5-[(4-sulfofenil)azo]benzojeve kiseline

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Kinetics of the Surface Redox Reaction
of 2-Hydroxy-5-[(4-sulfophenyl)azo]benzoic Acid

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The standard surface redox reaction rate constant of the quasireversible electroreduction of 2-hydroxy-5-[(4-sulfophenyl)azo]benzoic acid adsorbed on the static mercury drop electrode has been determined as $\bar{k}_s = 24$ ($\pm$ 6) s^{-1} using the method of split square-wave voltamograms.

INTRODUCTION

In square-wave voltammetry of fast and reversible electrode reactions of strongly adsorbed redox couples, the net response may split into two peaks under suitable experimental conditions.[1–5] This phenomenon was observed in square-wave voltammetry of adsorbed methylene blue,[1] cytochrome-c,[2] azobenzene,[3] alizarine-red S[4] and cinnoline.[5] Splitting is a consequence of the separation of the maximum of the reduction component of the net response from the minimum of the oxidation component. The difference between the potentials of two peaks of the split net response is a linear function of the square-wave amplitude:[4] $\Delta E_p = (2 \cdot E_{sw} - (50 - 5 \cdot \kappa))$ mV, where κ is the dimensionless ratio of the standard redox reaction rate constant and the square-wave frequency ($\kappa = k_s / f$). This equation was calculated for $n = 1$, $\alpha = 0.5$ and d$E =$ 5 mV, where n is the number of electrons in the electrode reaction, α is the transfer coefficient and dE is the step increment of the staircase wave-form to which the square-

wave signal is superimposed, and it applies to $\kappa > 3$, *i.e.*, for fast and reversible surface redox reactions. Our recent calculations have shown that for quasireversible surface redox reactions the intercept of the linear relationship between ΔE_p and E_{sw} depends on both n and α, so that the general form of this relationship is: $\Delta E_p = 2E_{sw} - f(\kappa, n, \alpha)$.

In this short communication, the function $f(\kappa, n, \alpha)$ is calculated theoretically for $\alpha = 0.5$ and used for determination of the standard rate constant of the surface redox reaction of 2-hydroxy-5-[(4-sulfophenyl)azo]benzoic acid (SPAB, see Scheme 1). This compound has been designed as a precursor of 5-aminosalicylic acid (5-ASA),
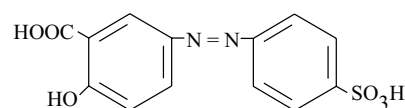
Scheme 1. Structural formula of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid (SPAB).

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which was identified as an active component in the therapy of inflammatory bowel diseases.[6] The electrochemical reduction of SPAB on carbon electrodes in aqueous solution is an ECE process, in which the first step is the electroreduction of azo bond to the hydrazo intermediate.[7] In acidic media, the hydrazo form is chemically cleaved into sulfanilic acid and the oxidized, quinone-imine form of 5-ASA. On the electrode surface, the latter is immediately reduced to 5-ASA. In neutral and weakly basic media, the intermediate is stable within the time scale of cyclic voltammetry. On mercury electrodes, both azo and hydrazo forms of SPAB are strongly adsorbed.[8,9] In square-wave voltammetry of SPAB adsorbed on a mercury electrode, at pH = 4, the surface redox reaction appears quasireversible, while the influence of the following chemical reaction is negligible.[8]

EXPERIMENTAL

2-Hydroxy-5-[(4-sulfophenyl)azo]benzoic acid (SPAB) was synthesized according to the literature procedure.[6] SPAB identification was performed by IR, NMR and MS spectroscopy, and purity was determined by HPLC. All other chemicals were of analytical grade and were obtained from Merck. Water was demineralized by ionic exchangers Millipore Milli Q until its specific resistance was 18.2 MΩ cm. 0.4 M Britton-Robinson buffer, pH = 4, was used as supporting electrolyte. Standard solution of SPAB was prepared daily by diluting the stock solution (5×10^{-3} M) with the supporting electrolyte.

Measurements were performed with a multimode polarograph EG&G Model 273A in conjunction with PAR 303 A Static Mercury Drop Electrode (both Princeton Applied Research). The area of the working mercury drop electrode was 0.015 cm^2. The Pt wire served as an auxiliary electrode, and Ag/AgCl/KCl(sat.) was the reference electrode.

Solutions were degassed with high-purity nitrogen for 10 min prior to measurements. A nitrogen blanket was maintained thereafter. All measurements were carried out at room temperature.

The Model

Electrode reaction of two compounds, both strongly and totally irreversibly adsorbed to the working electrode surface, is investigated:

$$(Ox)_{ads} + ne^- \leftrightarrows (Red)_{ads} \tag{1}$$

It is assumed that there are no interactions between the adsorbed molecules in the case of submonolayer surface coverage, and that the additional adsorption and the redox reaction of the dissolved reactant can be neglected. Under these conditions, reaction (1) is described by the differential equations:[4]

$$d\Gamma_{ox} / dt = -k_s \exp(-\alpha\varphi)\,[\Gamma_{ox} - \Gamma_{red}\exp(\varphi)] \tag{2}$$

$$d\Gamma_{ox} / dt = -I / nFS \tag{3}$$

$$d\Gamma_{ox} / dt = -d\Gamma_{red} / dt \tag{4}$$

with the following initial and boundary conditions:

$$t = 0: \qquad \Gamma_{ox} = \Gamma_{ox}{}^*, \qquad \Gamma_{red} = 0 \tag{5}$$

$$t > 0: \qquad \Gamma_{ox} + \Gamma_{red} = \Gamma_{ox}{}^* \tag{6}$$

where $\varphi = nF(E - E°)/RT$ is dimensionless potential, Γ_{ox} and Γ_{red} are surface concentrations of Ox and Red species, respectively, $\Gamma_{ox}{}^*$ is the initial surface concentration of the reactant Ox, k_s is the standard redox reaction rate constant, α is the cathodic transfer coefficient, I/S is the current density, E is the working electrode potential, $E°$ is the standard electrode potential, S is the electrode surface area, while n, F, R, T and t have their usual significance.

For numerical calculation, Eqs. (2) – (4) can be transformed into the following system of recursive formulae:[10]

$$\Phi_1 = \frac{\kappa \cdot \exp(-\alpha\varphi_1)}{1 + \kappa \cdot \exp(-\alpha\varphi_1)[1 + \exp(\varphi_1)]/50} \tag{7}$$

$$\Phi_m = \frac{\kappa \cdot \exp(-\alpha\varphi_m) \cdot \left\{1 - [1 + \exp(\varphi_m)]\sum_{j=1}^{m-1}\Phi_j/50\right\}}{1 + \kappa \cdot \exp(-\alpha\varphi_m)[1 + \exp(\varphi_m)]/50} \tag{8}$$

where $\Phi = I/nFS\Gamma_{ox}{}^* f$ is the dimensionless current, $\kappa = k_s/f$ is the dimensionless kinetic parameter, $d = (50 \cdot f)^{-1}$ is the time increment and f is square-wave frequency.

The square-wave signal is a train of alternating pulses, which is superimposed to a staircase ramp (see Scheme 2). Each square-wave period occurs during one staircase period τ. Hence, the frequency of the excitation signal is $f = \tau^{-1}$, and the pulse duration is $t_p = \tau/2$. The square-wave amplitude, E_{sw}, is one-half of the peak-to-peak amplitude, and the potential increment dE is the step height of the staircase waveform. Relative to the scan direction, dE, the forward and backward pulses can be distinguished. The currents are
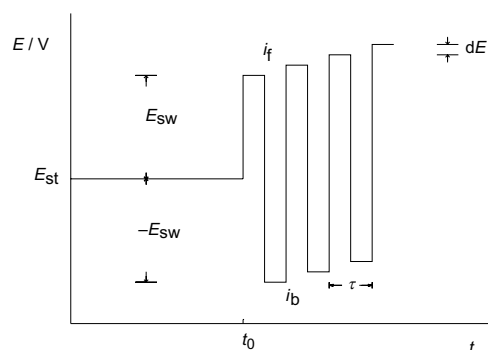
Scheme 2. The square-wave excitation signal. E_{st} is the starting potential, t_0 is delay time, E_{sw} is SW amplitude, $E_{sw} - (-E_{sw})$ is the peak-to-peak amplitude, dE is the scan increment, τ is the SW period and symbols i_f and i_b denote the points at the end of pulses where the forward and backward current components are sampled, respectively.

measured at the end of each pulse and the difference between the currents measured on two successive pulses is recorded as a net response. It is plotted as a function of the corresponding potential of the staircase ramp. The net response consists of two components corresponding to the forward and backward series of pulses, respectively.

RESULTS AND DISCUSSION

Theoretical Results

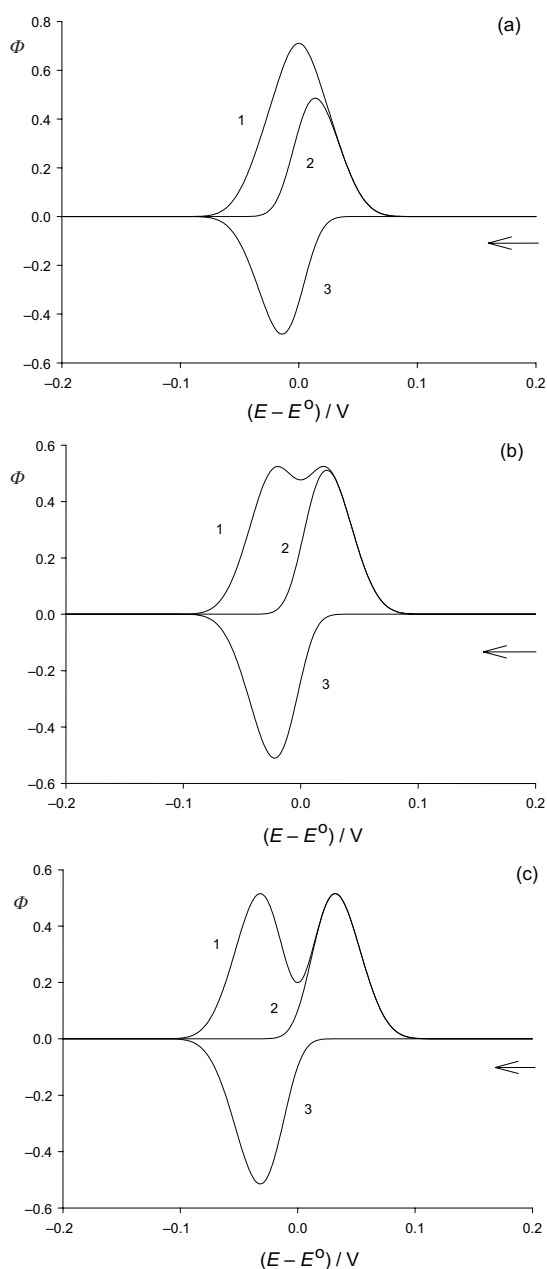Figure 1 shows the theoretical dependence of square-wave voltamograms of the quasireversible surface redox

Figure 1. Theoretical square-wave voltamograms of the quasireversible surface redox reaction. The net response (1) and its reduction (2) and oxidation (3) components; $\kappa = 1.4$, $n = 2$, $\alpha = 0.5$, $dE = -1$ mV and $E_{sw} = 30$ (a), 40 (b) and 50 mV (c).
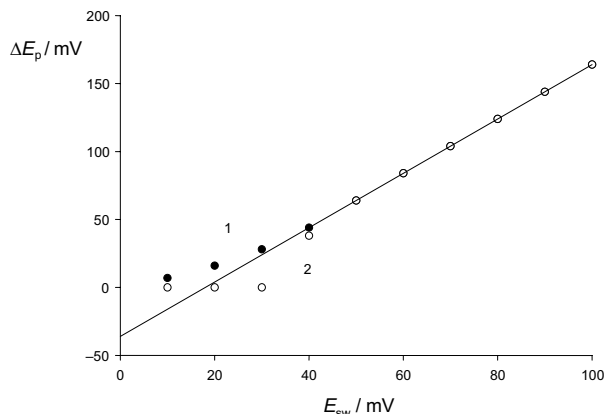
Figure 2. Theoretical dependence of the difference between the potentials of the extremes of the components (1, full points) and the difference between the potentials of two peaks of the split net response (2, open circles) on the square-wave amplitude. Straight line: $\Delta E_p = (2 E_{sw} - 36)$ mV. All parameters are as in Figure 1.

reaction on square-wave amplitude. If $E_{sw} = 30$ mV, the difference between the potentials of the maximum of the reduction component and the minimum of the oxidation component is 28 mV, but the net response is a single peak at 0 V $vs.$ E^o. If E_{sw} is increased to 40 mV, this difference is 44 mV, and the net response appears split into two peaks separated by 38 mV. At $E_{sw} = 50$ mV, separation between the two peaks of the net response is 64 mV, which is equal to the difference between the potentials of the maximum and the minimum of the components.

Figure 2 shows that for higher pulse amplitudes, the separation of peaks of the net response satisfies the linear relationship: $\Delta E_p = (2 E_{sw} - 36)$ mV. However, if $E_{sw} < 40$ mV, the difference between the potentials of the extremes of the components tends to zero, while the separation of peaks of the net response is abruptly diminished to zero in the narrow range $30 < E_{sw} < 40$ mV. Kinetic parameters of the surface redox reaction can be determined by fitting the current-potential relationship of both components of the square-wave response,[2,3] but a simpler way is to calculate the theoretical relationship between the intercept $f(\kappa, n, \alpha)$ and the dimensionless kinetic parameter κ, for the known values of n and α.

The theoretical influence of the transfer coefficient α on square-wave voltamograms of reaction (1), for $n = 2$, is shown in Figure 3. The peak currents of the split net response are equal if $\alpha = 0.5$, but if $\alpha = 0.3$ and $\alpha = 0.7$, the ratios between the reduction and the oxidation peak currents are 1.42 and 0.70, respectively, as predicted previously.[4] However, if $\alpha = 0.5$, separation of the peaks of the net response is 104 mV, corresponding to the intercept –36 mV, but if $\alpha = 0.3$ and $\alpha = 0.7$, the separation is 100 mV, which corresponds to the intercept –40 mV. Thus, in this work, we calculated the theoretical relationships between the intercept $f(\kappa, n, \alpha)$ and the parameter κ for $\alpha = 0.5$, $dE = 1$ mV and $n = 2$ and $n = 1$. For $n = 2$, $dE = 1$ mV, and $\alpha = 0.5$, the results are presented in

Figure 4. Square-wave voltamograms of 5×10^{-6} M SPAB in Britton-Robinson buffer, pH = 4. $E_{sw} = 50$ mV, d$E = -2$ mV and $f = 20$ (a) and 100 Hz (b).
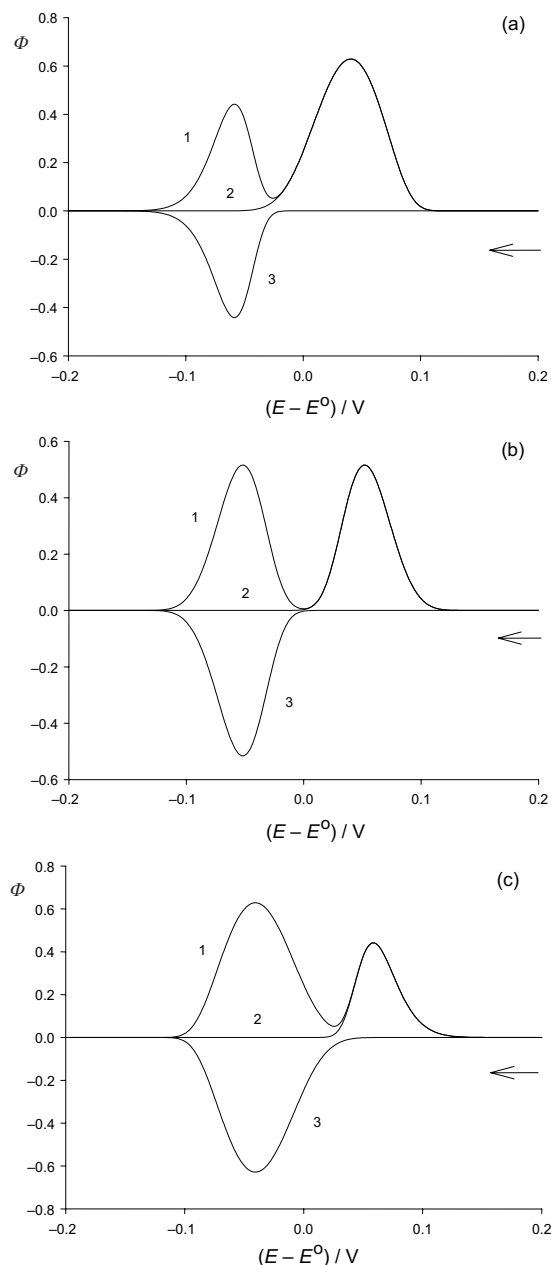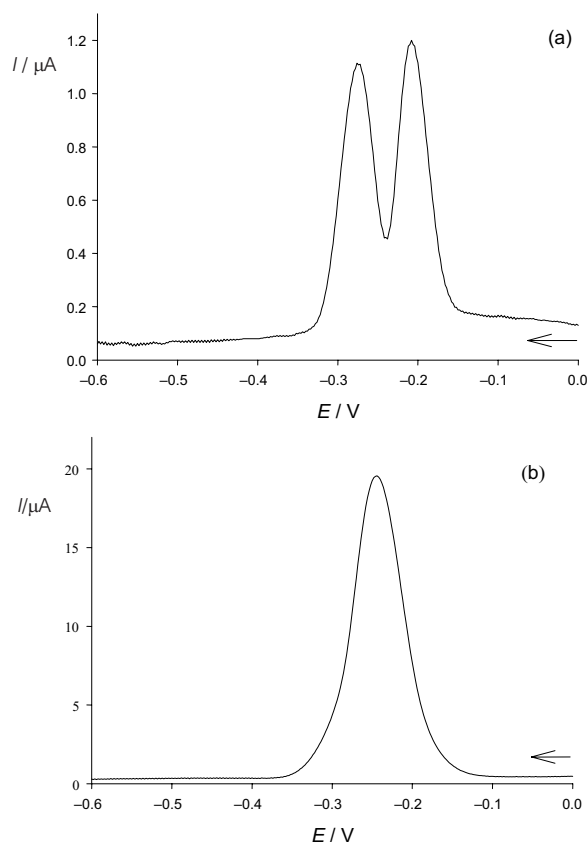
Figure 3. Dependence of the theoretical net square-wave voltamogram (1) and its reduction (2) and oxidation (3) components on the transfer coefficient; $\kappa = 1.4$, $n = 2$, $E_{sw} = 70$ mV, d$E = -1$ mV and $\alpha = 0.3$ (a), 0.5 (b) and 0.7 (c).

square-wave frequency is equal or higher than 40 Hz, but smaller than 200 Hz, the response is a single peak appearing between –0.240 V and –0.250 V *vs*. Ag/AgCl/KCl (sat.). At frequencies lower than 40 Hz, the response is split into two peaks, but the potential of the minimum between the peaks is equal to the potential of the maximum of the response corresponding to $f = 50$ Hz. The peak currents of the split response are almost equal, which indicates that the transfer coefficient is $\alpha = 0.5$.[4,8] The

Table I. If $n = 1$ and $\alpha = 0.5$, the intercept is exactly two times bigger than the intercept corresponding to $n = 2$, regardless of whether dE is 1 mV or 2 mV:

$$f(\kappa, 2, 0.5) = f(\kappa, 1, 0.5) / 2 \qquad (9)$$

Experimental Results

Figure 4 shows the square-wave voltamograms of the surface redox reaction of SPAB. They correspond to reduction of the azo bond to the hydrazo bond and involve two electrons and two protons.[8] If $E_{sw} = 50$ mV and the

TABLE I.

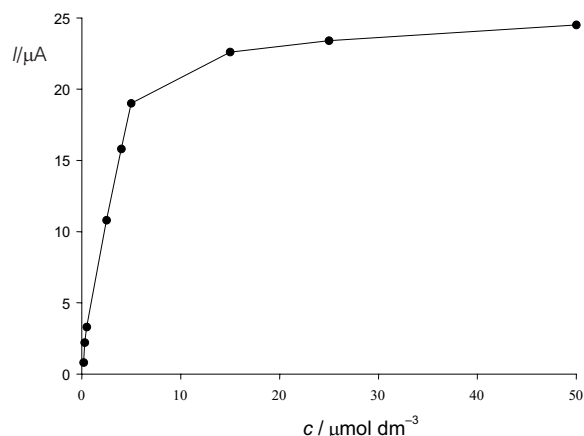| κ	$f(\kappa, 2, 0.5)$	κ	$f(\kappa, 2, 0.5)$	κ	$f(\kappa, 2, 0.5)$
0.1	156	1.1	44	2.5	22
0.2	120	1.2	42	3	18
0.3	100	1.3	38	4	14
0.4	86	1.4	36	5	12
0.5	76	1.5	34	6	10
0.6	68	1.6	32	7	10
0.7	62	1.7	30	8	8
0.8	56	1.8	30	9	8
0.9	52	1.9	28	10	8
1	48	2	26		

Figure 5. Dependence of square-wave voltammetric peak currents of SPAB on its concentration in Britton-Robinson buffer, pH = 4. E_{st} = 0 V, t_{acc} = 0 s, E_{sw} = 50 mV, dE = –2 mV and f = 100 Hz.

TABLE II.

f / Hz	$\overline{f(\kappa, 2, 0.5)}$	κ	k_s / s^{-1}
20	34.0	1.5	30.0
30	54.6	0.835	25.05
40	73.5	0.531	21.24
50	92.3	0.355	17.75
100	110.0	0.25	25.0

bols). The straight lines in Figure 6 correspond to the average intercepts ($\Delta E_p = 2\,E_{sw} - \overline{f(\kappa, 2, 0.5)}$), which were calculated using the equation: $\overline{f(\kappa, 2, 0.5)} = \sum\limits_{j=1}^{m}(2\,E_{sw} - \Delta E_p)_j / m$, where m is the number of points in the ΔE_p vs. E_{sw} graphs. Average intercepts, $\overline{f(\kappa, 2, 0.5)}$, are listed in Table II, together with the corresponding values of the dimensionless kinetic parameters κ (see Table I) and the standard surface redox reaction rate constants, which were calculated using the equation: $k_s = \kappa \cdot f$. The average value of the rate constants is: $\overline{k_s} = (24 \pm 6)$ s^{-1}. This result is in agreement with the value $k_s = (26 \pm 2)$ s^{-1}, which was calculated by the method of the quasireversible maximum in square-wave voltammetry.[8]
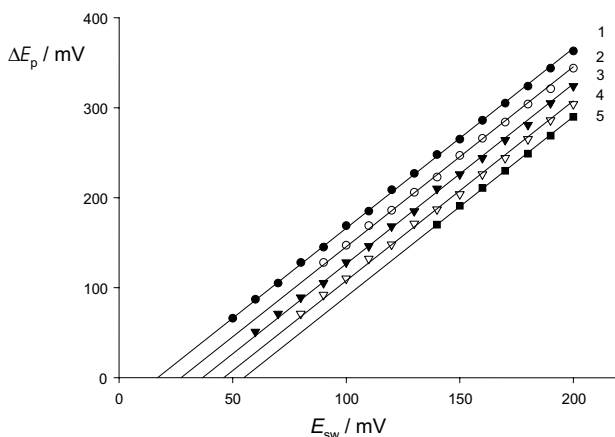

Figure 6. Dependence of separation of the peaks of the split square-wave voltamograms of SPAB on the square-wave amplitude (symbols); f = 20 (1), 30 (2), 40 (3), 50 (4) and 100 Hz (5). Straight lines: $\Delta E_p = 2\,E_{sw} - \overline{f(\kappa, 2, 0.5)}$.

dependence of SWV peak currents on the concentration of SPAB is shown in Figure 5. Saturation of the electrode surface at concentrations higher than 1×10^{-5} mol dm^{-3} can be observed. A similar sigmoidal relationship exists between the peak current and the accumulation time.

In the frequency range $20 \le f \le 100$ Hz, the square-wave voltammetric response of SPAB splits into two peaks if the square-wave amplitude is higher than 40 mV, depending on the frequency. The linear relationship between separations of the two peaks of the net responses of SPAB and square-wave amplitudes are shown in Figure 6 (sym-

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SAŽETAK

Kinetika površinske redoks reakcije 2-hidroksi-5-[(4-sulfofenil)azo]benzojeve kiseline

Šebojka Komorsky-Lovrić i Biljana Nigović

Rabeći metodu rascijepljenih pravokutnovalnih voltamograma, određena je standardna konstanta brzine površinske redoks reakcije ($\bar{k}_s$ = 24 (± 6) s^{-1}) kvazireverzibilne elektroredukcije 2-hidroksi-5-[(4-sulfofenil)azo]benzojeve kiseline adsorbirane na površini statične živine kapi.