Original Scientific Paper

Pulse Polarography of Surface EC Mechanism

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A theoretical model for pulse polarographic response of surface redox reaction followed by totally irreversible, first-order chemical reaction is developed. Adsorption of both the reactant and the product and reversible redox reaction are assumed. The model is tested on benzidine rearrangement of electrochemically produced hydrazobenzene in 3 M $HClO_4$ in 20% v/v aqueous acetonitrile. The rate constant $\log(k^*/s^{-1}) = 2.2 \pm 0.2$, referred to $E^* = -0.006$ V $vs.$ Ag/AgCl/4 M NaCl, is obtained.
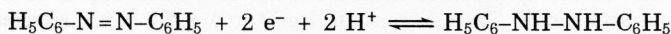
INTRODUCTION

In normal pulse polarography, a dropping mercury electrode is charged to a short pulse of potential which is superimposed on a certain constant potential E_i.[1,2] The pulse is applied near the end of drop life-time and a current response is sampled at the end of pulse. From drop to drop, the pulse amplitude increases linearly. If at the initial potential E_i no redox reaction occurs, the NPP i–E curve resembles a dc polarographic wave. The NPP is highly discriminative against a capacitive current which, as a rule, decreases during the pulse faster than faradaic current and contributes minimally to the total current sampled at the end of the pulse.[1]

If a reactant of a certain redox reaction adsorbs at the surface of the working electrode, the pulse polarogram may exhibit a maximum and a heavily depressed limiting current.[3-14] Such anomalous pulse polarograms consist of adsorptive and diffusive current components which are well separated.[3] The maximum originates only from the redox reaction of initially adsorbed reactant and its peak potential is equal to the half-

wave potential of the postwave in dc polarography.[10] This adsorptive component is added to the limiting current which itself is the consequence of diffusion of redox species.[6-8] Because of the current sampling procedure, the maximum cannot be recorded if the Nernst equilibrium at the electrode surface is established almost immediately after the beginning of the pulse.[4,14] If, for instance, both the reactant and the product of a certain reversible redox reaction are strongly adsorbed at electrode surface, the equilibrium between them is established simultaneously with the pulse application and the adsorptive current is a spike which does not last until the end of the pulse and does not contribute to the total sampled current.[5,11] Maximum appears either if the product of reversible redox reaction is not surface active and continuously disturbs the equilibrium by diffusing off the electrode surface,[9] or if the product adsorbs, but the reaction is not reversible.[10] Redox reactions may appear irreversible either because of slow charge transfers, or because of fast and irreversible homogeneous chemical reactions, such as protonation or rearrangements, which follow the charge transfer and cause electroinactivation of the final product (an EC mechanism).[15] In both cases, the reaction rate constants can be calculated from polarographic data.[13,15-22] The theory for the volume EC mechanism is well developed for several electrochemical techniques[16-22] and Laviron[22] has analyzed the surface EC mechanism by cyclic and linear scan voltammetry. To discriminate between the surface and the volume rate constants, an effective separation of adsorptive from diffusion current components is required.[22-24] As shown above, this can be achieved by the application of normal pulse polarography. In this paper, a simple model of pulse polarographic response of first-order, irreversible, surface EC mechanism is developed. The model is tested on benzidine rearrangement of hydrazobenzene.[25,26]

Azobenzene and hydrazobenzene are a well known, reversible redox couple.[27-32] In aqueous and alcoholic solutions, at a dropping mercury electrode, their polarogram is a single, reversible, two-electrons wave corresponding to the redox reaction:[32]

$$H_5C_6-N=N-C_6H_5 + 2\ e^- + 2\ H^+ \rightleftharpoons H_5C_6-NH-NH-C_6H_5$$

The half-wave potential is pH and medium dependent. For example, in 1 M KNO_3 in 15% v/v aqueous ethanol, it is:[27] $E_{1/2} = 0.07 - 0.06$ pH. Hydrazobenzene, being a product of azobenzene reversible electroreduction at mercury electrode surface, undergoes in the acidic medium intramolecular, irreversible rearrangement to benzidine (4′,4′-diaminobiphenyl) which is electroinactive.[16-26,34-38] The rearrangement is second-order in acid and first-order in hydrazobenzene.[25,26,34-38] Both azobenzene and hydrazobenzene[22-24,27,31,39,40] and probably also benzidine[41] are strongly adsorbed to the mercury electrode surface. In 0.1 M solution of $HClO_4$ in 50% v/v aqueous ethanol, adsorption constants of azobenzene and hydrazobenzene are equal.[24,40] The system was used for testing theoretical models of surface[22] as well as simple[16-21] and adsorption complicated[23,24] volume EC mechanisms.

EXPERIMENTAL

Acetonitrile, perchloric acid and azobenzene (all »Merck«, analytical grade) were used as received. Water was double distilled. Azobenzene was dissolved in acetonitrile and a stock solution containing 10^{-3} M azobenzene in 50% v/v aqueous acetonitrile was prepared. The supporting electrolyte was 3 M $HClO_4$ in 20% v/v aqueous acetonitrile.

The pulse polarographic measurements were performed with a multimode polarograph Autolab (ECO chemie, Utrecht), which was connected to a personal computer AT 286–16 and a printer KX–P 1191 (Panasonic). The working electrode was PAR 303 A Static Mercury Drop Electrode (Princeton Applied Research) with a constant area of 0.015 cm². The Pt wire was an auxiliary electrode and Ag/AgCl/4 M NaCl was the reference. To ensure a constant adsorption time ($t_1 = 1$ s) while changing a pulse duration time (t_p), the drop life time was also changed: $t_d = (1 + t_p)$ s. The initial potential was 0.2 V and a step increment was –2 mV.

Extra pure nitrogen was passed through the solution 15 minutes prior to the measurement and a nitrogen blanket was maintained thereafter.

THEORY

The model is based on several simplifying conditions. It is assumed that both the reactant and the product are strongly adsorbed, well below the surface saturation, and any interaction with the solution is neglected. So, there is no change in the total quantity of the adsorbed material by adsorption/desorption processes during the NPP pulse. The current calculated by this model corresponds to the adsorptive component of the total response. It is equal to the difference between the maximum and the limiting currents.[10] It is also supposed that only the adsorbed reactant is initially present at the electrode surface.

Under these assumptions, a first-order, irreversible, surface EC mechanism:

$$O_{ads} + ne^- \underset{E^0}{\rightleftharpoons} R_{ads} \underset{k}{\rightleftharpoons} B$$

can be mathematically described with the following differential equations:

$$d\Gamma_0/dt = -i/nFS \tag{1}$$

$$d\Gamma_r/dt = i/nFS - k\Gamma_r \tag{2}$$

$$\Gamma_0 = \Gamma_r \exp(\varphi) \tag{3}$$

where $\varphi = nF(E–E^0)/RT$, Γ_0 and Γ_r are surface concentrations of the reactant and the product, respectively, E^0 is a standard potential, k is the first order reaction rate constant and S is an electrode surface area.

The initial time $t=0$ is set at the very moment of the pulse application. Because of the reversible redox reaction, the pulse causes an immediate reaction of the adsorbed reactant to the adsorbed product to satisfy the Nernst equilibrium. The current caused by this initial reaction is a spike similar to the capacitive current. As the current is sampled only at the end of the pulse, both of these currents can be neglected in a simple model like this one. Thus, $\Gamma_{r,t=0} = \Gamma_0^* (1 + \exp(\varphi))^{-1}$ and $\Gamma_{0,t=0} = \Gamma_0^* \exp(\varphi)(1 + \exp(\varphi))^{-1}$, where Γ_0^* is the surface concentration of reactant adsorbed before the pulse application.

The solution of Eqs. (1) – (3) is:

$$I = \omega \exp(\varphi) (1 + \exp(\varphi))^{-2} \exp\{-\omega (1 + \exp(\varphi))^{-1}\} \tag{4}$$

where $\omega = kt_p$, $I = it_p(nFS\Gamma_0^*)^{-1}$ and t_p is the pulse duration time. Eq. (4) describes the dimensionless maximum in pulse polarography. Its peak potential depends on the kinetic parameter ω:

$$\exp(\varphi_{max}) = (\omega + (\omega^2 + 4)^{1/2})/2 \tag{5}$$

If $\omega >> 1$, the solution of Eq. (5) is $\exp(\varphi_{max}) = \omega$ and consequently:

$$E_{max} = E^0 + RT \ln(kt_p)/nF \tag{6}$$

$$\partial E_{max} / \partial \log t_p = 2.303 \, RT /nF \tag{7}$$

$$I_{max} = e^{-1} \tag{8}$$

$$\Delta E_{p/2} = 63/n \text{ mV} \tag{9}$$

where $\Delta E_{p/2}$ is a half-peak width and e is the base of natural logarithms. As shown in Figure 1, the condition $\omega >> 1$ is satisfied to the first approximation already if $kt_p > 3$.
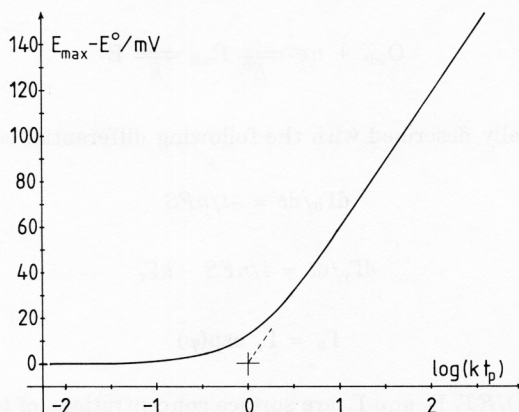

Figure 1. Theoretical dependence of the potential of the maximum in the pulse polarography on the logarithm of the kinetic parameter kt_p. The first-order, irreversible, surface EC mechanism (Eq. 5) for $n = 1$ and $t = 25$ °C.

The solution of Eq. (5) for $\omega << 1$ is $\exp(\varphi_{max}) = 1$, and consequently:

$$E_{max} = E^0 \tag{10}$$

$$\partial E_{max} / \partial \log t_p = 0 \tag{11}$$

$$I_{max} = kt_p / 4 \tag{12}$$

$$\Delta E_{p/2} = 90.5/n \text{ mV} \tag{13}$$

As shown in Figure 1, this condition is satisfied approximately if $kt_p < 0.3$. At this limit, neither the real peak current i_{max} nor the peak potential depend on the pulse duration time. These maxima can be recorded only with very short pulses. Thus, they can be more significantly influenced by capacitive and pseudo capacitive currents flowing in the very beginning of the pulse, the currents neglected in this model.

The solution of a steady-state equation:

$$d\Gamma_0 / dt = -k\Gamma_0 \exp(-\varphi) \tag{14}$$

which can be derived from Eqs. (1)–(3), assuming that $d\Gamma_r / dt = 0$ and $\Gamma_{0,t=0} = \Gamma_0^*$, is:

$$I = \omega \exp(-\varphi) \exp(-\omega \exp(-\varphi)) \tag{15}$$

If $\omega > 3$, Eqs. (4) and (15) are characterized by the same I_{max}, E_{max} and $\Delta E_{p/2}$ (Eqs. 6–9). So, the steady-state solution applies if $kt_p > 3$.

Eqs. (6), (8), (12) and (15) can be used for the calculation of the reaction rate constant. The initial surface concentration of the reactant can be calculated from Eq. (8):

$$i_{max}t_p e(nFS)^{-1} = \Gamma_0^* \tag{16}$$

The value Γ_0^* can be used for the calculation of the rate constant from Eq. (12):

$$k = 4 \, i_{max}(nFS\Gamma_0^*)^{-1} \tag{17}$$

Besides, the rate constant can be calculated independently from Eqs. (6) and (15). If the overall reaction is totally irreversible, the rate constant can be referred to an arbitrary potential E^*. If the potential of maximum is measured against the reference potential E^*, its dependence on the logarithm of the pulse duration time is linear:

$$E_{max} - E^* = 2.303(RT/nF) \log k^* + 2.303(RT/nF) \log t_p \tag{18}$$

where $k^* = k \exp(-nF(E^*-E^0)/RT)$ is the rate constant referred to the reference potential E^*. Another set of values of k^* can be obtained by measuring the dependence of the current on pulse width at various potentials (Eq. 15):

$$\log(i / nFS\Gamma_0^*) = \log(k^* \exp(-\varphi^*)) - 0.4343 \, (k^* \exp(-\varphi^*)) \, t_p \tag{19}$$

where $\varphi^* = nF(E-E^*)/RT$. The rate constant can be calculated from both, the slope and the intercept of this linear relationship.

RESULTS AND DISCUSSION

A pulse polarogram of azobenzene in 3 M $HClO_4$, as shown in Figure 2, consists of a well developed maximum and a rather small limiting current. If [azobenzene] < 10^{-4} M, the peak currents depend linearly on the reactant concentration and a drop
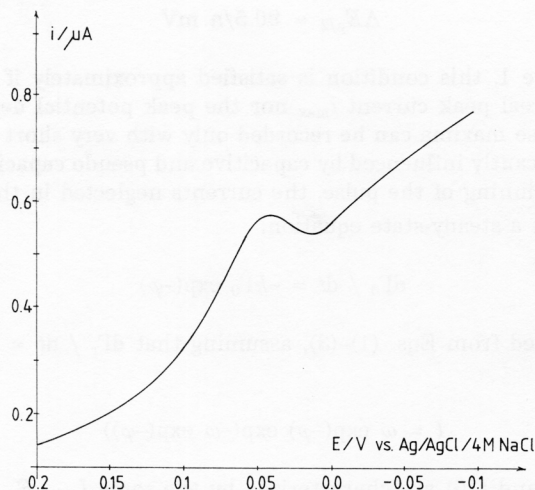
Figure 2. Pulse polarogram of 5×10^{-5} M azobenzene from 3 M $HClO_4$ in 20% v/v aqueous acetonitrile. Static mercury drop electrode, drop life-time 1.04 s, pulse duration time 40 ms, initial potential 0.2 V *vs.* Ag/AgCl/4 M NaCl and a step increment –2 mV.

life-time (for $t_d \leq 5$ s) and peak potentials are independent of these variables. Cyclic voltammograms recorded in this medium, after 30 s accumulation at 0.2 V *vs.* Ag/AgCl/4 M NaCl, are highly symmetrical: cathodic and anodic peak currents are almost equal and their peak potentials are equal to 0.02 V, if $dE/dt \geq 500$ mV/s. This indicates strong adsorption of both azobenzene and hydrazobenzene in agreement with previous reports.[22–24,27,31,39,40] The second, totally irreversible peak, which corresponds to the reduction of hydrazobenzene to aniline, appears at 100 – 200 mV more negative potential and does not interfere with kinetic measurements of benzidine rearrangement.

The dependence of pulse polarographic peak potentials (E_p) on the logarithm of the pulse duration time (t_p) is shown in Figure 3. For very short pulses, the maxima are relatively high ($i_{max} = nFS\Gamma_0^* k/4$) and both i_{max} and E_p are independent of t_p. As t_p increases, i_{max} becomes inversely proportional to it ($i_{max} = nFS\Gamma_0^* / et_p$) and E_p shifts towards more positive potentials. For the longest t_p, a constant gradient $\partial E_p/\partial \log t_p$ = 59/n mV (for 25 °C) exists, but i_{max} diminishes drastically and the maximum gradually vanishes. This is the main difference between the fast, irreversible, surface EC mechanism and the surface redox reaction controlled by a slow charge transfer. In the latter case, the constant gradient $\partial E_p/\partial \log t_p = 59/\alpha n$ mV exists only for the shortest pulses.[9–13] With an increasing of t_p, the peak potentials may either become t_p independent (if the product is also adsorbed; in this case the maximum disappears rapidly), or depend linearly on t_p, with the slope $\partial E_p/\partial \log t_p = 29/n$ mV, if only reactant is adsorbed, in which case the product $i_{max} t_p$ is a constant.[9,10]

The results of azobenzene NPP measurements may be divided into two groups. If $t_p \leq 10$ ms, the maxima are independent on the pulse duration time: $i_{max} = 0.62 \pm 0.05$ μA, $E_p = -0.006 \pm 0.005$ V and $\Delta E_{p/2} = 120 \pm 10$ mV. Using Eq. (13), the apparent number of electrons transferred per molecule is $n = 0.75 \pm 0.05$. The average
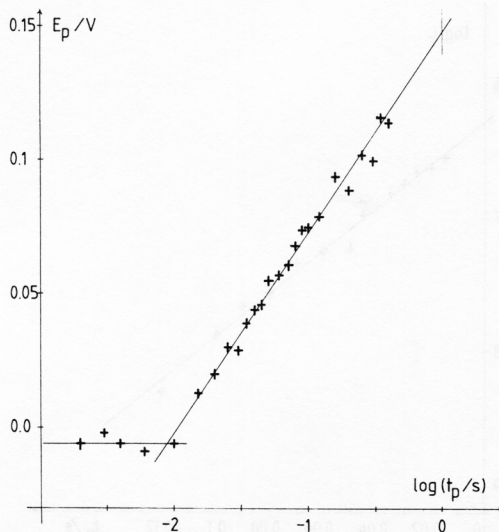
Figure 3. Dependence of peak potentials of pulse polarographic maxima of azobenzene on the logarithm of pulse duration time. All data as in Figure 2.

peak potential is chosen as the reference ($E^* = -0.006$ V) for the calculation of rate constants according to Eqs. (18) and (19). In the acid concentration range $1 \leq [HClO_4]/M \leq 5$, the reference potentials E^* chosen in this way satisfy the relationship $E^* = -0.060 - 0.059\, H_0$, where H_0 is the acidity function[42] which is formally equivalent to pH of diluted acids. In the same media, the medians of cathodic and anodic peak potentials in cyclic voltammetry are equal to $\overline{E} = -0.050 - 0.050\, H_0$. This indicates that the potentials E^* are closely related to the reversible half-wave potentials of redox reactions between adsorbed azobenzene and adsorbed hydrazobezene. In 3 M aqueous $HClO_4$, the acidity function is $H_0 = -1.23$. The influence of 20% acetonitrile on H_0 function is not known and a possible difference is neglected as nonessential.

Azobenzene pulse polarographic maxima recorded with $t_p \geq 40$ ms are characterized by the constant product $i_{max} t_p = (4.4 \pm 0.5)\, 10^{-9}$ C. Using Eq. (16), the initial surface concentration of azobenzene is estimated as the product: $n\Gamma_0^* = (8.2 \pm 0.4)\, 10^{-12}$ mol/cm^2. This value was introduced to Eq. (17) to calculate the rate constant of benzidine rearrangement from the t_p independent peak currents: $k^* = 209 \pm 17$ s^{-1}. Furthermore, if $t_p \geq 40$ ms, the half-peak widths of NPP maxima are equal $\Delta E_{p/2} = 56 \pm 10$ mV (wherefrom $n = 1.1 \pm 0.2$, according to Eq. (9)) and their peak potentials depend linearly on the logarithm of pulse duration time, as shown in Figure 3. The slope of this relationship is $\partial E_p / \partial \log t_p = 0.075$ V, which indicates $n = 0.8$. Eq. (18), the rate constant was calculated from the intercept of this straight line: $k^* = 115$ s^{-1} (referred to E^*).

Independent estimations of rate constants were obtained by correlating the logarithms of the current recorded at an arbitrarily chosen constant potential E to the pulse duration time. This relationship is linear, as predicted by Eq. (19), and shown
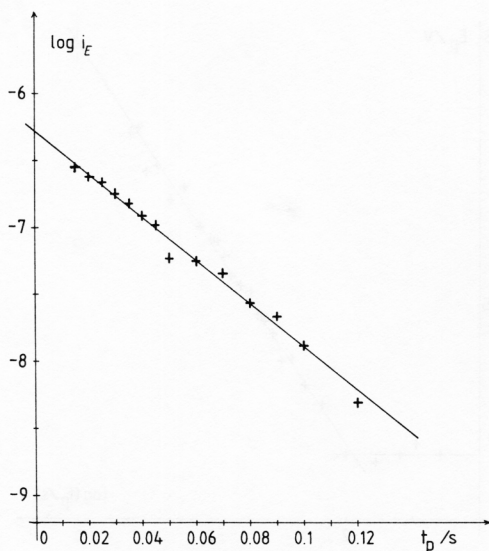
Figure 4. Dependence of the logarithm of the pulse polarographic current of azobenzene measured at E = 0.050 V on the pulse duration time. All data as in Figure 2.

in Figure 4 for E = 0.050 V *vs.* Ag/AgCl. Using experimental data for $n\Gamma_0^*$ and n = 0.8, the rate constants k^* = 206 s^{-1} (from the slope) and k^* = 250 s^{-1} (from the intercept) were calculated. From similar correlation, corresponding to E = 0.100 V, the results k^* = 122 s^{-1} and k = 119 s^{-1} were obtained from the slope and the intercept, respectively. An average value of all these calculations is k^* = 170 ± 70 s^{-1}, or $\log(k^*/\mathrm{s}^{-1})$ = 2.2 ± 0.2 and satisfies an approximative relation $\log(k^*/\mathrm{s}^{-1}) \approx -2\ H_0$. This result is in good agreement with previously published data[16,20,22,23,40] and indicates that the rate of benzidine rearrangement of adsorbed hydrazobenzene is not significantly different from the rate of the rearrangement of dissolved hydrazobenzene.

The apparent number of electrons calculated from the NPP measurements is twice smaller than reported for alcoholic solutions.[27-32] As a possible explanation, it can be assumed that, in aqueous acetonitrile, the second subsequent charge transfer (in the reduction) is not much faster than the first one, as it is in alcoholic solutions.[27] If individual half-wave potentials of two subsequent reversible charge transfers are similar, the polarogram may indicate the apparent number of electrons as equal, or close to one.[33] For azobenzene, this problem requires further investigation.

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SAŽETAK

Pulsna polarografija površinskog EC mehanizma

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Razvijen je teorijski model pulsno-polarografskog odziva površinske redoks-reakcije za kojom slijedi posve ireverzibilna kemijska reakcija prvoga reda. Pretpostavljeno je da su reaktant i produkt adsorbirani na površini radne elektrode i da je redoks-reakcija reverzibilna. Model je provjeren mjerenjem kinetike benzidinske pregradnje elektrokemijski stvorenog hidrazobenzena. Osnovni elektrolit bila je $HClO_4$ (c = 3 mol dm^{-3}) u 20%-tnoj vodenoj otopini acetonitrila. Konstanta brzine pregradnje u tom mediju jest $lg(k^*/s^{-1}) = 2.2 \pm 0.2$, izražena prema potencijalu $E^* = -0.006$ V (prema Ag/AgCl/4 M NaCl).