Stepped-polarographies of Nernstian systems with potential-dependent reactant adsorption

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Abstract

An analytical solution for any single pulse polarography in the case of reversible systems with linearly potential-dependent reactant adsorption is derived. The consequences of the variation of the adsorption constants with potential have been studied in normal pulse polarography and associated methods.

Keywords: Stepped-polarography; Adsorption; Potential dependence

1. Introduction

We have recently established a solution for stepped-potential polarographies of reversible systems with linear reactant adsorption [1] assuming adsorption constants independent of potential. This assumption is not always justified in normal pulse polarography (NPP) and reverse pulse polarography (RPP) where potential steps of large amplitude are used. Actually, for a step of 0.5 V, adsorption constants may change by a factor of four or more [2,3]. Some consequences of the potential dependence of reactant adsorption in NPP have been predicted either qualitatively [4] or by digital simulation [5] and have been observed experimentally [6,7].

It has been proved possible to solve the problem by taking into consideration the potential dependence of adsorption constants. This has served as a basis for the analysis of NPP, RPP and associated methods [8].

2. Potential-dependent reactants’ adsorption

It is considered that:
- the electrochemical reaction is reversible;
- reactant adsorption occurs at \( t > 0 \);
- surface concentrations \( \Gamma_0 \), \( \Gamma_R \) and volume concentrations at the electrode/solution interface \( c_0 \) and \( c_R \) of Ox and Red species respectively, are in equilibrium and \( \Gamma_0 = k_0 c_0, \Gamma_R = k_R c_R \) (Henry’s law);
- adsorption constants \( k_0 \) and \( k_R \) depend on potential \( E \) so that

\[
0 < t < t_1 \quad E = E_1 \quad k_0 = k_{0,1} \quad k_R = k_{R,1}
\]

\[
t > t_1 \quad E = E_2 \quad k_0 = k_{0,2} \quad k_R = k_{R,2}
\]

Under these conditions, using the methodology we have previously developed in Ref. [1], the following expression for the current \( I \) is derived. The convention of a negative reduction current is assumed.

\[
I = \frac{nFA}{\sqrt{D_0 c_0^* + \sqrt{D_R c_R^*}}} \left[ \frac{k_{R,1}}{\sqrt{D_0 c_0^* + \sqrt{D_R c_R^*}}} \left( \frac{k_{R,1}}{k_{R,1} + k_{O,1} \lambda_1} \right) \frac{1}{\sqrt{\pi t}} \right. \\
+ \left. \frac{k_{R,1} \lambda_1 - \sqrt{D_R}}{k_{R,1} + k_{O,1} \lambda_1} F_1(t) \right]
\]

\( t > t_1 \)

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\[
\frac{I}{nFA} = \left( \frac{\sqrt{D_R} c^*_R}{\sqrt{D_R} c^*_R + \sqrt{D_R} c^*_R} \right) \times \frac{1}{\sqrt{\pi t}} \times \left[ \frac{\sqrt{D_R}}{k_{r_1} + k_{o_1} \lambda_1} - \frac{x_1}{(x_1 + x_2)(k_{r_2} + k_{o_2} \lambda_2)} \right] \times \left[ 1 - \frac{2}{\pi} \arctan \left( \frac{1 - F_i(t)}{x_i \sqrt{\pi \Delta t}} \right) \right] \times \left( \frac{\sqrt{D_R}}{k_{r_1} + k_{o_1} \lambda_1} - \frac{x_1}{(x_1 + x_2)(k_{r_2} + k_{o_2} \lambda_2)} \right) \times \left( \frac{x_1^2 - x_2^2 [1 - F_i(t)]}{x_1 (x_1 + x_2)} \right) \times \left( \sqrt{\pi} \right) \times a_i(t) \right)
\]

(2b)

In these equations, \( c^*_o \) and \( c^*_r \) are the initial concentrations of the Ox and Red species respectively. \( A \) is the surface area of the electrode, and:

\[
\Delta t = t - t_i
\]

(3)

\[
\lambda_i = \exp \left( \frac{n \xi (E_i - E^0)}{RT} \right) \quad i = 1, 2
\]

(4)

\[
x_i = \frac{\sqrt{D_R} + \lambda_i \sqrt{D_O}}{k_{r,i} + k_{o,i} \lambda_i} \quad i = 1, 2
\]

(5)

\[
F_i(u) = \exp \left( x_i^2 u \text{erfc} \left( x_i \sqrt{u} \right) \right) \quad i = 1, 2
\]

(6)

\[
a_i(t) = \int_{t_i}^{t} \frac{F_i(u) du}{\sqrt{\pi u}}
\]

(7)

\[
a_2(t) = \int_{0}^{\Delta t} \frac{F_i(u) du}{\sqrt{\pi u}}
\]

(8)

Other symbols have their usual meaning.

Functions \( F_i \) and \( a_i \) \( i = 1, 2 \) can be calculated as indicated in Ref. [1].

Letting \( k_{o,1} = k_{o,2} = k_o \) and \( k_{r,1} = k_{r,2} = k_r \), from Eq. (2a) and Eq. (2b), eqs. (24a) and (24b) in Ref. [1] are found.

3. Polarographies with potential steps of variable amplitude

In order to apply the general solution of Eq. (2b) to normal or reverse pulse polarography, the species initially present in solution needs to be specified. If only Ox species is initially present, in NPP \( \lambda_1 \to +\infty \) and in RPP, \( \lambda_1 \to 0 \). 'Intermediate' polarization modes can also be carried out using less important overpotentials \(|E_1 - E^0|\) than in NPP and RPP [8].

In the following development, for the sake of simplicity, it is considered that \( D_o = D_r = D \).

3.1. Relations between the different polarograms

Let

\[
J = \frac{I}{nFA (\sqrt{D} (c^*_o + c^*_r))} \quad (9)
\]

We shall denote as \( J_0 \) the curve \( J = f(E) \) when \( c^*_r = 0 \) and as \( J_r \) this curve when \( c^*_o = 0 \). From the general solution of Eq. (2b), it follows that:

(i) \( J_0(\lambda_1 = a) = J_0(\lambda_1 = a) = 1/\sqrt{\pi t} \). Therefore, the curve \( J_{r,\text{RPP}} \) in RPP (\( \lambda_1 \to +\infty \)) is obtained from the curve \( J_{o,\text{NPP}} \) in NPP (\( \lambda_1 \to +\infty \)) by a vertical translation of \(|1/\sqrt{\pi t}| \). This allows us to restrict our study to the case where only Ox species is initially present;

(ii) for a given value of \( x_1 \), the difference \( J_0(\lambda_1 = a) - J_0(\lambda_1 = b) \) is constant. Consequently, there is always a curve in NPP (\( \lambda_1 \to +\infty \)) superimposable to a curve obtained in RPP (\( \lambda_1 \to 0 \)) or in an 'intermediate' polarization mode;

(iii) the curve \( J_{o,\text{NPP}}(k_{o,1} = a, k_{o,2} = b, k_{r,2} = c) \) in NPP is superimposable to the curve \( J_{r,\text{RPP}}(k_{r,1} = a, k_{o,2} = c, k_{r,2} = b) \) in RPP by a rotation of \( \pi \) around the point (0,0) and by a vertical translation of \(-1/\sqrt{\pi t}\). This seems to be in disagreement with previous published conclusions on correspondences between waves in NPP and in RPP [9].

3.2. Limiting currents

Waves in RPP and in 'intermediate' polarization modes develop on both sides of the zero current line. However, whatever the method used, from Eq. (2b), the amplitude \( \Delta J = J_o(\lambda_2 = +\infty) - J_o(\lambda_2 = 0) \) is:

\[
\Delta J = \frac{1}{\sqrt{\pi t}} + \frac{1 - F_i(t)}{\sqrt{\pi \Delta t}} - x_i F_i(t) - \frac{x_i^2}{\sqrt{\pi}} a_i(t) + x_i \left( 1 - \frac{2}{\pi} \arctan \frac{1}{\sqrt{\pi \Delta t}} \right)
\]

(10)

In NPP, \( x_1 = \sqrt{D}/k_{o,1} \) and in RPP \( x_i = \sqrt{D}/k_{r,1} \). Therefore, \( \Delta J \) is independent of \( k_{r,1} \) in NPP and of \( k_{o,1} \) in RPP.

When \( x_i \to +\infty \) we find \( \Delta J = 1/\sqrt{\pi \Delta t} \) which is the amplitude of curves \( J_o \) in the absence of reactant adsorption. In the case of curve \( J_{o,\text{NPP}} \), this limit is reached when there is no adsorption of Ox at \( E_i \) (\( k_{o,1} = 0 \)). Otherwise, it can be approached to better than 1% for \( x_i \sqrt{\Delta t} > 7 \). Under usual conditions, this corresponds to \( k_{o,1} < 5 \times 10^{-4} \) cm.

When \( x_1 \sqrt{\Delta t} \to 0 \), we find \( \Delta J = 1/\sqrt{\pi t} \), which is the amplitude of the wave in d.c. polarography in the absence
of reactant adsorption. For curves $J_{O,NPP}$, this limit can be approached for a reasonable value of $k_{0,1}$ if $t_i$ is small and $\Delta \tau$ large. Actually, for $t_i = 0.5$ s, $\Delta \tau = 0.05$ s and $k_{0,1} = 5 \times 10^{-2}$ cm, $\Delta \sqrt{\pi} \tau = 1.1$

3.2.1. Detection of adsorption of Red species from the limiting currents in RPP

Whatever the value of $k_{R,1}$, the limit of $J_{O,RPP}$ as $\lambda_3 \to 0$ (foot of the wave) is $-1/\sqrt{\pi} \tau$. Then, if $r_{Lin}$ is the ratio, in absolute value, of the limits of $J_{O,RPP}$ as $\lambda_3 \to +\infty$ (plateau of the wave) and $\lambda_3 \to 0$, that is:

$$r_{Lin} = |J_{O,RPP}(\lambda_3 = +\infty)/J_{O,RPP}(\lambda_3 = 0)|$$

we have

$$0 < r_{Lin} \leq \sqrt{1/\Delta \tau} - 1$$

$r_{Lin}$ is equal to $\sqrt{1/\Delta \tau} - 1$ when there is no adsorption of Red species at $E_i$. The ratio $r_{Lin}$ in RPP provides an intrinsic diagnosis criterion for the adsorption of Red species at $E_i$. This criterion is all the more sensitive as $t_i$ decreases and $\Delta \tau$ increases. If $t_i = 0.5$ s and $\Delta \tau = 0.05$ s, in the absence of adsorption, $r_{Lin} = 2.32$ and for $k_{R,1} = 5 \times 10^{-4}$ cm, which corresponds to a weak adsorption of Red species at $E_i$, $r_{Lin} = 1.96$.

3.3. Shapes of the polarograms

Taking into account the correspondences between curves in NPP and RPP (Section 3.1. (iii)), it is sufficient to study only the curves $J_{O,NPP}$. Conclusions that will be drawn also apply in RPP by inverting $k_0$ and $k_R$.

In general, adsorption of both redox species has to be considered. Adsorption of Ox species only occurs in the case of reduction of some Cd(II) complexes which lead to amalgam formation. [3,4,6,7].

Curves $J_{O,NPP}$ may or may not exhibit an extremum before reaching a limiting amplitude. The appearance of this extremum depends on the respective weights of $k_{0,1}$ at $E_i$ and of $k_{O,2}$ and $k_{R,2}$ in the short potential interval where the rising part of the wave develops.

In the following, the value zero will be attributed to an adsorption constant which is effectively equal to zero or very low.

3.3.1. Curves $J_{O,NPP}$ without extremum

Curves $J_{O,NPP}$ have a sigmoidal shape without extremum appearance:

(a) when $k_{0,1} = 0$ whatever the values of $k_{O,2}$ and $k_{R,2}$: Under these conditions the equation of the wave becomes:

$$J_{O,NPP} = -\frac{k_{R,2}}{k_{R,2} + k_{O,2} \lambda_3} \frac{1}{\sqrt{\pi \Delta \tau}} \frac{k_{R,2} x_2 - \sqrt{D}}{k_{R,2} x_2 + k_{O,2} x_2} r_2(\Delta \tau)$$

The limiting value of $J_{O,NPP}$ $(\lambda_3 \to 0)$ is equal to $-1/\sqrt{\pi} \Delta \tau$. The location of the half-wave potential $E_{1/2}$ depends on the ratio $k_{R,2}/k_{O,2}$. The overpotential $E_{1/2} - E^0$ is negative for $0 \leq k_{R,2}/k_{O,2} < 1$ and positive for $k_{R,2}/k_{O,2} > 1$.

(b) when, in the potential domain corresponding to the rising part of the curve, $k_{O,2}$ and $k_{R,2}$ are of the same order of magnitude. If $k_0 = k_R$ at any potential, a single curve $J_{O,NPP}/\Delta J$ exists the equation of which is

$$J_{O,NPP}/\Delta J = -1/(1 + \lambda_3)$$

where $\Delta J$ is given by Eq. (10). As $1/\sqrt{\pi} \tau < \Delta J \leq 1/\sqrt{\pi} \Delta \tau$, equal adsorption of Ox and Red species at any potential leads to a simple contraction of ordinates of the wave that would be obtained in the absence of reactant adsorption ($\Delta J = 1/\sqrt{\pi} \Delta \tau$).

3.3.2. Curves $J_{O,NPP}$ with extremum

Curves $J_{O,NPP}$ can exhibit either a minimum (negative reduction current) if $k_{0,1} > 0$ and $k_{O,2} > k_{R,2}$ or a maximum if $k_{0,1} > 0$ and $k_{O,2} < k_{R,2}$. These cases are illustrated by curves in Fig. 1 where $k_{O,2}$ and $k_{R,2}$ are kept constant. Actually, the contribution of these constants is significant only in the potential interval where the extremum appears. Since this interval is short, the variation of the adsorption constants is low. Curve 1, which presents a minimum, is obtained with $k_{0,1} = k_{O,2} = 4 \times 10^{-3}$ cm and $k_{R,2} = 10^{-3}$ cm. The rather unusual curve 2, which presents a maximum, is obtained with $k_{0,1} = k_{R,2} = 4 \times 10^{-3}$ cm and $k_{O,2} = 10^{-3}$ cm, conditions which are plausible. According to Section 3.1 (i) and (iii), curve 1 is superimposposable on curve 2 by a rotation of $\pi$ around (0,0) and by a vertical translation of $-\Delta J$.

From a practical point of view, it is interesting to consider the ratio $r_{Lin}$ of 1 of the amplitude of the extremum over the limiting amplitude $\Delta J$ of the curve. $r_{Lin}$ increases when $t_i$ increases and $\Delta \tau$ decreases. However, variation of
3.3.3. Adsorption of a single redox species

When only Ox species is adsorbed and $\Delta t = 10$ ms, the outgrowth of the curve with respect to its limiting current becomes appreciable ($r_{ex} > 1.1$) for $k_{0.1} = k_{0.2} > 5 \times 10^{-4}$ cm. As both $k_{0.1}$ and $k_{0.2}$ increase, $r_{ex}$ increases and tends to a limiting value which is practically reached for $k_{0.1}$ and $k_{0.2}$ of the order of 0.1 cm. The minimum shifts towards positive potentials in increasing $k_{0.1}$ and towards negative potentials in increasing $k_{0.2}$. However, under usual experimental conditions ($\Delta t/t_i < 1$) and for $k_{0.2} \geq 5 \times 10^{-3}$ cm, the overpotential at which the minimum appears depends essentially on $k_{0.2}$ and can be approximated with an error of less than 5 mV by

$$E_2 - E^0 = \frac{RT}{nF} \ln \frac{\sqrt{D\Delta t}}{0.9k_{0.2}}$$  \hspace{1cm} (15)

An equivalent approximation has been previously proposed [9].

Adsorption of Ox species only can be treated quantitatively by introducing in the calculations the following law for the variation of $k_{0}$ as a function of the potential $[10-12]$

$$k_{0} = k_{M} \exp \left[ - \alpha \left( E - E_{M} \right)^{2} \right]$$  \hspace{1cm} (16)

$k_{M}$ is the value of $k_{0}$ at the potential of maximum adsorption $E_{M}$. Usually, the constant $\alpha$ lies between $10^{-6}$ and $5 \times 10^{-6}$ mV$^{-2}$ [11,13]. Curves shown in Fig. 4 represent the function $J' = -J_{O,NPP} \sqrt{\pi \Delta t} / \mathcal{F} \mathcal{A} c_{ox}$, that is the ratio in NPP of the current when Ox is adsorbed over the limiting current in absence of Ox adsorption, as a function of the overpotential $E_{2} - E^0$. In all cases, the polarization overpotential $E_{1} - E^0$ is 350 mV. In calculations, $t_i = 1$ s, $\Delta t = 10$ ms, $k_{M} = 2 \times 10^{-3}$ cm have been used. Curve 1, in Fig. 3, is obtained assuming $k_{0}$ independent of potential ($\alpha = 0$). For curves 2-4, where $k_{0}$ is potential dependent, $\alpha$ is $5 \times 10^{-6}$ mV$^{-2}$ and $E_{M} - E^0$ is respectively 350 mV, 0 mV and $-350$ mV. It can be observed that the outgrowth decreases when $k_{0.1}$ or $k_{0.2}$ decrease and that curves 1 and 2, for which $k_{0}$ at $E_1$ is the same, have the same limiting amplitude.
For curve 4, where $E_M$ is located on the plateau of the curve, the influence of Ox adsorption is practically not observable. However, in this case, an ‘intermediate’ polarization mode permits us to underscore Ox adsorption, as is shown in Fig. 4. Actually, as was revealed in Section 3.1, a curve in NPP and a curve in an ‘intermediate’ polarization mode are isometric for the same value of $x_i$. Therefore, as the outgrowth of a curve $I_{O,NPP}$ increases when $x_i$ decreases, $E_{1i}$ in the ‘intermediate’ mode, should be chosen so that $x_i$ is a minimum. Taking into account Eq. (5) and Eq. (16), in the actual example, $x_i$ is a minimum for $E_1 - E^0 = 55$ mV.

4. Conclusions

Reactant adsorption in NPP and RPP is not always easy to detect. However, some conclusions can be pointed out. When Ox species are initially present, the appearance of a minimum in NPP (negative reduction current) shows a predominant adsorption of Ox species in the whole polarization domain. Similarly, a maximum in RPP indicates a predominant adsorption of Red species formed at the electrode.

The absence of an extremum in NPP and RPP does not exclude a significant reactant adsorption. In such a case, the ratio of the current at the plateau over the current at the foot of the wave in RPP allows us to underscore an eventual adsorption of Red species at the constant polarization potential.

An ‘intermediate’ polarization mode allows us to detect an adsorption which is not observable in NPP or in RPP.

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References