POLAROGRAPHIC IRREVERSIBLE BULK CATALYTIC HYDROGEN WAVES

Corresponding Member, Acad. Sci. USSR V. G. Levich
and B. I. Khaikin

Electrochemistry Institute, Academy of Sciences, USSR

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In [1], equations were found for the volt-ampere characteristics of the polarographic bulk catalytic hydrogen waves produced by the following cycle of reactions:

$$B + DH \underset{k_2}{\overset{k_1}{\rightleftarrows}} BH^+ + D^-; \qquad (I)$$

$$BH^+ + e^- \overset{el}{\leftrightarrows} BH; \qquad (II)$$

$$2BH \xrightarrow{k} 2B + H_2. \qquad (III)$$

In the scheme (I)-(III) B and BH^+ are the two forms of the catalyst present in protolytic equilibrium before electrolysis; BH is the product of the electrode reaction, regenerating the catalyst; and DH and D^- are the components of the buffer system.

In the derivation in [1], it was assumed that the electrochemical reaction (II) is reversible (close to the electrode, the concentrations of the substances taking part in the electrochemical reaction obey the thermodynamic Nernst equation). This assumption is justified experimentally in the case, for example, of the catalytic waves produced by pyridine [2].

Analysis of the solutions of the differential equations which describe the processes taking place in the scheme (I)-(III) leads, however, to the following criterion for polarographic reversibility:

$$\mu_2 \gg \frac{D}{k_{b,h}}, \qquad (1)$$

where μ_2 is the thickness of the kinetic layer of the bimolecular process (III); $k_{b,h}$ is the rate constant of the reversible electrochemical reaction; and D is the diffusion coefficient, which for the sake of simplicity in the calculations we shall subsequently assume to be the same for all forms of the catalyst.

For the standard potential, the inequality (1) has the form

$$\mu_2 \gg \frac{D}{k_{s,h}}, \qquad (1')$$

where $k_{s,h}$ is the rate constant of the electrochemical reaction at the standard potential.

Comparison of condition (1') with the usual criterion for polarographic reversibility in electrode processes without subsequent bulk chemical reaction [3] shows that reversibility in the processes taking place according to the scheme (I)-(III) requires extremely high values for the rate constant of the electrochemical reaction $k_{s,h}$. The value of $k_{s,h}$ in the case of catalytic processes should be greater than the usual value of $k_{s,h}$ for which an electrochemical reaction is usually considered reversible ($k_{s,h} \gg 10^{-2}$ cm/sec) by a factor equal to the factor by which the thickness of the diffusion layer exceeds the thickness of the kinetic layer of the subsequent chemical reaction. It is therefore natural to assume that in a number of cases the processes under consideration should have an irreversible electrochemical stage. In actual fact, in the case of the bulk catalytic waves produced by tetrahydroquinoline and di-N,N'-piperidinium-1,3-propane dibromide, S. G. Mairanovskii and L. D. Klyukina found that the electrochemical reaction showed marked irreversibility.

Equations are derived below for the volt-ampere characteristics of irreversible bulk catalytic hydrogen waves for the case where the inequality corresponding to the reverse of inequality (1) applies.

Since the thickness of the kinetic layer is much less than the thickness of the diffusion layer and a stationary state is established in the electrolysis process in an extremely small time interval (of the order of μ_2^2/D), the following boundary value problem applies for the processes under consideration (it is assumed that the solution contains an excess of indifferent electrolyte):

$$D\frac{d^2c_1}{dx^2} + \rho\,(c_2 - \sigma c_1) = 0,$$

$$D\frac{d^2c_2}{dx^2} - \rho\,(c_2 - \sigma c_1) + kc_3^2 = 0, \qquad (2)$$

$$D\frac{d^2c_3}{dx^2} - kc_3^2 = 0;$$

$x = 0$:

$$D\frac{dc_1}{dx} = k_{s,h}c_1\exp\left[\frac{\alpha F}{RT}(\varphi^{(0)} - \varphi)\right],$$

$$\frac{dc_1}{dx} = -\frac{dc_3}{dx} = \frac{j}{FD},\quad \frac{dc_2}{dx} = 0; \qquad (3)$$

$x \to \infty$:

$$c_1 + c_2 + c_3 = \gamma,\quad c_2 = \sigma c_1,\quad c_3 = 0. \qquad (4)$$

In formulas (2), (3), and (4), the symbols have the following significance: c_1, c_2, and c_3 are the concentrations of the substances BH^+, B, and BH respectively; $\rho = k_1[DH]$ (the concentrations of the components of the buffer system are much greater than the catalyst concentration and can be included in the effective rate constant); σ is the constant for the equilibrium between the inactive and active forms of the catalyst ($\sigma = [B]/[BH^+]$, where [B] and $[BH^+]$ are the concentrations before the start of electrolysis); $\underline{j}$ is the current density; $\varphi^{(0)}$ is the standard potential; and γ is the analytical concentration of the catalyst in the bulk of the solution.

The third equation of system (2), which contains only one unknown function c_3 and does not contain a clearly independent variable, is easily solved. Substitution of the solution of the third equation in the second equation of system (2) gives a system of linear differential equations. Solution of the latter, to find the relationship between the current density and potential, gives the following transcendental equation:

$$\frac{k\gamma}{6\rho(1+\sigma)}\beta^3 - \beta^2 - \beta^3e^{\beta}\,\mathrm{Ei}\,(-\beta) = 2\,(1+\sigma)\,[1 + \varkappa\,(\varphi)], \qquad (5)$$

where

$$\mathrm{Ei}\,(-\beta) = -\int_{\beta}^{\infty}\frac{e^{-t}}{t}\,dt,$$

$$\varkappa\,(\varphi) = \frac{\sqrt{D\rho\,(1+\sigma)}}{k_{s,h}}\exp\left[-\frac{\alpha F}{RT}(\varphi^{(0)} - \varphi)\right], \qquad (6)$$

$$\beta = 12^{1/3}\,\frac{F^{1/3}D^{1/6}\rho^{1/6}(1+\sigma)^{1/2}}{k^{1/3}j^{1/3}}. \qquad (7)$$

Equation (5), from which the value of β should be found [β is related to the current density $\underline{j}$ by the relationship (7)], is the equation for the volt-ampere characteristic of the irreversible process. The numerical solution of Eq. (5)

for any values of the parameters defining the kinetics of the process and for any potential does not present any great difficulty. In practice, however, an important part is played by various limiting cases, which are examined below.

If the condition

$$\left\{\frac{12\rho\,(1+\sigma)^2}{k\gamma}\,[1+\varkappa(\varphi)]\right\}^{1/3} \ll 1 \tag{8}$$

applies, the value of β is much less than unity. Equation (5) then reduces to the following equation for the volt-ampere characteristic:

$$\varphi = \varphi_{1/2} + \frac{RT}{\alpha F}\ln\frac{j_{\text{lim}} - j}{j}, \tag{9}$$

where

$$j_{\text{lim}} = \gamma F\sqrt{\frac{D\rho}{1+\sigma}}, \tag{10}$$

$$\varphi_{1/2} = \varphi^{(0)} + \frac{RT}{\alpha F}\ln\frac{k_{s,h}}{\sqrt{D\rho\,(1+\sigma)}}. \tag{11}$$

The limiting current, as expected, coincides with the limiting current for reversible processes [1]. The expression for the half-wave potential contains the rate constant of the electrochemical reaction (II) and can be used for the experimental determination of this constant.

The value of β is much greater than unity if at least one of the following two inequalities applies:

$$\left\{\frac{12\rho\,(1+\sigma)}{k\gamma}\,[1+\varkappa(\varphi)]\right\}^{1/3} \gg 1; \tag{12}$$

$$\left[\frac{6\rho\,(1+\sigma)}{k\gamma}\right]^{1/2} \gg 1. \tag{13}$$

In this case Eq. (5) leads to the following expression for the volt-ampere characteristic:

$$\gamma = \frac{j}{FD}\left[\frac{(1+\sigma)\,D}{\rho}\right]^{1/2}\left[1 + \frac{\sqrt{D\rho\,(1+\sigma)}}{k_{s,h}}\,e^{-\frac{\alpha F}{RT}(\varphi^{(0)}-\varphi)}\right] + \left(\frac{j}{FD}\right)^{1/3}\left(\frac{3D}{2k}\right)^{1/2}. \tag{14}$$

Equation (14) describes, in particular, the case where the limiting stage is the regeneration of the catalyst. If, together with (13), the inequality

$$\left[\frac{\rho}{k\gamma\,(1+\sigma)}\right]^{1/2} \gg 1 \tag{15}$$

applies, the limiting current density is in fact equal to

$$j_{\text{lim}} = F\gamma\,({}^2/_3\,Dk\gamma)^{1/2}. \tag{16}$$

From the inequalities (13) and (15), Eq. (14), and the inequality corresponding to the reverse of inequality (1), it follows that regeneration of the catalyst may be the limiting stage only if the concentration of the inactive form of the catalyst is not greater than (or less than) the concentration of the active form by too large a factor (σ small) and the potential is sufficiently negative (sufficiently close to the value at which the limiting current is attained).

If, in addition to the inequality (12), the inequality

$$\left\{\frac{12\rho}{k\gamma(1+\sigma)[1+\varkappa(\varphi)]}\right\}^{1/3} \ll 1. \tag{17}$$

applies, Eq. (14) reduces to Eqs. (9), (10), and (11). This may be the case only at very large values of σ.

If σ is very large, the thickness of the kinetic layer of the preceding reaction ($\mu_1 = \sqrt{D/\rho\sigma}$) is small and may prove to be commensurable with the thickness of the diffusion part of the double layer. In this case the structure of the double layer has a significant influence on the volt-ampere characteristic of the process. Calculations similar to those carried out in [4] give an equation for the volt-ampere characteristic in this case. If the inequality (17) applies, the following expressions for the limiting current density and the half-wave potential apply:

$$j_{\lim} = F\gamma\sqrt{\frac{D\rho}{\sigma}}\,G^{-1}, \tag{18}$$

$$\varphi_{1/2} = \varphi^{(0)} + \frac{RT}{\alpha F}\ln\frac{k_{s,h}}{\sqrt{\sigma D\rho}} + \frac{RT}{\alpha F}\ln G, \tag{19}$$

where G is a coefficient taking account of the influence of the double layer. Its values are given in [4]. Comparison of (19) with the formula for the half-wave potential of reversible processes shows that if, in the case of reversible waves, the value $(RT/F)\ \ln G$ is preceded by the coefficient 2/3, the corresponding coefficient for the case of irreversible waves is equal to $1/\alpha$ ($\alpha < 1$). The influence of the structure of the double layer on the half-wave potential of irreversible processes is therefore more marked than its effect on the half-wave potential of reversible processes.

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