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Abstract

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POLAROGRAPHIC IRREVERSIBLE VOLUME CATALYTIC WAVES OF HYDROGEN

In work (1), equations were found for the current-voltage characteristics of polarographic volume catalytic waves of hydrogen caused by the occurrence of the following cycle of reactions:

$$\mathrm{B} + \mathrm{DH} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{BH}^+ + \mathrm{D}^-; \tag{I}$$

$$\mathrm{BH}^+ + e \underset{\mathrm{el}}{\rightleftarrows} \mathrm{BH}; \tag{II}$$

$$2\mathrm{BH} \xrightarrow{k} 2\mathrm{B} + \mathrm{H}_2. \tag{III}$$

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

In deriving the equations in work (1), it was assumed that the electrochemical reaction (II) is reversible (near the electrode the concentrations of the substances participating in the electrochemical reaction obey the thermodynamic Nernst equation). This assumption is justified experimentally in the case, for example, of catalytic waves caused by pyridine (2).

Analysis of the solutions of the differential equations that describe the processes proceeding according to scheme (I)–(III), however, leads to the following criterion of polarographic reversibility:

$$\mu_2 \gg \frac{D}{k_{b,h}}, \tag{1}$$

where μ_2 is the thickness of the kinetic layer of the bimolecular process (III); $k_{b,h}$ is the rate constant of the reverse electrochemical reaction; D is the diffusion coefficient, which, in what follows, in order to simplify the calculations, we shall consider the same for all forms of the catalyst.

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

$$\mu_2 \gg \frac{D}{k_{s,h}}, \tag{1'}$$

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

Comparison of condition (1′) with the usual criterion of polarographic reversibility of electrode processes without a subsequent volume chemical reaction ([3]) shows that the reversibility of processes proceeding according to scheme (I)—(III) requires very large values of the rate constant of the electrochemical reaction $k_{s,h}$. In the case of catalytic processes, the quantity $k_{s,h}$ must be greater than the usual value of $k_{s,h}$, at which it is customary to regard the electrochemical reaction as reversible ($k_{s,h} \gtrsim 10^{-2}$ cm/sec), by as many times as the thickness of the diffusion layer is greater than the thickness of the kinetic layer of the subsequent chemical reaction. It is therefore natural to suppose that, in a number of cases, the processes under consideration must have an irreversible electrochemical stage. Indeed, in the case

volume catalytic waves caused by tetrahydroquinoline and di-N,N′-piperidinium-1,3-propane dibromide, S. G. Mairanovskii and L. D. Klyukina found a strong irreversibility of the electrochemical reaction.

Below, equations are derived for the current-voltage characteristics of irreversible volume catalytic hydrogen waves in the case where the inequality opposite to (1) is satisfied.

Since the thickness of the kinetic layer is much smaller than the thickness of the diffusion layer and, in the course of electrolysis, a steady state is established within a very short time interval (of the order of μ_2^2/D), the following boundary-value problem is valid for the processes under consideration (it is assumed that the solution contains an excess of indifferent electrolyte):

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

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

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

$$x = 0:$$

$$D\frac{dc_1}{dx} = k_{s,h} c_1 \exp\left[\frac{\alpha F}{RT}\left(\varphi^{(0)} - \varphi\right)\right], \tag{3}$$

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

$$x \to \infty:$$

$$c_1 + c_2 + c_3 = \gamma, \qquad c_2 = \sigma c_1, \qquad c_3 = 0. \tag{4}$$

In formulas (2), (3), and (4) the notation has the following meaning: c_1, c_2, c_3 are the concentrations of the substances BH^+, B, and BH, respectively; $\rho = k_1[\mathrm{DH}]$ (the concentrations of the buffer-system components considerably exceed the concentration of the catalyst and may be included in the effective rate constants); σ is the equilibrium constant of the inactive and active forms of the catalyst ($\sigma = [\mathrm{B}]/[\mathrm{BH}^+]$, where [B] and $[\mathrm{BH}^+]$ are the concentrations before the beginning of electrolysis); j is the current density; $\varphi^{(0)}$ is the standard potential; γ is the analytical concentration of the catalyst in the bulk of the solution.

The third equation of system (2), containing only one unknown function c_3 and not explicitly containing the independent variable, can be solved easily. Substitution of the solution of the third equation into the second equation of system (2) makes it possible to obtain a system of linear differential equations. Solving the latter in order to find the dependence between the current density and the potential leads to the following transcendental equation:

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

where

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

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

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

Equation (5), from which the quantity β must be found (β is related to the current density j by relation (7)), represents the current-

of the current-voltage characteristic of the irreversible process. A numerical solution of equation (5) for any values of the parameters determining the kinetics of the process, and for any potential, presents no special difficulty. However, in practice the main role is played by various limiting cases, which are examined below.

If the condition

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

is satisfied, then the quantity β is much less than unity. Then equation (5) leads to the following equation for the current-voltage characteristic:

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

where

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

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

The limiting current, as was to be expected, coincides with the limiting current of 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 quantity β is much greater than unity when at least one of the following two inequalities is satisfied:

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

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

In this case equation (5) leads to the following expression for the current-voltage characteristic:

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

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

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

is satisfied, then the limiting-current density is equal to

$$j_{\mathrm{pr}} = F\gamma^{2/3}(Dk\gamma)^{1/2}. \tag{16}$$

From inequalities (13), (15), equation (14), and the inequality reciprocal to (1), it follows that regeneration of the catalyst can be the limiting stage only in the case where the concentration of the inactive form of the catalyst does not greatly exceed (or is less than) the concentration of the active form (σ is small), and the potential is sufficiently negative (close to the value at which the limiting current is attained).

If, together with inequality (12), the inequality

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

is also satisfied, then equation (14) reduces to equations (9), (10), and (11). The latter can occur only at very large values of σ.

If σ is very large, then the thickness of the kinetic layer of the preceding reaction ($\mu_1 = \sqrt{D/\rho\sigma}$) is small and may prove comparable with the thickness

diffuse part of the double layer. In this case the structure of the double layer has a noticeable influence on the current-voltage characteristic of the process. Calculations similar to those carried out in work [4] make it possible to obtain an equation for the current-voltage characteristic in this case. If inequality (17) is satisfied, the following expressions are valid for the limiting-current density and the half-wave potential:

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

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

where G is a coefficient taking into account the influence of the double layer. Its values are given in work [4]. Comparison of (19) with the formula for the half-wave potential of reversible processes shows that, whereas in the case of reversible waves the coefficient before the quantity $\frac{RT}{F}\ln G$ is $^2/_3$, the corresponding coefficient in the case of irreversible waves is $1/\alpha$ $(\alpha < 1)$. Therefore, the influence of the structure of the double layer on the half-wave potential of irreversible processes is more pronounced than on the half-wave potential of reversible processes.

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Note: Figure translations are in progress. See original paper for figures.