Corresponding Member of the Academy of Sciences of the USSR V. G. LEVICH, B. I. KHAIKIN

and S. G. MAIRANOVSKII

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. G. LEVICH,
B. I. KHAIKIN
and S. G. MAIRANOVSKII

THE INFLUENCE OF THE DOUBLE LAYER ON POLAROGRAPHIC BULK CATALYTIC WAVES OF HYDROGEN

Polarographic catalytic waves of hydrogen are caused by the occurrence of the following cycle of reactions:

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

$$\mathrm{BH}^+ + \mathrm{e}^- \underset{\leftarrow}{\overset{\mathrm{el}}{\rightarrow}} \mathrm{BH}; \tag{II}$$

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

According to scheme (I)–(III), the catalyst exists in two forms, B and BH^+, which are in protolytic equilibrium. The active form of the catalyst is discharged at the electrode, while the product of the electrode reaction, BH, regenerates, by a bimolecular mechanism, the inactive form of the catalyst B with simultaneous evolution of hydrogen. DH and D^- are components of the buffer solution (the concentrations of D and DH considerably exceed the concentration of the catalyst).

In the case of catalytic waves produced by pyridine, the preceding and subsequent chemical reactions (I) and (III) occur only in the bulk of the solution (the catalyst, at the potentials at which the catalytic wave appears, is practically not adsorbed) in the so-called kinetic layers μ_1 and μ_2, respectively. In determining the rate constants of protonation of pyridine from polarographic data it was found that the rate constants are not constant, but that their value changes with changes in the pH of the solution ([1,2]) or in the concentration of indifferent electrolyte ([3]). This was attributed to the double layer. Indeed, the rate of the preceding reaction (I) is so high that the thickness of the kinetic layer μ_1 corresponding to this reaction is comparable with the thickness of the diffuse part of the double layer δ. Therefore the electric field within the kinetic layer μ_1 has a substantial influence both on the distribution of concentrations and on the process of ion transport. A change in the pH of the solution or in the concentration of indifferent electrolyte changes the ratio δ/μ_1 and thereby changes the values of the current density from which the magnitudes of the rate constants of the preceding reaction were calculated.

The aim of the present work is to determine the current-voltage characteristics of the reaction cycle under consideration, taking into account the influence of the double layer, and to compare the results obtained with experimental data.

Let us consider the practically most important case, when the concentration of the inactive form of the catalyst B in the solution considerably exceeds the concentration of the active form BH^+ ($\sigma = [\mathrm{B}]_0/[\mathrm{BH}^+]_0 \gg 1$, where $[\mathrm{B}]_0$ and $[\mathrm{BH}^+]_0$ are the concentrations in the bulk of the solution), and the thickness of the kinetic layer of the subsequent reaction μ_2 is considerably greater than μ_1 and σ.

Let us denote the concentrations $[\mathrm{BH}^+]$, $[\mathrm{B}]$, and $[\mathrm{BH}]$ by C_1, C_2, C_3, respectively, and introduce the effective rate constant of the monomolecular reaction $\rho = k_1[\mathrm{DH}]$. Choosing the origin of coordinates at the Helmholtz plane, for the region $x < \delta$ ($\delta > \mu_1$) or $x < \mu_1$ ($\mu_1 > \delta$) one can write the system

equations analogous to the equations in work (^{4}), but supplemented with terms describing the occurrence, within the region under consideration, of reaction (I):

$$D_1 \frac{d}{dx}\left\{\frac{dC_1}{dx} + \frac{C_1 F}{RT}\frac{d\varphi}{dx}\right\} - \rho\sigma C_1 e^{F\varphi/RT} + \rho C_2 = 0,$$

$$D_2 \frac{d^2 C_2}{dx^2} + \rho\sigma C_1 e^{F\varphi/RT} - \rho C_2 = 0, \tag{1}$$

$$\frac{d\varphi}{dx} = \frac{RT}{F\delta} e^{-F\varphi/RT}.$$

Boundary conditions for system (1):

$x = 0:$

$$F D_1 \left\{\frac{dC_1}{dx} + \frac{C_1 F}{RT}\frac{d\varphi}{dx}\right\} = j,$$

$$F D_2 \frac{dC_2}{dx} = 0, \qquad \varphi = \psi_1; \tag{2}$$

$x = \mu_1$ ($\mu_1 > \delta$) or $x = \delta$ ($\delta > \mu_1$) :

$$C_2 = C_2^{\mu_1}, \qquad C_1 = \frac{C_2^{\mu_1}}{\sigma} - \mu_1 \frac{dC_1}{dx}^{*}. \tag{3}$$

In formulas (1), (2), and (3) the notation has the following meaning: $\delta = (RT/8\pi F^2 C)^{1/2}$ is the thickness of the diffuse part of the double layer; C is the total concentration of electrolyte in solution, approximately equal to the concentration of indifferent electrolyte; ψ_1 is the potential at the Helmholtz plane ($\exp[F(\psi_1)/RT] \gg 1$); $C_2^{\mu_1}$ is the concentration value that must be determined from the solutions of the equations outside the region under consideration.

In the region $x > \mu_1, \delta$, where the electric field is practically absent and reaction (I) does not occur, the following differential equations are valid:

$$D_2 \frac{d^2 C_2}{dx^2} + kC_3^2 = 0,$$

$$D_3 \frac{d^2 C_3}{dx^2} - kC_3^2 = 0. \tag{4}$$

In equations (4) the motion of the drop is not taken into account, since it is assumed that the thickness of the layer μ_2 is much less than the thickness of the diffusion layer and, consequently, the influence of the motion of the drop may be neglected (^{5}). In these equations the terms containing time derivatives of the concentrations have also been omitted, since a special calculation shows that the time required for establishing the steady-state electrolysis regime is less than μ_2^2/D. The latter quantity, in turn, is much less than the drop time.

In view of the smallness of μ_1 and δ, these quantities may be taken to be zero for the region $x > \mu_1, \delta$. Therefore the boundary conditions for system (3) have the form:

$x = 0:$

$$FD_2 \frac{dC_2}{dx} = -FD_3 \frac{dC_3}{dx} = j;$$

$x \to \infty:$

$$C_2 = \gamma, \qquad C_3 = 0, \tag{5}$$

where γ is the analytical concentration of the catalyst in the bulk of the solution.

---

* At the boundary of the kinetic layer μ_1, the substance BH$^+$ is in chemical equilibrium with substance B ($C_1 \simeq C_2^{\mu_1}/\sigma$), and its flux is very small compared with the flux of substance B ($\mu_1 dC_1/dx \ll j\mu_1/FD,\ C_2^{\mu_1}/\sigma$). The solutions of equations (1) must be such that these requirements are fulfilled.

Following the method applied in work (^{6}), one can find the solution of the system of equations (1)*. For $x = 0$ we have:

$$(C_1)_{x=0} = e^{-F\psi_1/RT}\left\{\frac{C_2^s}{\delta} - \frac{j\mu_1}{FD}G\right\}, \tag{6}$$

where $\mu_1 = \sqrt{D/\rho\delta}$, and the coefficient G takes into account the influence of the double layer.

If $\exp\left\{-\frac{F|\psi_1|}{RT}\right\}\frac{\delta}{\mu_1} \ll 1$, then

$$G = 0.47\left(\frac{\delta}{\mu_1}\right)^{-1/2}\frac{I_{-1/4}(\delta/\mu_1) + I_{3/4}(\delta/\mu_1)}{I_{-3/4}(\delta/\mu_1) + I_{1/4}(\delta/\mu_1)}, \tag{7}$$

where I_ν are Bessel functions of imaginary argument.

If the condition $\delta/\mu_1 \ll 1$ is satisfied, then

$$G = 1 - 1.33\frac{\delta}{\mu_1}. \tag{8}$$

In the opposite limiting case, when $\exp\left\{-\frac{F|\psi_1|}{RT}\right\}\frac{\delta}{\mu_1} \gg 1$, the coefficient G is equal to

$$G = \exp\frac{\psi_1 F}{2RT}. \tag{9}$$

Solving the system of equations (4) leads to the following concentration values:

$$C_2^{\mu_1} = \gamma - \left(\frac{j}{F}\right)^{2/3}\left(\frac{3}{2D_3k}\right)^{1/3}\frac{D_3}{D_2}; \tag{10}$$

$$(C_3)_{x=0} = \left(\frac{j}{F}\right)^{2/3}\left(\frac{3}{2D_3k}\right)^{1/3}. \tag{11}$$

To find the current-voltage characteristic, we use the equation of the theory of slow discharge (7)

$$\begin{aligned} j = Fk_{s,h}\{&(C_1)_{x=0}\exp\left[\frac{\alpha F\psi_1}{RT}\right]\exp\left[-\frac{\alpha F}{RT}(\varphi - \varphi^{(0)})\right] \\ &- (C_3)_{x=0}\exp\left[\frac{(\alpha-1)F}{RT}\psi_1\right]\exp\left[-\frac{(\alpha-1)F}{RT}(\varphi - \varphi^{(0)})\right]\}, \end{aligned} \tag{12}$$

where $\varphi^{(0)}$ is the standard potential, and $k_{s,h}$ is the rate constant at the standard potential.

In the case of catalytic waves caused by pyridine, the electrode stage is reversible (8). Substituting expressions (6), (10), and (11) into (12) and taking into account the reversibility of the electrode stage, one can find the equation of the current-voltage characteristic:

$$\gamma = \frac{j}{FD_1}\left(\frac{\delta D_1}{\rho}\right)^{1/2} G + \left(\frac{j}{FD_3}\right)^{2/3}\left(\frac{3D_3}{2k}\right)^{1/3}\left(\frac{D_3}{D_2} + \delta \exp\left[\frac{E}{RT}(\varphi - \varphi^{(0)})\right]\right). \tag{13}$$

When the condition

$$\frac{D_1^{1/3} D_2^{2/3}}{D_2}\left(\frac{\rho}{\delta k \gamma}\right)^{1/3} G^{-2/3} \ll 1 \tag{14}$$

is fulfilled the following relations hold for the limiting-current density and the half-wave potential:

$$j_{\mathrm{lim}} = F\gamma\sqrt{\frac{D_1\rho}{\sigma}}\, G^{-1}, \tag{15}$$

$$\varphi_{1/2} = \varphi^{(0)} + \frac{1}{3}\frac{RT}{F}\ln\frac{k\gamma D_3}{3\sigma^2\rho D_1} + \frac{2}{3}\frac{RT}{F}\ln G. \tag{16}$$

For an experimental verification of the formulas obtained, let us use the data (3) on the dependence of the limiting current on the total concentration of electrolyte C. For small values of the ratio δ/μ_1, the following formula can be obtained:

$$\lg\left(\frac{j'_{\mathrm{lim}}}{j_{\mathrm{lim}} - j'_{\mathrm{lim}}}\right)^2 = -2\lg\frac{4\cdot 10^{-8}}{\mu_1} + \lg C, \tag{17}$$

where j'_{lim} is the limiting-current density without taking into account the influence of the double layer (9), the electrolyte concentration C is expressed in

---

* In equations (1) the variables are replaced by $\xi = e^{-\psi/2}$, $\dfrac{d}{dx} = -\dfrac{\xi^2}{2\delta}\dfrac{d}{d\xi}$. In order that the boundary conditions (3), in the case $\mu_1 > \delta$, remain valid, the region under consideration should be divided into two: $0 \le x < \delta$ and $\delta \le x \le \mu_1$. In the region $\delta \le x \le \mu_1$, equations (1) are solved with the values $\varphi = \dfrac{d\varphi}{dx} = 0$. The solutions are then matched at the point $x = \delta$.

moles per liter, and μ_1 in centimeters. Experimentally it is observed that, at very large values of the electrolyte concentration, a further increase in concentration almost does not change the limiting current (Fig. 2 in (^{3})). This value was approximately taken as the limiting current on which the structure of the double layer no longer has an effect. In Fig. 1 the points show the experimentally found dependence of the quantity

$$\lg\left(\frac{j'_{\text{lim}}}{j_{\text{lim}}-j'_{\text{lim}}}\right)^2$$

on $\lg C$. As is seen from the figure, the experimental points fit well on a straight line with a slope of 45° (in accordance with formula (16)). The deviations lie within the limits of experimental error; in part, they are apparently due to salt effects not taken into account. With the aid of the intercept cut off by the straight line on the ordinate axis, the thickness of the kinetic layer μ_1 was found, and the curve shown in Fig. 1 was constructed.

Fig. 1

There are many experimental data on the influence of the pH of the solution (^{1},^{2}) (with a change in pH, μ_1 changes) on the values of the limiting current and the half-wave potential. These data are in qualitative agreement with the theoretical results. However, an exact comparison of these experimental data with the theory is difficult because the true values of the thickness of the kinetic layer μ_1 are unknown.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
5 IV 1962

CITED LITERATURE

1. S. G. Mairanovskii, Ya. Koutecký, V. Hanuš, *ZhFKh*, **36**, No. 8-9 (1962).
2. S. G. Mairanovskii, L. I. Lishtet, Izv. AN SSSR, OKhN, 1962, No. 2.
3. S. G. Mairanovskii, *J. Electroanalyt. Chem.*, **3** (1962).
4. V. G. Levich, *DAN*, **67**, 309 (1949).
5. V. G. Levich, *Physicochemical Hydrodynamics*, 1959.
6. H. Matsuda, *J. Phys. Chem.*, **64**, 336 (1960).

7. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, B. N. Kabanov, *Kinetics of Electrode Processes*, Moscow, 1952.

8. S. G. Mairanovskii, *DAN*, **114**, 1272 (1959).

9. Ya. Koutecký, V. Hanuš, S. G. Mairanovskii, *ZhFKh*, **34**, 651 (1960).

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