THE EFFECT OF THE DOUBLE LAYER ON POLAROGRAPHIC VOLUME CATALYTIC HYDROGEN WAVES

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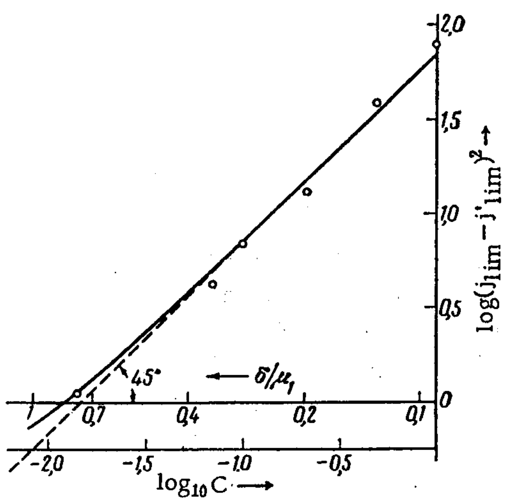
Polarographic catalytic hydrogen waves are caused by the following reaction cycle:

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

$$BH^+ + e^- \overset{el}{\rightleftarrows} BH; \quad \text{(II)}$$

$$2BH \overset{k}{\longrightarrow} 2B + H_2. \quad \text{(III)}$$

According to the scheme (I)−(III) the catalyst exists in the two forms B and BH^+ in protolytic equilibrium. The active form of the catalyst is discharged on the electrode and the product of the electrode reaction, BH, according to the bimolecular mechanism, regenerates the inactive form of the catalyst, B, at the same time liberating hydrogen. DH and D^- are components of the buffer solution (the concentrations of D and DH are considerably in excess of the concentration of the catalyst).



In the catalytic waves produced by pyridine, the preceding and the following chemical reactions (I) and (III) only go in the body of the solution (for all practical purposes the catalyst is not adsorbed at the potentials at which it occurs in the catalytic wave) in the so-called kinetic layers μ_1 and μ_2 respectively. If the pyridine protonation rate constants were found from the polarographic data, it was observed that the rate constants are not constant, but their value changes with change in pH of the solution [1, 2] or in the concentration of the indifferent electrolytes [3]. This was referred to the action of the double layer. Actually, the rate of the preceding reaction (I) is so high that the thickness of the kinetic layer μ_1 corresponding with this reaction is comparable with the thickness of the diffuse part of the double layer δ. Accordingly, the electric field contained within the kinetic layer μ_1 exerts a substantial effect on both the distribution of concentrations and the ionic transfer process. However a change in pH of the solution or in the concentration of the indifferent electrolyte changes the ratio δ/μ_1 and thus changes the values of current density, which were used to calculate the rate constants of the preceding reaction.

The purpose of the present paper is to find the volt-ampere characteristics of the reaction cycle under discussion including the effect of the double layer, and to compare the results obtained with experimental data.

Let us consider the case of most interest in practice, where the concentration of the inactive form of the catalyst, B, in the solution is considerably in excess of the concentration of the active form, BH^+ ($\sigma = [B]_0/[BH^+]_0 \gg 1$, where $[B]_0$ and $[BH^+]_0$ are the concentrations in the body of the solution) and the thickness of the kinetic layer of the following reaction, μ_2, is considerably greater than μ_1 and σ.

Let us designate the concentrations $[BH^+]$, $[B]$ and $[BH]$ by C_1, C_2, and C_3 respectively and introduce the effective rate constant of the monomolecular reaction, $\rho = k_1[DH]$. Taking the origin of coordinates at the Helmholtz plane, for the region $x < \delta$ ($\delta > \mu_1$) or $x < \mu_1$ ($\mu_1 > \delta$) we can write a system of equations similar to the equations in [4] but containing terms which describe how reaction (I) goes inside the region under discussion:

$$D_1 \frac{d}{dx}\left\{\frac{dC_1}{dx} + \frac{C_1 F}{RT}\frac{d\varphi}{dx}\right\} - \rho\sigma C_1 e^{F\varphi/RT} + \rho C_2 = 0,$$
$$D_2 \frac{d^2C_2}{dx^2} + \rho\sigma C_1 e^{F\varphi/RT} - \rho C_2 = 0,$$
$$\frac{d\varphi}{dx} = \frac{RT}{F\delta} e^{-F\varphi/RT}. \qquad (1)$$

The boundary conditions for the system (1) are:

$x = 0$:

$$FD_1\left\{\frac{dC_1}{dx} + \frac{C_1 F}{RT}\frac{d\varphi}{dx}\right\} = j,$$
$$FD_2 \frac{dC_2}{dx} = 0, \quad \varphi = \psi_1; \qquad (2)$$

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

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

In Eqs. (1), (2) and (3), the symbols have 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 concentration of the indifferent electrolyte, Ψ_1 is the potential at the Helmholtz plane ($\exp[F(\Psi_1)/RT] \gg 1$); $C_2^{\mu_1}$ is the value of the concentration which is to be found from the solutions of the equations outside the limits of the region under discussion.

In the range $x > \mu_1, \delta$, where there is practically no electric field and reaction (I) does not occur, the following differential equations hold:

$$D_2 \frac{d^2C_2}{dx^2} + kC_3^2 = 0,$$
$$D_3 \frac{d^2C_3}{dx^2} - kC_3^2 = 0. \qquad (4)$$

In Eqs. (4), no account is taken of the motion of the drop, since it is assumed that the thickness of the layer μ_2 is considerably less than the thickness of the diffuse layer and accordingly any effect of motion of the drop may be neglected [5]. Omitted from these equations are also terms containing derivatives of the concentration with respect to time, since a special calculation has shown that the time required to establish the stationary electrolysis state is less than μ_2^2/D. This latter quantity is in turn considerably less than the dropping period.

In view of the smallness of μ_1 and δ these quantities may be considered equal to zero for the range $x > \mu_1, \delta$. Accordingly the boundary conditions for the system (3) take the form

$x = 0$:

$$FD_2 \frac{dC_2}{dx} = -FD_3 \frac{dC_3}{dx} = j; \qquad (5)$$

$x \to \infty$:

$$C_2 = \gamma, \quad C_3 = 0,$$

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

* At the boundary of the kinetic layer μ_1, the substance BH^+ is in chemical equilibrium with the substance B($C_1 \approx C_2^{\mu_1}/\sigma$) and its current is very small compared with the current of the substance B ($\mu_1 dC_1/dx \ll j\mu_1/FD$, $C_2^{\mu_1}/\sigma$). The solutions of Eqs. (1) must be such as to satisfy the requirements mentioned.

Following the method used in [6] we can find the solution of the system of equations (1)*. For x=0 we have:

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

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

If $\left\{-\frac{F|\psi_1|}{RT}\right\}\frac{\delta}{\mu_1} \ll 1$, 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 where $\left\{-\frac{F|\psi_1|}{RT}\right\}\frac{\delta}{\mu_1} \gg 1$, the coefficient G is equal to

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

The solution of the system of Equations (4) leads to the following values for the concentrations:

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

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

To find the volt-ampere characteristic we use the equation of delayed discharge theory [7]

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

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

In the catalytic waves produced by pyridine, the electrode stage is reversible [8]. Substituting Eqs. (6), (10), and (11) in (12), and keeping in mind the reversibility of the electrode stage, we can find the equation for the volt-ampere characteristic:

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

If the condition is satisfied that

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* In Eqs. (1) we make the change of variables $\xi = e^{-\psi/2}$, $\frac{d}{dx} = -\frac{\xi^2}{2\sigma}\frac{d}{d\xi}$. For the boundary conditions (3) to continue to hold in the case $\mu_1 > \delta$, the region under consideration must be divided in two: $0 \le x < \delta$ and $\delta \le x \le \mu_1$. In the region $\delta \le x \simeq \mu_1$ we solve Eqs. (1) with the values $\varphi = \frac{d\varphi}{dx} = 0$. Further, the solutions fit at the point $x=\delta$.

$$\frac{D_1^{1/3} D_3^{2/3}}{D_2}\left(\frac{\rho}{\sigma k \gamma}\right)^{1/3} G^{-2/3} \ll 1 \quad (14)$$

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

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

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

To get an experimental check on these equations we shall use the data [3] of limiting current variation with the total electrolyte concentration C. For small values of the ratio δ/μ_1 we can get the following equation:

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

where j'_{lim} is the limiting current density neglecting the effect of the double layer [9], the electrolyte concentration C is expressed in moles per liter, and μ_1 is expressed in centimeters. It is observed experimentally that at very large values of electrolyte concentration increasing the concentration any more produces almost no change in the limiting current (Fig. 2 in [3]). This value was taken approximately as the limiting current at which the structure of the double layer no longer has any effect. The points in Fig. 1 show the experimentally determined values of $\log\left(\frac{j'_{\mathrm{lim}}}{j_{\mathrm{lim}} - j'_{\mathrm{lim}}}\right)^2$ as a function of $\log_{10}$ C. As may be seen from the figure, the experimental points give a good fit to a straight line running at 45° (in accordance with Eq. (16)). The deviations lie within the limits of experimental error, and they are apparently due in part to not having taken salt effects into consideration. The intercept which the line makes on the ordinate axis was used to find the thickness of the kinetic layer μ_1 and to construct the curve shown in Fig. 1.

There is a great deal of experimental data on the effect which the pH of the solution [1, 2] (μ_1 changes with change in pH) has on the values of the limiting current and the half-wave potential. These data are in qualitative agreement with the theoretical results. However an accurate comparison between these experimental data and the theory is rendered difficult by the fact that we do not know the true values for the thickness of the kinetic layer μ_1.

LITERATURE CITED

1. S. G. Mairanovskii, Ya. Koutetskii, and V. Ganush, ZhFKh, 36, No. 8-9 (1962).
2. S. G. Mairanovskii and L. I. Lishcheta, 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, Physico-Chemical Hydrodynamics [in Russian] (1959).
6. H. Matsuda, J. Phys. Chem., 64, 336 (1960).
7. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, Kinetics of Electrode Processes [in Russian] Moscow (1952).
8. S. G. Mairanovskii, DAN, 114, 1271 (1959).
9. Ya. Koutetskii, V. Ganush, and S. G. Mairanovskii, ZhFKh, 34, 651 (1960).
