KINETIC AND CATALYTIC CURRENTS AT A HANGING DROP ELECTRODE

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The stationary (hanging) drop electrode is widely used in analytical work on highly dilute solutions. In recent years, the hanging drop electrode has been sucessfully used in a number of electrochemical papers to investigate the mechanism of electrode processes [1].

It has been shown by V. Kemula and coworkers that the hanging drop electrode combined with a cyclically varying polarizing voltage is very convenient for making a study of the free radicals and instable intermediate products occurring in electrochemical reactions. This method has been used to investigate a wide range of electrode reactions involving organic compounds.

In polarization with a slowly varying voltage, the kinetic currents produced by volume changes in the depolarizer have a form in the case of a hanging drop electrode which is different from the plane electrode case [2,3]. The effect of electrode curvature on the kinetic and catalytic currents may be taken account of theoretically.

Consider the simplest kinetic reaction, going according to the scheme

$$A \underset{\rho}{\overset{\rho\sigma}{\rightleftarrows}} B \text{ (in the vol)}; \quad A \rightarrow C \text{ (at electrode)}. \tag{1}$$

We shall further assume that the electrode reaction is fast.

The system may be described by the following equations:

$$\begin{aligned} \frac{\partial a}{\partial t} &= D\left(\frac{\partial^2 a}{\partial r^2} + \frac{2}{r}\frac{\partial a}{\partial r}\right) + \rho\,(b - \sigma a), \\ \frac{\partial b}{\partial t} &= D\left(\frac{\partial^2 b}{\partial r^2} + \frac{2}{r}\frac{\partial b}{\partial r}\right) - \rho\,(b - \sigma a), \end{aligned} \tag{2}$$

where a and b are the concentrations of substances A and B, and it is assumed that $D_A = D_B = D$.

The initial concentrations a_0 and b_0 are related by the chemical equilibrium condition

$$b_0 = \sigma a_0. \tag{3}$$

For the kinetic reaction (1), the conditions on the electrode may be written in the form

$$a = 0, \quad \left(\frac{\partial b}{\partial r}\right) = 0 \text{ where } r = r_0 \tag{4}$$

Introduce further the dimensionless variables

$$x = \frac{r - r_0}{r_0}, \quad \tau = \frac{Dt}{r_0^2} \tag{5}$$

and the new functions

$$\Psi = \frac{r}{r_0}\,(b - \sigma a), \quad \Phi = \frac{r}{r_0}\,(a + b). \tag{6}$$

After this substitution, Eq. (2) reduces to

$$\begin{aligned} \frac{\partial \Phi}{\partial \tau} &= \frac{\partial^2 \Phi}{\partial x^2}, \\ \frac{\partial \Psi}{\partial \tau} &= \frac{\partial^2 \Psi}{\partial x^2} - \varkappa \Psi, \end{aligned} \tag{7}$$

where

$$\varkappa = \frac{\rho(1+\sigma) r_0^2}{D}. \tag{8}$$

The boundary conditions take the form:
at the electrode (x = 0)

$$\begin{gathered}\Phi(0, \tau) = \Psi(0, \tau),\\ \sigma\left(\frac{\partial \Phi}{\partial x}\right)_0 + \left(\frac{\partial \Psi}{\partial x}\right)_0 - (1+\sigma)\Phi(0, \tau) = 0;\end{gathered} \tag{9}$$

far from the electrode ($x \to \infty$) (and the initial conditions for $\tau = 0$)

$$\Psi = 0, \qquad \Phi = a_0(1+\sigma)(1+x). \tag{10}$$

The desired kinetic current is written in the following way:

$$j = D\left(\frac{\partial a}{\partial r}\right)_{r=r_0} = \frac{D}{r_0(1+\sigma)}\left[\left(\frac{\partial \Phi}{\partial x}\right)_0 - \left(\frac{\partial \Psi}{\partial x}\right)_0\right]. \tag{11}$$

We shall further solve the diffusion problem posed, by reduction to integral equations. For this purpose we introduce the two unknown functions

$$\left(\frac{\partial \Phi}{\partial x}\right)_{x=0} = u(\tau), \quad \left(\frac{\partial \Psi}{\partial x}\right)_{x=0} = v(\tau).$$

Using the Duhamel integral [4] for the values of the functions $\Phi(x, \tau)$ and $\Psi(x, \tau)$ at the boundary (x = 0), we can write the following expressions:

$$\Phi(0, \tau) = a_0(1+\sigma)\left(1 + 2\sqrt{\frac{\tau}{\pi}}\right) - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{u(\theta)\,d\theta}{\sqrt{\tau-\theta}}; \tag{12}$$

$$\Psi(0, \tau) = -\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{e^{-\varkappa(\tau-\theta)}}{\sqrt{\tau-\theta}}\, v(\theta)\,d\theta. \tag{13}$$

Equation (13) is a modification of the Duhamel integral for the case of a diffusion equation with volume sources.

Substituting (12) and (13) in the boundary conditions (at x = 0), gives a system of integral equations for finding $u(\tau)$ and $v(\tau)$.

$$\begin{gathered}a_0(1+\sigma)\left(1 + 2\sqrt{\frac{\tau}{\pi}}\right) - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{u(\theta)\,d\theta}{\sqrt{\tau-\theta}} = -\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{v(\theta)\,e^{-\varkappa(\tau-\theta)}}{\sqrt{\tau-\theta}}\,d\theta,\\ \sigma u + v = (1+\sigma)\left[a_0(1+\sigma)\left(1 + 2\sqrt{\frac{\tau}{\pi}}\right) - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{u(\theta)\,d\theta}{\sqrt{\tau-\theta}}\right].\end{gathered} \tag{14}$$

The kinetic current may be written in the form

$$j = D\left(\frac{\partial a}{\partial r}\right)_{r=r_0} = \frac{D}{r_0(1+\sigma)}[u(\tau) - v(\tau)]. \tag{15}$$

The solution of the system of integral equations (14) will be looked for with the aid of the Laplace transformation. Introduce the expressions

$$U(p) = p\int_0^\infty e^{-p\tau} u(\tau)\,d\tau, \quad V(p) = p\int_0^\infty e^{-p\tau} v(\tau)\,d\tau. \tag{16}$$

After carrying out the Laplace transformation in the system of integral equations (14), we obtain a system of algebraic equations for finding U(p) and V(p):

$$\begin{gathered}U - V\sqrt{\frac{p}{p+\varkappa}} = a_0(1+\sigma)(1+\sqrt{p}),\\ \left(\frac{\sigma\sqrt{p}}{1+\sigma} + 1\right)U + \frac{\sqrt{p}}{1+\sigma}V = a_0(1+\sigma)(1+\sqrt{p}).\end{gathered} \tag{17}$$

From the solution of the system (17) we obtain for the Laplace transform of the desired current

$$\mathcal{L}(j) = \frac{D}{r_0(1+\sigma)}(U-V) = \frac{Da_0(1+\sigma)}{r_0}\,\frac{(1+\sqrt{p})(1+\sqrt{p+\varkappa})}{(1+\sqrt{p+\varkappa})+\sigma(1+\sqrt{p})}\,. \tag{18}$$

Finding the original of the above expression in general form is a complicated problem.

We shall limit ourselves to a discussion of some limiting cases, which, however, are of most interest to the theory of kinetic currents.

We shall further assume that the chemical equilibrium is shifted toward the substance B, i.e., $\sigma \gg 1$. In the usual way, we introduce the thickness of the kinetic layer [3]

$$\mu = \sqrt{\frac{D}{p\sigma}}\,. \tag{19}$$

a) In case there are rapid volume chemical changes in the depolarizer ($\varkappa \gg 1$, or $r_0 \gg \mu$) for instants of time $\tau > 1/\varkappa$, it may be assumed that a quasi-steady state chemical equilibrium is set up. The Laplace transform of the current at the electrode for these values of the time may be represented in the form

$$\mathcal{L}(j) = \frac{Da_0\sigma}{r_0}\,\frac{\sqrt{\varkappa}(1+\sqrt{p})}{\sqrt{\varkappa}+\sigma(1+\sqrt{p})}\,. \tag{20}$$

From Eq. (20) using [5], we obtain the following expression for the kinetic current expressed in dimensional variables:

$$j = \frac{Db_0}{r_0+\sigma\mu}\left\{1 - e^{(1/r_0+1/\sigma\mu)^2 Dt}\,\operatorname{erfc}\left[\left(\frac{1}{r_0}+\frac{1}{\sigma\mu}\right)\sqrt{Dt}\right]\right\}. \tag{21}$$

As $r_0 \to \infty$, Eq. (21) assumes the form of the kinetic current at a plane electrode [3]

$$j_{\text{plane}} = \frac{Db_0}{\sigma\mu}\,e^{Dt/(\sigma\mu)^2}\,\operatorname{erfc}\left(\frac{\sqrt{Dt}}{\sigma\mu}\right). \tag{22}$$

As $t \to \infty$, (21) reduces to

$$j = \frac{Db_0}{r_0+\sigma\mu} \tag{23}$$

and, in contrast with a plane electrode, remains finite.

Two cases are possible: 1) $r_0 \gg \sigma\mu$, and 2) $r_0 \ll \sigma\mu$. In these cases, Eqs. (21) and (23) become simpler. It should be noted that since $\sigma \gg 1$, neither case contradicts the condition $r_0 \gg \mu$.

For $r_0 \gg \mu\sigma$, it follows from Eq. (21) that at the initial instants of time (but for $t > 1/p\sigma$), electrode curvature is not very important, and the kinetic current may be represented in the form (22). However as $\tau \to \infty$, (21) reduces to $j = Db_0/r_0$. As in the case of a plane electrode, the kinetic current (21) is determined by the supply to the electrode of the nondischarging substance B. However, in the case of a hanging drop electrode, the diffusion current of the substance B shows the features characteristic of a spherical electrode.

b) For slow volume chemical reactions ($\varkappa \ll 1$, or $r_0 \ll \mu$), the Laplace transform (18) may be expanded in a convergent infinite series. Limiting ourselves to the first term of the series, we obtain the following expression for the current at the electrode:

$$j = \frac{Da_0}{r_0}\left[1 + \frac{r_0 e^{-Dt/\mu^2}}{\sqrt{\pi Dt}} + \frac{r_0}{\mu}\operatorname{erf}\sqrt{\frac{Dt}{\mu^2}}\right]. \tag{24}$$

It follows from (24) that the volume chemical reaction introduces a small correction to the usual diffusion current of substance A.

Consider the case of a catalytic reaction going by a quasi-monomolecular mechanism, which may be represented by the scheme

$$\mathrm{A} \underset{p}{\overset{p\sigma}{\rightleftarrows}} \mathrm{B}\ \text{(in the vol.)},\quad \mathrm{A} \to \mathrm{B}\ \text{(at the electrode)} \tag{25}$$

Assuming the electrode reaction to be fast, instead of (4), the following boundary conditions must be imposed on the electrode

$$a = 0, \quad \left(\frac{\partial a}{\partial r}\right) = -\left(\frac{\partial b}{\partial r}\right) \text{ where } r = r_0. \tag{26}$$

Retaining the previous notation, we obtain for x = 0, instead of (9)

$$\begin{gathered} \Phi(0, \tau) = \Psi(0, \tau) \\ \left(\frac{\partial \Phi}{\partial x}\right)_0 - \Phi(0, \tau) = 0. \end{gathered} \tag{27}$$

Further, instead of (17) we obtain the system of algebraic equations

$$\begin{gathered} U - V\sqrt{\frac{p}{p+\varkappa}} = a_0(1+\sigma)(1+\sqrt{p}), \\ U(1+\sqrt{p}) = a_0(1+\sigma)(1+\sqrt{} \end{gathered} \tag{28}$$

[illegible]

The density of the catalytic current to the electrode may easily be found exactly. It is of the form (24). In contrast with the kinetic current, Eq. (24) is the catalytic current for any degree of reversibility of the volume chemical reaction. Introduce the quantity

$$\mu = \sqrt{\frac{D}{\rho(1+\sigma)}}. \tag{29}$$

As $r_0 \to \infty$, Eq. (24) reduces to the expression for the catalytic current at a plane electrode [6]. For large values of the time ($t \to \infty$), Eq. (24) reduces to

$$j = Da_0\left(\frac{1}{r_0} + \frac{1}{\mu}\right). \tag{30}$$

It follows from an analysis of Eq. (24) for the catalytic current on a hanging drop electrode that the effective electrode curvature is only important in the case of a slow volume chemical reaction ($r_0 \ll \mu$), and for instants of time, $t > r_0^2/D$.

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