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Abstract

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KINETIC AND CATALYTIC CURRENTS AT A HANGING DROP ELECTRODE

The stationary (hanging) drop electrode is widely used in analytical studies of highly dilute solutions. In recent years, in a number of electrochemical works the hanging drop electrode has been successfully used to study the mechanism of electrode processes ([1]).

As V. Kemula and his coworkers have shown, the hanging drop electrode, in combination with a cyclically varying polarizing voltage, is very convenient for investigating free radicals and unstable intermediate products of electrochemical reactions. By this method a broad range of electrode processes involving organic compounds has been studied.

When polarization is carried out with a slowly varying voltage, the kinetic currents arising as a result of bulk transformations of the depolarizer have, in the case of the hanging drop electrode, a form different from that for a plane electrode ([2,3]). The influence of the curvature of the electrode on kinetic and catalytic currents can be taken into account theoretically.

Let us consider the simplest kinetic process proceeding according to the scheme

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

We shall further assume that the electrode reaction is fast. The system can be described by the following equations:

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

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

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 condition of chemical equilibrium

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

For the kinetic process (1), the conditions at the electrode may be written in the form

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

We next introduce dimensionless variables

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

and new functions

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

After the indicated substitution, equations (2) become

$$\frac{\partial \Phi}{\partial \tau} = \frac{\partial^2 \Phi}{\partial x^2},$$

$$\frac{\partial \Psi}{\partial \tau} = \frac{\partial^2 \Psi}{\partial x^2} - \chi \Psi, \tag{7}$$

where

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

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

$$\Phi(0, \tau) = \Psi(0, \tau),$$

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

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

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

The kinetic current sought is written as follows:

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

We shall next solve the diffusion problem posed by reducing it to integral equations. For this purpose we introduce two unknown functions

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

With the aid of Duhamel' s integral [4], the following expressions may be written for the values of the functions $\Phi(x,\tau)$ and $\Psi(x,\tau)$ at the boundary ($x = 0$):

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

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

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

Substituting (12) and (13) into the boundary conditions (at $x = 0$), we obtain a system of integral equations for determining $u(\tau)$ and $v(\tau)$.

$$a_0(1+\sigma)\left(1 + 2\sqrt{\frac{\tau}{\pi}}\right) - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{u(\theta)\,d\theta}{\sqrt{\tau-\theta}} = -\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{v(\theta)e^{-\chi(\tau-\theta)}}{\sqrt{\tau-\theta}}\,d\theta,$$

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

The kinetic current may be written in the form

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

We shall seek the solution of the system of integral equations (14) by means of the Laplace transform. We introduce

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

Carrying out the Laplace transform in the system of integral equations (14), we obtain a system of algebraic equations for determining $U(p)$ and $V(p)$:

$$U - V\sqrt{\frac{p}{p+\chi}} = a_0(1+\sigma)(1+\sqrt{p}),$$

$$\left(\frac{\sigma\sqrt{p}}{1+\sigma}+1\right)U + \frac{\sqrt{p}}{1+\sigma}V = a_0(1+\sigma)(1+\sqrt{p}). \tag{17}$$

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

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

In general form, finding the inverse of the expression obtained is a difficult problem.

We shall restrict ourselves to considering certain limiting cases which, however, are of greatest interest in the theory of kinetic currents.

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

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

a) In the case of rapid bulk chemical transformations of the depolarizer ($\chi \gg 1$ or $r_0 \gg \mu$), for times $\tau > 1/\chi$ it may be assumed that a quasi-stationary chemical equilibrium is established. The Laplace transform of the current at the electrode for such time values may be represented in the form

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

From expression (20), with the aid of ([5]), we obtain the following expression for the kinetic current, written in dimensional variables:

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

For $r_0 \to \infty$, formula (21) takes 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) becomes

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

and, in contrast to the plane electrode, remains finite.

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

For $r_0 \gg \mu\sigma$, it follows from (21) that at the initial instants of time (but with $t > 1/\rho\sigma$) the curvature of the electrode is of little importance and the kinetic current may be represented in the form (22). However, as $t \to \infty$, (21) becomes $j = Db_0/r_0$. As in the case of a plane electrode, the kinetic current (21) is determined by the supply to the electrode of the uncharged substance B. However, in the case of a hanging drop electrode the diffusion flux of substance B has the features characteristic of a spherical electrode.

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

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

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

Let us consider the case of a catalytic reaction proceeding by a quasi-monomolecular mechanism, which can be represented by the scheme

$$\mathrm{A} \underset{\rho}{\overset{\rho\sigma}{\rightleftarrows}} \mathrm{B}\ \text{(in the bulk)}, \qquad \mathrm{A} \to \mathrm{B}\ \text{(at the electrode)}. \tag{25}$$

Assuming the electrode reaction to be fast, instead of (4) the following boundary conditions should be imposed at the electrode:

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

Keeping the previous notation, instead of (9) we obtain, at $x = 0$,

$$\Phi(0, \tau) = \Psi(0, \tau)$$

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

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

$$U - V\sqrt{\frac{p}{p + \varkappa}} = a_0(1 + \sigma)(1 + \sqrt{p}),$$

$$U(1 + \sqrt{p}) = a_0(1 + \sigma)(1 + \sqrt{p}). \tag{28}$$

The density of the catalytic current at the electrode can be readily found exactly. It has the form (24). In contrast to the kinetic current, expression (24) represents the catalytic current for any degree of reversibility of the bulk chemical reaction. Let us introduce

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

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

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

From analysis of formula (24) for the catalytic current at a hanging drop electrode, it follows that the curvature of the electrode has a substantial effect only in the case of a slow bulk chemical reaction ($r_0 \lesssim \mu$) and for times $t > r_0^2/D$.

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