

# INACTIVATION OF THE DEPolarIZER CATALYZED BY THE DEPolarIZATION PRODUCT AT THE ELECTRODE\*

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A theory for galvanostatic electrolysis was derived where the depolarizer is inactivated at the electrode with a rate proportional to the product of its concentration and the amount or concentration of the electrode reaction product. The solution is given for the case where the depolarization product is completely adsorbed on the electrode surface, as well as for the case where it diffuses back into the solution. The inactivation rate constant and the diffusion coefficient of the depolarizer can be determined by comparing the dependence of the quantity  $i\sqrt{\tau}/c_0^*$  on  $\log(c_0^*\tau)$  with calculated dependences, where  $c_0^*$  denotes depolarizer concentration in solution,  $\tau$  transition time and  $i$  current density.

The solution of many cases of preceding and interposed chemical reactions in the galvanostatic method<sup>1-5</sup> showed always that the mechanisms influencing the limiting current in polarography manifest themselves also in the transition times. To supplement the possibilities of the galvanostatic method, we present the results for the case of a catalytic inactivation of the depolarizer by the depolarization product, which was discovered with some chromium complexes and solved in polarography<sup>6</sup>.

## RESULTS AND DISCUSSION

Catalytic inactivation of the depolarizer, O, by the depolarization product, R, is described schematically as



where Z means an electroinactive substance. We shall distinguish two limiting cases: a) R is completely adsorbed on the electrode surface so that inactivation proceeds only just on the electrode, b) R is not adsorbed and diffuses into the solution so that inactivation proceeds in the diffusion layer. We assume that the depolarizer is not

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adsorbed and is transported to the electrode surface by diffusion. In polarography, only the case *a* was solved.

*Case a.* The problem is described mathematically by the following equations (compare<sup>6</sup>).

$$\partial c_0 / \partial t = D \partial^2 c_0 / \partial x^2, \quad (1)$$

$$t = 0, \quad x \geq 0: \quad c_0 = c_0^*; \quad t \geq 0, \quad x \rightarrow \infty: \quad c_0 = c_0^*, \quad (2a)$$

$$x = 0, \quad t > 0: \quad D \partial c_0 / \partial x = i/nF + itkc_0/nF. \quad (2b)$$

We introduce the following dimensionless parameters:

$$\varphi = c_0/c_0^*, \quad y = kc_0^*t, \quad g = 2i/nFc_0^*(\pi kc_0^*D)^{1/2}, \quad (3)$$

and obtain the solution in the form

$$\varphi = 1 - g \sqrt{y} - \frac{1}{2}gy^{3/2} \int_0^1 \varphi(u)y(1-u)^{-1/2} u \, du. \quad (4)$$

For the transition time  $\tau$  we have

$$\varphi_\tau = 0, \quad y_\tau = kc_0^*\tau, \quad g \sqrt{y_\tau} = 2i \sqrt{\tau/nFc_0^*} \sqrt{(\pi D)} = i \sqrt{\tau}/(i \sqrt{\tau})_0, \quad (5)$$

where  $(i \sqrt{\tau})_0$  denotes the value of  $i \sqrt{\tau}$  for the case where no inactivation takes place ( $k = 0$ ). We assume that the dependence of  $\varphi$  on  $y$  has the form of a power series:

$$\varphi(y) = \sum_i a_i y^{\alpha_i} \quad (6)$$

and obtain from Eq. (4)

$$\alpha_i = i/2, \quad a_0 = 1, \quad a_1 = -g, \quad a_2 = a_{3k+2} = 0, \\ i > 2: \quad a_i = \frac{1}{2}g \sqrt{\pi} [\Gamma(\alpha_{i-3} + 2)/\Gamma(\alpha_{i-3} + \frac{3}{2})] a_{i-3}. \quad (7)$$

The beginning of the expansion has the form

$$\varphi = 1 - g \sqrt{y} - \frac{3}{2}gy^{3/2} + (3\pi/16)g^2y^2 + (5\pi/48)g^2y^2 - \dots \quad (8)$$

With increasing  $y$  the convergence of this series becomes worse. The dependence of  $g \sqrt{y_\tau}$  on  $\log y_\tau$  calculated for  $y_\tau < 50$ , i.e.  $g \sqrt{y_\tau} > 0.68$ , is shown in Fig. 1. The calculation was performed on a computer in two ways. First, from Eqs (5)–(7),

the series being stopped at the term which was smaller than  $10^{-7}$ . Second, by solving Eq. (4) numerically by the method developed previously<sup>7</sup>. The results obtained were in both cases the same for  $y_\tau < 50$  but differed for  $y_\tau > 50$  as a result of both the worsening convergence of the series (6) and abruptly changing dependence of  $\varphi$  on  $y$ . Therefore, the dependence of  $g \sqrt{y_\tau}$  on  $\log y_\tau$  in Fig. 1 ends at  $y_\tau = 50$ .

Case b. The problem is described by the equations

$$\partial c_O / \partial t = D \partial^2 c_O / \partial x^2 - k c_O c_R, \quad \partial c_R / \partial t = D \partial^2 c_R / \partial x^2, \quad (9a, b)$$

$$(10a)$$

$$t = 0, \quad x \geq 0: \quad c_O = c_O^*, \quad c_R = 0; \quad t \geq 0, \quad x \rightarrow \infty: \quad c_O = c_O^*, \quad c_R = 0,$$

$$x = 0, \quad t > 0: \quad D \partial c_O / \partial x = -D \partial c_R / \partial x = i / n F. \quad (10b)$$

We assume for simplicity that the diffusion coefficients of the substances O and R are the same and we introduce dimensionless parameters  $y$  and  $g$  defined by Eq. (3) and

$$\varphi_O = c_O / c_O^*, \quad \varphi_R = c_R / c_O^*, \quad z = x \sqrt{(k c_O^* / D)}. \quad (11)$$

Thus, the system of the above equations can be rewritten as

$$\partial \varphi_O / \partial y = \partial^2 \varphi_O / \partial z^2 - \varphi_O \varphi_R, \quad \partial \varphi_R / \partial y = \partial^2 \varphi_R / \partial z^2, \quad (12a, b)$$

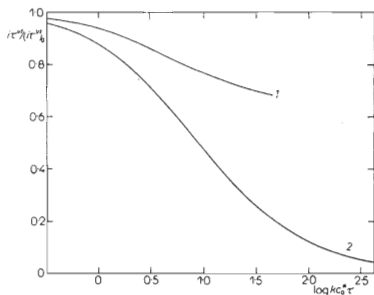


FIG. 1

Theoretical Dependence of the Ratio  $i\sqrt{\tau}/(i\sqrt{\tau})_0$  on  $\log(kc_0^*\tau)$  for the Case of Inactivation Catalyzed by the Depolarization Product

The product is 1 completely adsorbed on the electrode, 2 diffuses into the solution.

$$\begin{aligned} y = 0, \quad z \geq 0: \quad \varphi_O = 1, \quad \varphi_R = 0; \quad y > 0, \quad z \rightarrow \infty: \quad \varphi_O = 1, \quad \varphi_R = 0, \\ z = 0, \quad y < 0: \quad \partial\varphi_O/\partial z = -\partial\varphi_R/\partial z = \frac{1}{2}g\sqrt{\pi}. \end{aligned} \quad (13b)$$

This system of equations together with (5) define the dependence of  $y_x$  on  $g$ . The numerical solution was carried out by the previously elaborated method of network with extrapolation<sup>8</sup>. The calculated dependence of  $g\sqrt{y_x}$  on  $\log y_x$  is shown in Fig. 1.

It is seen that in both cases the inactivation rate constant,  $k$ , and the diffusion coefficient,  $D$ , can be determined by comparing the experimental dependence of  $i\sqrt{\tau}/c_0^*$  on  $\log(c_0^*\tau)$  with the dependences shown in Fig. 1. The agreement of the dependences is an evidence for the validity of the presumed reaction mechanism. If the behaviour of the substance R is intermediate between the discussed limiting cases of total adsorption and pure diffusion, the course of the studied dependence can be expected to lie between the limiting ones.

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