IRREVERSIBLE FOLLOW-UP REACTIONS ACCELERATED BY ELECTRODE SURFACE IN GALVANOSTATIC CURRENT REVERSAL METHODS*
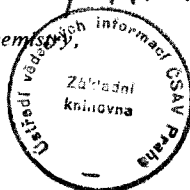
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The cases of an irreversible follow-up first-order reaction and an irreversible follow-up second order reaction proceeding homogeneously and at the same time heterogeneously on the electrode surface are solved for the galvanostatic method with current reversal. For a sufficiently long time of the reversal, t_1, the transition time, τ', after the reversal is independent of t_1. The solution is presented in the form of diagrams with which the experimental results can be compared to determine the rate constants of the homogeneous and heterogeneous reactions. For a first-order reaction, the dependence of $\log \tau'$ on $\log u$ can be used, while for a second-order reaction the $\log \tau'$–$\log j$ dependence is preferred, where j is the current density before the current reversal and u the ratio of current intensities after and before the current reversal. With both reactions, the slope of these dependences increases with the rate of the surface reaction, however in the case of a second-order reaction only slightly.

If chemical reactions coupled with electrode processes are studied by electrochemical methods, the results can be considerably influenced by the electrode surface, which is manifested most often by adsorption. Another influence of the electrode surface consists in accelerating the chemical reaction of electroactive substances.

For the galvanostatic method of the current reversal, the influence of adsorption on the measurement of chemical reaction rates was already treated mathematically[1,2]. To broaden the possibilities of the galvanostatic method, also the other mentioned effect should be studied. The most suitable, simple model of the influence of the electrode surface on a chemical reaction rate is represented by a chemical reaction proceeding homogeneously in the bulk of the electrolyte and at the same time heterogeneously on the electrode surface. At the usual conditions of measurement by the mentioned method, the accelerating effect of the electrode surface is in the case of reversible, follow-up chemical reactions not manifested in the form of the found dependences. Only the values of the found kinetic parameters are changed. Hence, such a case cannot be experimentally distinguished from others. In contrast, in the case of

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irreversible follow-up reactions such an influence can be revealed, as shown below. We therefore solved the cases of irreversible follow-up first-order and second-order reactions for the mentioned model.

THEORETICAL

Irreversible Follow-up First-Order Reaction

For an irreversible follow-up first-order reaction proceeding both in the solution with a homogeneous rate constant k and on the electrode surface with a heterogeneous rate constant m, the problem is for the galvanostatic method with current reversal described by the equations

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - kC, \tag{1}$$

$$t = 0: \quad C = 0; \quad x \to \infty: \quad C \to 0, \tag{2a}$$

$$x = 0, \quad t < t_1: \quad D\partial C/\partial x = -j/nF + mC, \tag{2b}$$

$$x = 0, \quad t > t_1: \quad D\partial C/\partial x = ju/nF + mC, \tag{2c}$$

where the other symbols are the same as in the preceding paper[2]. The solution of this system by the method of the Laplace transformation gives the Laplace transform of the concentration,

$$\bar{C} = \frac{j[1 - (u + 1) e^{-pt_1}]}{nFp \sqrt{D}[m/\sqrt{D} + (p + k)^{1/2}]} \exp\left[-x(p + k)^{1/2}/\sqrt{D}\right], \tag{3}$$

whose retransformation gives for the concentration on the electrode surface

$$t > t_1: \quad C_{x=0} = \left[jm/nF(m^2 - kD)\right]\{1 - [(kD)^{1/2}/m] \operatorname{erf}(kt)^{1/2} -$$
$$- \exp\left(m^2 t/D - kt\right) \operatorname{erfc}\left(m \sqrt{t}/\sqrt{D}\right) -$$
$$- (u + 1)\{1 - [(kD)^{1/2}/m] \operatorname{erf}[k(t-t_1)]^{1/2} -$$
$$- \exp\left[(m^2/D - k)(t-t_1)\right] \operatorname{erfc}[(t-t_1)^{1/2} m/\sqrt{D}]\}\}. \tag{4}$$

We introduce the dimensionless parameter

$$g = m/(kD)^{1/2}, \tag{5}$$

which is a measure for the acceleration of the chemical reaction by the electrode surface. From Eq. (3) it follows further that

$$t < t_1, \quad kt \to \infty: \quad C_{x=0} = j/nF[m + (kD)^{1/2}], \tag{6}$$

whence it is seen that the concentration of the depolarization product at the electrode surface prior to the current reversal is at a sufficiently long duration of the electrolysis such as it would be in the case of a chemical reaction without the surface effect proceeding at a rate given by the effective rate constant

$$k_{ef} = k(g + 1)^2. \tag{7}$$

As in the preceding work[2], we shall further discuss only the case where the time of current reversal, t_1, is sufficiently large. If the inequality

$$k_{ef}t_1 > 6 \tag{8}$$

is fulfilled, we obtain from Eq. (4) analogously as before[2] a simplified expression for the transition time τ' after the current reversal:

$$g - 1 = (u + 1)\{g - \mathrm{erf}\,[(k_{ef}\tau')^{1/2}/(g + 1)]$$
$$-g \exp\,[k_{ef}\tau'(g - 1)/(g + 1)]\,\mathrm{erfc}\,[(k_{ef}\tau')^{1/2}g/(g + 1)]\}. \tag{9}$$

This is an implicit form of the dependence of $k_{ef}\tau'$ on u and g. For $g = 1$, Eq. (9) takes the form of an identity. By performing the limit, we obtain for this case

$$g = 1: \quad 2/(u + 1) = 2 - (2 + k_{ef}\tau')\,\mathrm{erfc}\,[(k_{ef}\tau')^{1/2}/2] +$$
$$+ (k_{ef}\tau')^{1/2} \exp\,(-k_{ef}\tau'/4). \tag{10}$$

The curves obtained by solving Eq. (9) or (10) numerically are shown in Fig. 1.

Irreversible Follow-up Second-Order Reaction

For an irreversible follow-up second-order reaction proceeding in the solution with a homogeneous rate constant k and on the electrode surface with a heterogeneous rate constant m, the mathematical formulation of the problem is as follows:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - kC^2, \tag{11}$$

$$t = 0: \quad C = 0; \quad x \to \infty: \quad C \to 0, \tag{12a}$$

$$x = 0, \quad t < t_1: \quad D\partial C/\partial x = -j/nF + mC^2, \tag{12b}$$

$$x = 0, \quad t > t_1: \quad D\partial C/\partial \ = ju/nF + mC^2. \tag{12c}$$

For a sufficiently long time before the current reversal, if $kC_{x=0}\, t \gg 1$, the solution of Eq. (11) with the condition $(12a)$ for $t < t_1$ is[3]

$$C = [x(k/6D)^{1/2} + N]^{-2}\,,\qquad(13)$$

where N is an integration constant. We now introduce the dimensionless quantities

$$b = jm^3/nF(kD)^2\,,\quad \psi = m^2/kDN^2\,,\qquad(14),(15)$$

and obtain from Eq. $(12b)$

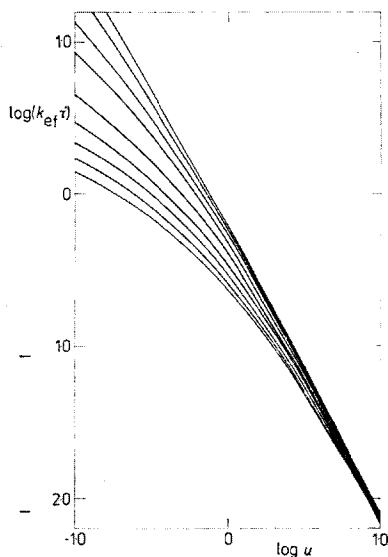$$\psi^2 + \psi^{3/2}\,\sqrt{(2/3)} = b\,.\qquad(16)$$

FIG. 1

Dependence of $\log(k_{\rm ef}\tau')$ on $\log u$ for Various g Values in the Case of an Irreversible Follow-up, First-Order Reaction

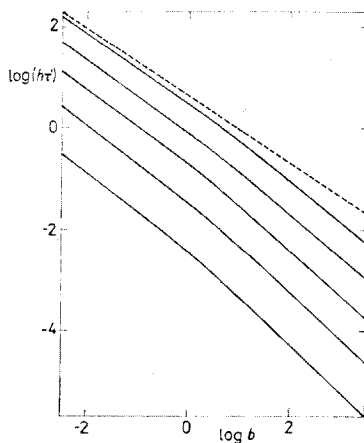Values of g for the curves beginning from below: 0, 0·2, 0·5, 1, 2, 5, 10, 30, 1 000.

FIG. 2

Dependence of $\log(h\tau')$ on $\log b$ for Various u Values in the Case of an Irreversible Follow-up, Second-Order Reaction

$h = k^2 D/m^2$. Values of u for the curves beginning from below: 10, 3, 1, 1/3, 1/10. Dashed curve indicates the slope of the dependence of $\log \tau'$ on $\log j$ for an irreversible follow-up, second-order reaction without the effect of the electrode surface $(b \sim j)$.

This equation gives the dependence of ψ on b in the implicit form. Further we shall use the dimensionless variables

$$\varphi = CN^2, \quad z = x\sqrt{k/N}\sqrt{D}, \quad y = k(t - t_1)/N^2 \qquad (17)$$

defined as in ref.[3], whereby we obtain for $t > t_1$ the following formulation of the problem:

$$\partial\varphi/\partial y = \partial^2\varphi/\partial z^2 - \varphi^2 \qquad (18)$$

$$z \to \infty: \quad \varphi \to 0; \quad y = 0: \quad \varphi = (1 + z/\sqrt{6})^{-2}, \qquad (19a, b)$$

$$y > 0, \quad z = 0: \quad \partial\varphi/\partial z = ub\psi^{-3/2} + \varphi^2\sqrt{\psi}. \qquad (19c)$$

It follows from Eqs (16), (18) and (19) that $\varphi = \varphi(z, y, u, b)$, so that we arrive in the same way as in ref.[3] to the equation

$$\tau'k^2D/m^2 = y_\tau/\psi = \mathrm{f}(u, b), \qquad (20)$$

where y_τ is defined as

$$\varphi(y_\tau, u, b)_{z=0} = 0. \qquad (21)$$

The system of equations (16), $(18)-(21)$ was solved numerically by the method described in our previous paper[4]. The value of $\varphi = \varphi_0$ for the electrode surface was calculated from the equation

$$\varphi_0 = \{[1 + 2\,\Delta z\sqrt{\psi}(\varphi_1 - ub\psi^{-3/2}\,\Delta z/2)]^{1/2} - 1\}/\Delta z\sqrt{\psi}, \qquad (22)$$

which follows from $(19c)$ for the mesh spacing used; φ_1 is the value of φ for the first knot on the z axis. The resulting dependences of $\log(\tau'k^2D/m^2)$ on $\log b$ for various u values are shown in Fig. 2.

DISCUSSION

As could be expected, also irreversible follow-up reactions accelerated by the electrode surface preserve the characteristic features of irreversible follow-up reactions: for a sufficiently long time of the current reversal, t_1, the transition time, τ', after the current reversal is independent of t_1. For irreversible follow-up, first-order reaction, also the independence of τ' on the current, j, is preserved.

It is seen from Fig. 1 that an increasing rate of an irreversible first-order reaction on the electrode surface (corresponding to an increasing value of g) is manifested by an increase of the slope of the $\log \tau'- \log u$ dependence (u = current after reversal/ /current before reversal). In contrast, adsorption of the depolarization product is

manifested by a decrease of the slope of this dependence[2]. Hence, if the dependence of log τ' on log u is more steep than would correspond to a homogeneous reaction without the influence of the electrode surface, it can be concluded that the reaction is accelerated by the electrode surface without a substantial adsorption of the depolarization product. If, on the contrary, it is less steep, it can be concluded that adsorption of the depolarization product plays a role, provided that the ECE mechanism, which would cause the same effect[5], is excluded (*e.g.*, by following the dependence of τ' on t_1 at small values of t_1).

By comparing the experimental dependence of log τ' on log u with the curves in Fig. 1 it is possible to determine the values of g and k_{ef} and then with the aid of Eqs (5) and (7) to evaluate the rate constants of the volume and surface reactions.

It is seen from Fig. 2 representing the dependence of log τ' on log j for an irreversible follow-up, second-order reaction that an increasing rate of the reaction on the electrode surface (corresponding to increasing b) is in this case not appreciably manifested on the experimental dependences. The dependence of log τ' on log j is somewhat convex and somewhat steeper than the straight line corresponding to a homogeneous reaction without the influence of the electrode surface, however in other known cases of such dependences the increase in the slope and curvature is much more pronounced[6]. Also the slope of the log τ'– log u dependence at constant j increases with the rate of the surface reaction, but only slightly as can be seen from the sequence of the curves in Fig. 2. By comparing these curves with experimental log τ' – log j dependences it is possible to determine the factors by which the quantities j and τ' in Eqs (11) and (20) are multiplied and from them to determine the rate constants of the volume and surface reactions. However, it follows from the weak influence of the rate of the surface reaction on the discussed dependences that the rate constant of the surface reaction will be subject to a large error.

Our simple model of a reaction proceeding homogeneously in the solution and at the same time heterogeneously on the electrode surface can be adequate, *e.g.*, in the case of a catalytic effect of the electrode material or adsorption of a catalyst on the electrode surface, and in some cases of the influence of the electrode double layer. The effect of an adsorbed catalyst on the inactivation of a substance was indeed observed[7] and the influence of the electrode double layer on the chemical reaction rate was investigated theoretically by numerous authors (for survey see *e. g.* [8,9]). In the case of changes of the rate constants in a layer at the electrode surface (*e.g.*, certain effects of the double layer), it is, of course, necessary for the application of our model that the thickness of this layer be much smaller than that of the reaction layer. For example, in the case of a first-order reaction the condition $(D/k_{ef})^{1/2} \gg d$ must be fulfilled, where d denotes the thickness of the layer in which the value of k is appreciably different from that in the solution. The formal surface rate constant, m, in our model is then given by the integral of the rate constant increment in this layer, $m = \int_0^\infty [k(x) - k(\infty)]\, dx$, where x denotes the distance from the electrode surface.

Further it is necessary for the application of our model in such a case that inside the mentioned layer no substantial changes of the concentration of the electroactive substances with the distance from the electrode surface take place (*e.g.*, by electrostatic repulsion). Electrostatic repulsion of the depolarizer in the double layer is manifested by a pronounced decrease of its concentration on the electrode surface[10] and such a case would require the use of a more complicated model. The model used can be also regarded as a limiting case of the one used earlier[2] for the case of a negligible adsorption and a very high reaction rate in the adsorbed state. Indeed, it follows directly from the comparison of Eqs $(1)-(3)$ in the cited paper with Eqs (1) and (2) in the present paper that $g = \lim (l/2a)$ for $a \to \infty$, where l and a are parameters defined previously[2].

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