

IRREVERSIBLE FOLLOW-UP SECOND-ORDER REACTION
WITH LINEAR ADSORPTION OF A SUBSTANCE
IN THE GALVANOSTATIC METHOD WITH CURRENT REVERSAL*

O. DRAČKA

*Department of Theoretical and Physical Chemistry,
J. E. Purkyně University, 611 37 Brno*

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The case of irreversible follow-up chemical reaction of the second order with adsorption of a substance obeying a linear adsorption isotherm is solved for the galvanostatic method with current reversal. It is assumed that an adsorption equilibrium is established with an equilibrium constant B and that a chemical reaction proceeds in the solution and in the adsorbed layer with rate constants k and k_{ad} , respectively. For a sufficiently long time of the current reversal, t_1 , the transition time τ' after the current reversal is independent of t_1 . The results are presented graphically as the dependences of $\log \tau'$ on $\log j$ for different u and λ values, where j denotes the current before the reversal, u ratio of the currents after and before the reversal, and $\lambda = k_{ad}B/k$. The inequality $\partial^2 \log \tau' / (\partial \log j \partial \log u) > 0$ is a suitable criterion for the realization of the case under study.

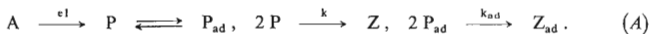
In an earlier work¹ we found a weak adsorption of the depolarization product in a follow-up irreversible reaction of the first order. A theoretical treatment of this case with a very rapid adsorption equilibrium characterized by a linear isotherm showed the possibility of the determination of the parameters of both the adsorption and the chemical reaction. The experimental results were in accord with the theory.

For an irreversible follow-up second-order reaction in the galvanostatic method with current reversal, the following cases were treated theoretically: homogeneous reaction^{2,3}, reaction in the completely adsorbed state⁴, and reactions accelerated by the electrode surface⁵. Similarly as with a first-order reaction¹, it can be expected that the course of the dependence of the transition time after the current reversal, τ' , on experimental parameters will lie in the case of a weak adsorption with a very rapid adsorption equilibrium between the courses corresponding to the mentioned cases. It can be also assumed that it will be possible to identify weak adsorption and to determine the parameters of both the adsorption and the chemical reaction in the case of a linear isotherm.

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THEORETICAL

We assume that a depolarization product, P, undergoes a homogeneous irreversible second-order reaction with a rate constant k and is besides adsorbed on the electrode. In the adsorbed state it undergoes the same reaction as in the solution but with a heterogeneous rate constant k_{ad} . Thus, we have the following reaction scheme:



For the galvanostatic method with current reversal, the problem is described by the equations

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC^2, \quad (1)$$

$$t = 0: C = 0; \quad x \rightarrow \infty: C \rightarrow 0, \quad (2a)$$

$$x = 0, \quad 0 < t < t_1: D \frac{\partial C}{\partial x} - \frac{\partial \Gamma}{\partial t} - k_{ad}\Gamma^2 = -\frac{j}{nF}, \quad (2b)$$

$$x = 0, \quad t > t_1: D \frac{\partial C}{\partial x} - \frac{\partial \Gamma}{\partial t} - k_{ad}\Gamma^2 = \frac{ju}{nF}, \quad (2c)$$

where the meaning of symbols (except for those defined above) is the same as in ref.¹. Further we assume that the rate of adsorption and desorption is so large that an adsorption equilibrium is practically always established and that the adsorption obeys the linear isotherm

$$\Gamma = BC(x = 0). \quad (3)$$

For a sufficiently long time of the current reversal, t_1 , so that

$$kC(x = 0)t_1 > 6, \quad (4)$$

the solution of Eqs (1)–(2c) for $t = t_1$ is with a sufficient accuracy given by²

$$C = [x(k/6D)^{1/2} + N]^{-2}, \quad (5)$$

where N is an integration constant. We introduce the dimensionless parameters

$$\beta = jkB^3/nFD^2 = wj; \quad \lambda = k_{ad}B/k; \quad \xi = B\sqrt{k/n}\sqrt{D}. \quad (6), (7), (8)$$

From Eq. (2b) we then obtain

$$\lambda \xi^4 + \xi^3 \sqrt{2/3} = \beta. \quad (9)$$

This is an implicit form of the dependence $\xi = \xi(\beta, \lambda)$, which is shown in Fig. 1 in bilogarithmic coordinates.

Further we introduce the dimensionless variables defined earlier^{2,5}:

$$\varphi = CN^2, \quad z = x \sqrt{k/N} \sqrt{D}, \quad y = k(t - t_1)/N^2, \quad (10)$$

and we obtain for $t > t_1$ from the preceding relations the following formulation of our problem:

$$\frac{\partial \varphi}{\partial y} = \frac{\partial^2 \varphi}{\partial z^2} - \varphi^2, \quad (11)$$

$$z \rightarrow \infty: \varphi \rightarrow 0; \quad y = 0: \varphi = [1 + z/\sqrt{6}]^{-2} \quad (12a,b)$$

$$y > 0, \quad z = 0: \frac{\partial \varphi}{\partial z} - \xi \frac{\partial \varphi}{\partial y} - \varphi^2 \lambda \xi = u \beta / \xi^3. \quad (12c)$$

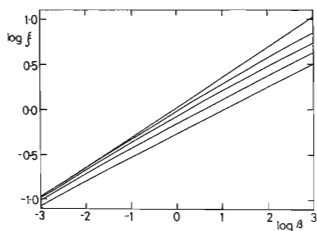


FIG. 1

Dependence of $\log \xi$ on $\log \beta$ for Different Values of λ from Eq. (9)

Values of λ from below: 0, 0.3, 1, 3, 10.

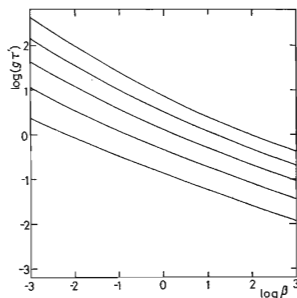


FIG. 2

Dependence of $\log \tau'$ on $\log j$ for Different Values of u at $\lambda = 0$

Values on the coordinate axes correspond to τ' and j expressed as dimensionless parameters $g\tau'$ and β . Values of u from above: 1/10, 1/3, 1, 3, 10.

It follows from Eqs (9), (11) and (12) that $\varphi = \varphi(z, y, u, \beta, \lambda)$, so that we obtain in the same way as in the preceding work^{2,5}

$$\tau' D|B^2 = g\tau' = y_{\tau'}|\xi^2 = f(u, \beta, \lambda), \quad (13)$$

where $y_{\tau'}$ is defined by

$$\varphi(y_{\tau'}, u, \beta, \lambda)_{z=0} = 0. \quad (14)$$

The system of equations (9), (11)–(14) was solved on a computer by the method described earlier³. The quantity φ for the electrode surface was calculated from the equations

$$\varphi_0^2 \lambda \xi + \varphi_0(2/\Delta z + 2\xi/\Delta y) + u\beta/\xi^3 - 2\varphi_1/\Delta z - 2\varphi_{0,p}\xi/\Delta y - (\partial\varphi_0/\partial y)_p \xi = 0, \quad (15)$$

$$\partial\varphi_0/\partial y = 2(\varphi_0 - \varphi_{0,p})/\Delta y - (\partial\varphi_0/\partial y)_p, \quad (16)$$

which can be analogously as earlier⁵ derived from Eq. (12c) for the network used. The indexes 0 and 1 denote the values for the electrode surface and for the first knot on the z axis, the index p refers to the values for $y - \Delta y$.

The result of the solution is the dependence of $\log(g\tau')$ on $\log \beta$ for different values of λ and u (Figs 2–6). The error of the calculation was controlled by the method described earlier³ so that it was under the limit of accuracy of the graphical representation. A network with $n_z = 40$ was sufficient in most cases; only for $\lambda = 0$, large β and small u values it was necessary to choose $n_z = 54 - 120$.

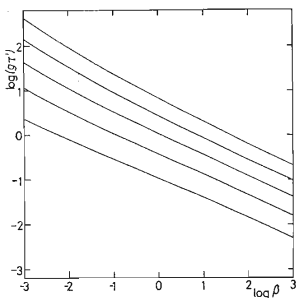


FIG. 3

Same as Fig. 2 but for $\lambda = 0.3$

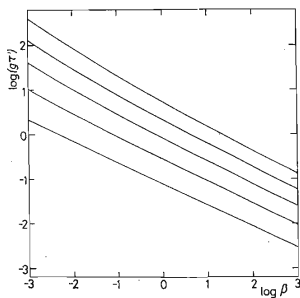


FIG. 4

Same as Fig. 2 but for $\lambda = 1$

DISCUSSION

Similarly as with other irreversible follow-up reactions¹⁻⁵, also in the case under study the transition time τ' after the current reversal is for a sufficiently long time t_1 of the current reversal independent of t_1 . The condition of large t_1 follows from the relations (4), (10) and (13) and can be expressed as $t_1/\tau' > 6/\xi^2(\beta, \lambda) f(u, \beta, \lambda)$. This can be verified with the aid of the dependences in Figs 1-6 and experimental results.

The dimensionless product $g\tau'$ is a function of three dimensionless parameters: u , β , and λ . The first two can be changed experimentally; u is the ratio of the current intensities after and before the reversal, β involves the current, j , before the reversal. The parameter λ expresses the ratio of the reaction rate in the adsorbed state to that in the solution.

It follows from Eqs (3), (5) and (8) that

$$\xi = \sqrt{6(\Gamma) \int_0^{\infty} C dx}_{t=t_1}, \quad (17)$$

hence the parameter ξ is proportional to the ratio of the quantity of the substance P in the adsorbed state to that in the solution in the instant of the current reversal. It is seen from Fig. 1 that the relative amount of the adsorbed substance increases with increasing current and diminishes with increasing reaction rate in the adsorbed state. Hence, the influence of adsorption becomes more pronounced with increasing current.

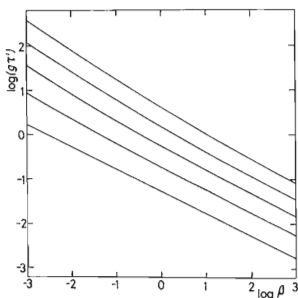


FIG. 5

Same as Fig. 2 but for $\lambda = 3$

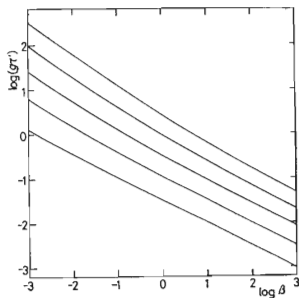


FIG. 6

Same as Fig. 2 but for $\lambda = 10$

The case under study can be reduced to the cases treated earlier and mentioned in the introduction. By comparing the basic equations and variables we obtain easily

$$\lim_{B \rightarrow 0} (g\tau' \beta^{2/3}) = f_2(u) ; \quad \lim_{B \rightarrow 0} (g\tau' \sqrt{(\beta\lambda)}) = f_2(u) \quad (18), (19)$$

$$\lim_{B \rightarrow 0, k_{ad} B^2 \rightarrow m} (g\tau'/\lambda^2) = h\tau' , \quad \lim_{B \rightarrow 0, k_{ad} B^2 \rightarrow m} (\beta\lambda^3) = b , \quad (20)$$

where $f_2(u)$ and $f_2(u)$ are dimensionless functions of the parameter u for a homogeneous chemical reaction^{2,3} and a chemical reaction in the completely adsorbed state⁴, h , m , and b are parameters defined for a reaction accelerated by the electrode surface⁵.

It follows further from Eqs (18) and (19) that

$$\lim_{\beta, \lambda \rightarrow 0} (\partial \log \tau' / \partial \log j)_u = -2/3 , \quad (21)$$

$$\lim_{\beta, \lambda \rightarrow \infty} (\partial \log \tau' / \partial \log j)_u = -1/2 . \quad (22)$$

From this it can be deduced that at least in a certain range of β and λ values the following inequality could apply:

$$\partial^2 \log \tau' / (\partial \log j)^2 > 0 . \quad (23)$$

It follows from Figs 2–6 that this is indeed the case in the range of u , β , and λ values under study, so that the dependences of $\log \tau'$ on $\log j$ are concave.

In all other solved cases^{2–7} there was $\partial^2 \log \tau' / (\partial \log j)^2 \leq 0$, hence the inequality (23) could principally serve as a criterion for the case corresponding to the reaction scheme (A). However, it is seen from Figs 2–6 that the curvature of the dependence of $\log \tau'$ on $\log j$ is so small that (in view of the experimentally limited range of j values) the proof of the validity of the relation (23) would be in most cases very difficult. At the same time it is apparent from Figs 2–6 that in the range of small β values the slope of the dependence of $\log \tau'$ on $\log j$ increases with decreasing value of u in accord with the inequality

$$\partial^2 \log \tau' / \partial \log j \partial \log u > 0 . \quad (24)$$

A comparison with other cases^{2–7} leads to the conclusion that the mentioned dependence is also typical for the case under study. In the range of small β values, this dependence can be easily determined even with a limited range of j values.

Figs 2–6 can serve as nomographs for the determination of the values of k , k_{ad} , and B . By comparing the experimental dependences of $\log \tau'$ on $\log j$ at various values of u with the curves in the diagrams, it is possible to determine the coefficients λ , w , and g , from which the values of k , k_{ad} , and B can be calculated if the diffusion coefficient D is known. In practice, however, in view of experimental errors and the similarity of the mentioned dependences it can be expected that (similarly as in the case of a reaction of the first order¹) only some of these quantities will be determined with a sufficient accuracy.

REFERENCES

1. Fischer O., Dračka O., Kaláb P.: This Journal 41, 703 (1976).
2. Dračka O.: This Journal 26, 2144 (1961).
3. Dračka O.: This Journal 35, 2480 (1970).
4. Dračka O.: This Journal 38, 1104 (1973).
5. Dračka O.: This Journal 41, 953 (1976).
6. Dračka O.: This Journal 36, 1889 (1971).
7. Dračka O.: This Journal 41, 498 (1976).

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