# IRREVERSIBLE FOLLOW-UP REACTION WITH LINEAR ADSORPTION OF THE PRODUCT STUDIED BY THE GALVANOSTATIC CURRENT REVERSAL METHOD* **

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The case of an irreversible follow-up reaction of the first order with adsorption obeying a linear isotherm was solved for the galvanostatic method with current reversal. Adsorption equilibrium and a different rate of the chemical reaction in the adsorbed phase from that in the solution are assumed. The transition time, $\tau'$, after the reversion of the current is in this case independent of the current, $j$, and time, $t_1$, before the reversion provided that the value of $t_1$ is large enough. The course of the dependence of the transition time, $\tau'$, on the ratio of the current intensities, $u = i/j$, depends on two parameters, namely the ratio of the reaction rates in the adsorbed state and in the solution, $l = k_{ad}/k$, and the ratio of the quantities of the substance in the solution and in the adsorbed state in the instant of the current reversal, denoted as $a$. The theoretical dependence of the product $k\tau'$ are for practical values of $u$ shown graphically for various values of $a$ and $l$. The possibility of evaluating all the parameters $a$, $k$, $l$, and distinguishing the given case from other cases of adsorption is discussed. The reduction of $p$-diacetylbenzene in water–alcohol mixtures is used as an illustrative example.

In the earlier work[1] devoted to the galvanostatic reduction of $p$-diacetylbenzene it was assumed that the measured rate constants of the follow-up reaction of the electrode product are influenced by its adsorption on the electrode. An analysis of the results showed that the adsorption was weak and therefore the results of the work[2] assuming complete adsorption of the electrode reaction product are not applicable. Instead, a model based on a mobile adsorption equilibrium characterized by a linear (Henry's) isotherm is plausible. The possibility of determining such an adsorbed product by the galvanostatic method with current reversal was already investigated[3].

The present work deals with the case where a chemical conversion of the electrode reaction product to an inactive substance proceeds both in the solution and in the adsorbed state parallel to its adsorption described by a linear isotherm. This inactivation is of the first order and irreversible.

**THEORETICAL**

We shall assume that the depolarization product, R, undergoes an irreversible follow-up reaction of the first order with a rate constant $k$ and besides is adsorbed on the electrode. In the adsorbed state it undergoes an irreversible follow-up reaction with a rate constant $k_{ad}$. For the method of reversing the direction of a constant current the problem is described by the equations

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

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

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

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

where $\Gamma$ denotes surface concentration of adsorbed substance R, $C$ its concentration in solution and $D$ its diffusion coefficient; other symbols have the same meaning as in ref.[4]. The rates of adsorption and desorption are so high that the adsorption equilibrium is practically always maintained; the adsorption obeys the linear isotherm

$$\Gamma = B(C)_{x=0}. \tag{3}$$

The Laplace transform of the solution of Eq. $(1)$ with the condition $(2a)$ is

$$\bar{C} = M \exp\left[-x[(p + k)/D]^{1/2}\right], \tag{4}$$

where $p$ is a complex variable and $M$ integration constant, which is a function of $p$. From $(2b)$, $(2c)$, and $(3)$ we obtain after transformation

$$x = 0: \quad D\frac{\partial \bar{C}}{\partial x} - Bp\bar{C} - k_{ad}B\bar{C} = -(j/nFp)\left(1 - (u + 1)\exp\left(-pt_1\right)\right). \tag{5}$$

From $(4)$ and $(5)$ we obtain

$$(\bar{C})_{x=0} = \left[j/nFp(Bp + k_{ad}B + (D(p + k))^{1/2})\right]\left[1 - (u + 1)\exp\left(-pt_1\right)\right]. \tag{6}$$

By decomposing the fractions, retransforming with the aid of tables[5] and rearranging we obtain from Eq. $(6)$

$$(C)_{x=0} = [j/nFkB(2a + l)] \{1 - [2a/(2a - l)] \operatorname{erfc}(kt)^{1/2} -$$
$$- [(2a - lg_1)/2z(2a - l)] \exp[(g_2^2 - 1) kt] \operatorname{erfc}[g_2(kt)^{1/2}] +$$
$$+ [(2a - lg_2)/2z(2a - l)] \exp[(g_1^2 - 1) kt] \operatorname{erfc}[g_1(kt)^{1/2}] -$$
$$- (u + 1) \{1 - [2a/(2a - l)] \operatorname{erfc}[k(t - t_1)]^{1/2} -$$
$$- [(2a - lg_1)/2z(2a - l)] \exp[(g_2^2 - 1) k(t - t_1)] \operatorname{erfc}[g_2(k(t - t_1))^{1/2}] +$$
$$+ [(2a - lg_2)/2z(2a - l)] \exp[(g_1^2 - 1) k(t - t_1)] \operatorname{erfc}[g_1(k(t - t_1))^{1/2}]\}\} . \quad (7)$$

Here we introduced the parameters

$$l = k_{ad}/k, \quad a = (D/k)^{1/2}/2B, \quad z = (1 + a^2 - l)^{1/2},$$
$$g_1 = a + z, \quad g_2 = a - z. \quad (8)$$

If the value of $kt_1$ is sufficiently large, we can neglect all terms containing the error function complement of this argument and its multiples (with small values of $g_2$ or $g_1$ this neglection is possible in view of the term $\exp(-kt_1)$). Practically the fulfillment of the same inequality is sufficient as in the case of a simple reaction[4]:

$$kt_1 > 6. \quad (9)$$

From this inequality and Eq. (7) we obtain the following equation for the transition time $\tau'$ after the current reversal:

$$2z(2a - l) = (u + 1) \{2z(2a - l) - 4az \operatorname{erfc}(k\tau')^{1/2} -$$
$$- (2a - lg_1) \exp[(g_2^2 - 1) k\tau'] \operatorname{erfc}[g_2(k\tau')^{1/2}] +$$
$$+ (2a - lg_2) \exp[(g_1^2 - 1) k\tau'] \operatorname{erfc}[g_1(k\tau')^{1/2}]\} . \quad (10)$$

Hence, it is seen that $k\tau'$ is a function of three dimensionless parameters, $a$, $l$, and $u$, and is independent of $t_1$ and $j$. This function can be expressed explicitly only by solving Eq. (10) numerically. Of the parameters $a, l, u$, the first two are parameters of the measured system while the third one is an experimental variable. It is therefore suitable to study the dependence of $k\tau'$ on $u$ at various values of $a$ and $l$.

The numerical solution of Eg. (10) is not possible in certain regions:

a) For $l = 2a$, Eq. (10) becomes an identity, so that the value of $k\tau'$ cannot be determined; nevertheless we obtain by performing the limit

$$2(a - 1)^2 = (u + 1) \{2(a - 1)^2 - (2a^2 + a + 1) \operatorname{erfc}(k\tau')^{1/2} -$$
$$- 16a(a - 1) k\tau' \operatorname{erfc}(k\tau')^{1/2} + 8a(a - 1)(k\tau')^{1/2} \exp(-k\tau') +$$
$$+ (5a - 1) \exp[4a(a - 1) k\tau'] \operatorname{erfc}([2a - 1)(k\tau')^{1/2}]\} . \quad (11)$$

This is an implicit dependence of $k\tau'$ on $a$ and $u$ for $l = 2a$. Eq. $(11)$ becomes an identity for $a = 1$ and it can be treated in this special case analogously.

b) For $l > a^2 + 1$, $g_1$ and $g_2$ are complex. The calculation of the error function of a complex argument is very difficult. This difficulty occurs either in the case of a weak adsorption (large value of $a$) and a substantially higher reaction rate in the adsorbed state than in the solution (large value of $l$), or in the case of a strong adsorption (small value of $a$) and $l > 1$. Both these cases lie beyond the scope of the present work.

c) For large values of $k\tau'$, the numerical solution of Eq. $(10)$ is unstable owing to a rapid convergence of the error function complement to zero with increasing argument. Since high values of $k\tau'$ are attained only in the case of a very strong adsorption, where the linear isotherm is not applicable, this region was not studied further and the solution was restricted to the values of $k\tau' < 6$.

The calculated dependences are shown in Figs $1-5$ in bilogarithmic coordinates. It is seen that their slope and curvature depend on the parameters $a$ and $l$. To evaluate experimental results, the experimental dependence of $\log \tau'$ on $\log u$ must be compared with the calculated curves. To distinguish reliably various cases, the range
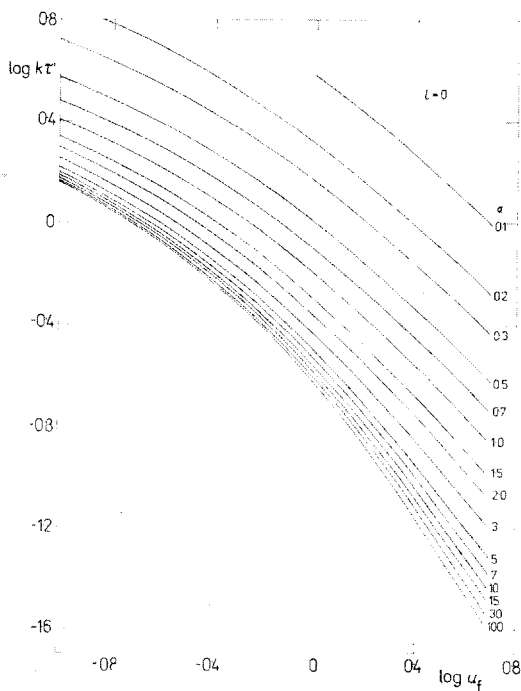


FIG. 1

Dependence of $\log k\tau'$ on the Logarithm of the Ratio of Currents $u$ for Various Values of the Adsorption Parameter $a$

The ratio of the chemical rate constants $l = 0$ (no chemical reaction proceeds in the adsorbed state).

of $u$ values should be as large as possible. Unfortunately the values of $\tau'$ can be determined with a sufficient accuracy only in a limited range of the $u$ values. The obtained value of $k$ must be used to verify the validity of the inequality $(9)$.

*Discussion of Theoretical Relations*

Our calculations show that even in the case where the follow-up irreversible reaction of the first order is complicated by an adsorption equilibrium with a linear isotherm, the transition time $\tau'$ preserves the general features characteristic for a system without adsorption: it is independent on the current $j$ and, if the condition $k\tau_1 > 6$ is fulfilled, also on the time of the reversion, $t_1$.

Of the parameters $a$ and $l$, which characterize the adsorption and reaction in the adsorbed state, the latter is clearly defined by Eq. $(8)$. The parameter $a$ can be interpreted as follows: From Eqs $(3)$, $(4)$, $(8)$, and the inequality $(9)$ follows

$$a = \frac{1}{2}\left(\int_0^\infty C\,dx/\Gamma\right)_{t=t_1}. \tag{12}$$
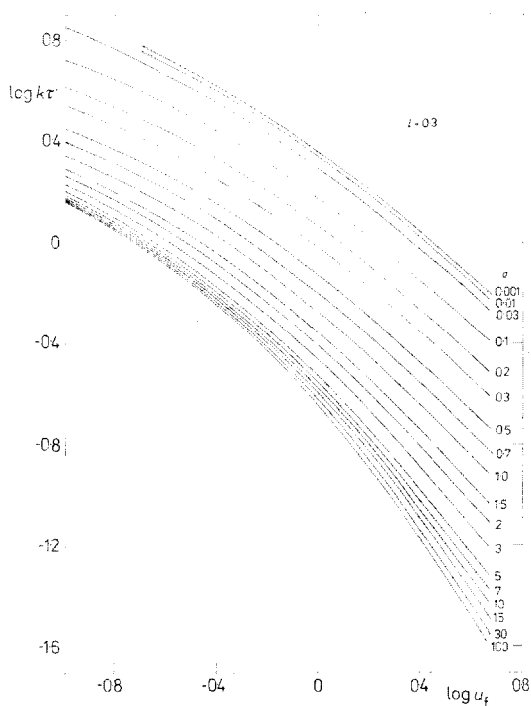


Fig. 2

Same Dependences as in Fig. 1 but for $l = 0.3$

hence the parameter $a$ is equal to one half of the ratio of the quantity of the substance R in the solution to its quantity in the adsorbed state at the instant of the current reversal. The relative quantity of R adsorbed on the electrode at $t = t_1$ is equal to $1/(2a + 1)$, and its absolute content in the solution at the electrode is equal to $(D/k)^{1/2} C_{x=0}$; according to Eq. (7) we have $C_{x=0} = j/nFkB(2a + l)$ at $t = t_1$.

As can be seen from Figs 1−5, the $\tau' - u$ dependence becomes flatter with increasing adsorption (except for $l = 10$), i.e., with decreasing $a$. In other words, if $l < 3$, the product $k\tau'$ increases at constant ratio of the currents, $u$, with increasing adsorption the more the slower is the reaction in the adsorbed state. This can be explained so that if the adsorption equilibrium is attained, the adsorbed product is completely consumed on the electrode after the reversion, whereas of the product in the solution only that fraction is consumed which diffuses back to the electrode during the transition time $\tau'$. Therefore at higher $u$ values where the transition time $\tau'$ is shorter and the participation of the adsorbed product in the electrode reaction more pronounced, both the stronger adsorption and retarding of the reaction in the adsorbed state is manifested by an increase of the quantity $k\tau'$. It is seen from Figs 1−5 that the $\log \tau' - \log u_f$ curves for $l \leqq 1$ are much less dependent on $l$ at constant $a$ than on $a$ at constant $l$, so that the value of $l$ will be in the analysis in this region subject to a much larger error than the value of $a$.

If the adsorption is governed by another isotherm than a linear one and the inequality (9) is fulfilled, $\tau'$ will be again independent of $t_1$. The ratio of $\Gamma/C_{x=0}$ is in this case a function of $C_{x=0}$ and hence also of the current $j$ before the reversion. The rela-
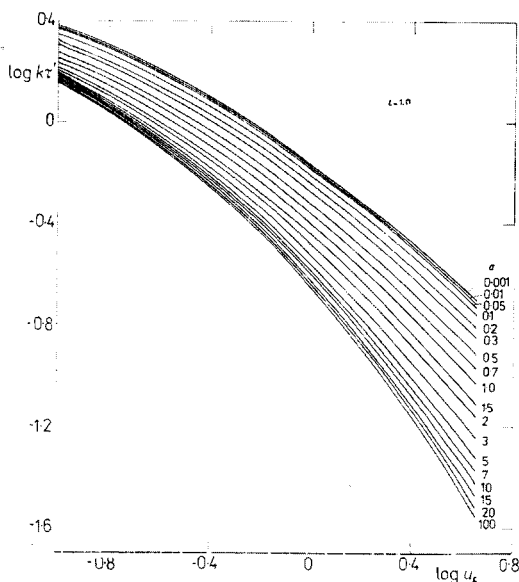


FIG. 3

Same Dependences as in Fig. 1 but for $l = 1$

tive amount of the adsorbed substance R at the moment of the reversion is a non-linear function of $j$ and therefore also $\tau'$ depends on $j$. The independence of $\tau'$ on $j$ in the case of an irreversible follow-up first-order reaction with adsorption is therefore a criterion for distinguishing the linear isotherm from other ones. If the ratio $\Gamma/C_{x=0}$ decreases with rising $C_{x=0}$, we can expect at $l \leqq 1$ decreasing $\tau'$ with increasing current density $j$.
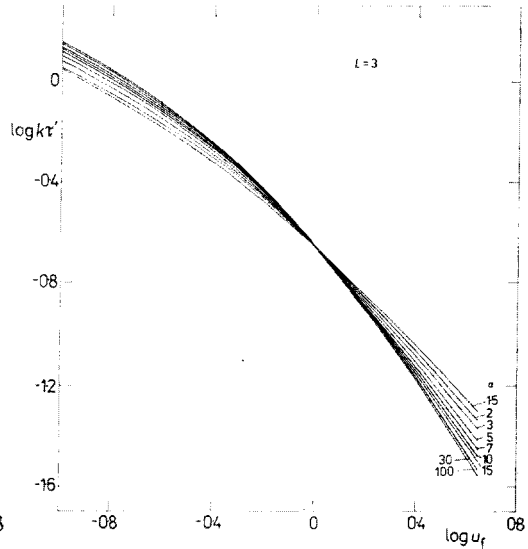


FIG. 4

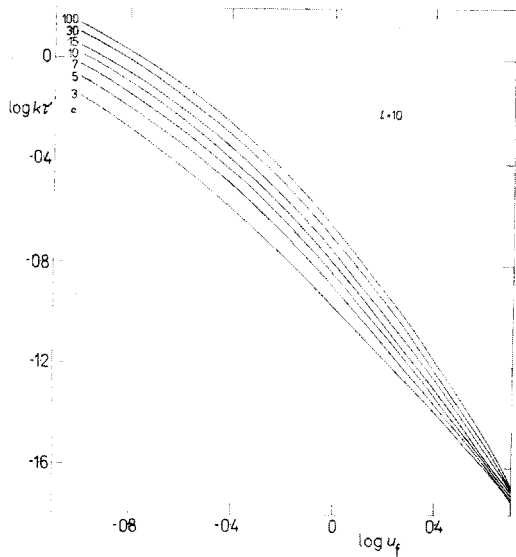Same Dependences as in Fig. 1 but for $l = 3$



FIG. 5

Same Dependences as in Fig. 1 but for $l = 10$

Another deviation from the assumed scheme may be a splitting of the transition after reversion in analogy to the splitting of polarographic waves[6]. This can occur: *a*) In the case of a sufficiently rapid, very strong adsorption if the electrode potential is determined by the concentration of the adsorbed substance on the electrode; *b*) in the case where the rates of adsorption and desorption are comparable with that of the chemical reaction. Then at a sufficiently large $t_1$ a stationary state with respect to the chemical reaction and adsorption is attained prior to the reversion. After the reversion, one form of the substance R will discharge more easily and when its concentration drops to zero (transition time $\tau_1'$), the concentration of the other form will be different from zero and its exhaustion will correspond to the time $\tau_2'$.

## EXPERIMENTAL

The experimental equipment was described in connection with the galvanostatic reduction of *p*-diacetylbenzene (PDAB)[1] and in[7]. A mercury pool electrode of $2.73 \text{ cm}^2$ geometric surface area was used. All chemicals were of reagent grade and were recrystallized from water when needed. The measured solutions contained $2 . 10^{-4}$M-PDAB in a 0.02M phosphate buffer (an equimolar mixture of $KH_2PO_4$ and $Na_2HPO_4$) in ethanol–water mixtures. Their pH was measured with a glass electrode standardized with respect to succinate and oxalate buffers in the same medium[8].

## RESULTS AND DISCUSSION

Since the solution were weakly alkaline (in the scales valid for the individual ethanol––water mixtures), it could be expected that the inactivation rate constants of the product R would be according to the previous results[1] of the order of unity $(s^{-1})$. Therefore, for the time of the reversion $t_1 > 5$ s the inequality (9) should be fulfilled enabling a simplified evaluation. We used for this purpose the method of comparing the dependences of log $\tau'$ on log $u_f$ with the diagrams in Figs $1 - 5$. The transition times $\tau'$ after the reversion of the current were well measurable and were in the range from 0.03 to 0.7 s fulfilling the inequality $\tau' \ll t_1$.

Since the transition times were short, it was necessary to introduce a correction for the charging current. Adsorption of the product of the electrode reaction and partially of the depolarizer changes the double layer capacity during the electrolysis, therefore we took its average value after the reversion of the current. The graphical method[9] cannot be used in the electrolysis with current reversion. Instead, we proceed as follows. The current can be thought to consist of a mean faradaic and a mean charging current[9]. The determination of the latter after the current reversion is possible under the assumption that the electrode and chemical reactions under consideration are such that the transition time $\tau'$ after the reversion is constant at constant ratio of the currents, *u*, and independent of the currents *i* and *j*. The contribution of the charging diminishes with increasing current. The experimentally de-

termined potential change during the transition time after the reversion, the additivity of the charging and faradaic currents and the constancy of $\tau'$ at constant $u$ enable us to calculate the effective average capacity of the double layer during reoxidation of the depolarization product.

A series of measurements leads to values increasing with the content of alcohol in the solution from 32 to 38 µF per total electrode surface area. Before the reversion of the current, the electrode potential changed little during the transition so that at $t_1 > 5$ s the charging correction was less than 1%. We therefore calculated the "faradaic" ratio of the currents, $u_f = i_f/j$.

One series of measurements of the $\tau' - u_f$ dependences in solutions of varying alcohol concentrations is shown in bilogarithmic coordinates in Fig. 6. It is obvious from the course of the curves that comparable values of the chemical rate constant $k$ and a decrease of the parameter $a$ with increasing alcohol content can be expected. From the comparison of the experimental curves with the theoretical diagrams follow the values given in Table I. It was possible to use the diagrams for $l$ from 0 to 1 and to a certain extent also for $l = 3$. Within the limits of accuracy of the experimental data, the value of $l$ could not be uniquely determined. If the chemical reaction proceeds in the adsorbed state, its rate constant is smaller or comparable with that for the free product at the electrode.

Regardless of this uncertainty, the values of $k$ and $a$ did not show a significant dependence on the chosen parameter $l$ and they could be averaged. The increase of $k$ with the alcohol concentration can be attributed to increasing pH values (base catalysis). With respect to the high value of the specific constant for $OH^-$ ions[1] this rate constant should increase already in the range from 7·5 to 8·0 linearly with the activity of $OH^-$ ions regardless of the changes in the activities of other components. Therefore, the difference $pH^* - \log k$ is constant (Fig. 7) within the
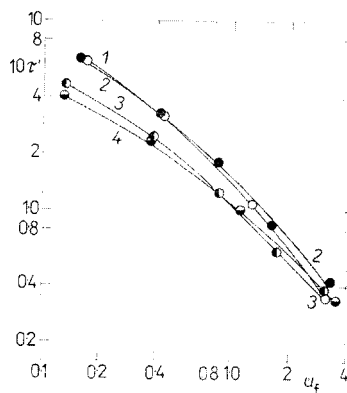


FIG. 6

Experimental Dependences of $\tau'$ on $u_f$ in Bilogarithmic Scale

Reduction of $2 \cdot 10^{-4}$M PDAB in 0·02M phosphate buffer at 25°C, $t_1 = 7·1$ s. Ethanol concentration (wt.%): 1 16·7; 2 25·5; 3 34·8; 4 44·4.

limits of errors. Small deviations can be attributed to an unperfect consistency of the pH* scales.

The distinct decrease of the parameter $a$ found with increasing alcohol concentration is influenced by the increase of the rate constant $k$, decrease of the diffusion coefficient $D$ (calculated from the transition timed for PDAB) as well as by changes of the adsorption constant $B$. Its values calculated from the second one of Eqs (8) exert a relatively large growth (Fig. 7), which is difficult to explain because of the competition of four substances on the surface (water, alcohol, PDAB, and product).

TABLE I

Evaluation of Experimental Data for the Reduction of $p$-Diacetylbenzene
$2 \cdot 10^{-4}$M-PDAB, 25°C, Hg electrode.

| % EtOH | pH* | $k$, s$^{-1}$ | $a$ | $D \cdot 10^{10}$ m$^2$ s$^{-1}$ | $B \cdot 10^6$, m |
|---|---|---|---|---|---|
| 16·7 | 7·55 | 1·8 | 13 | 3·9 | 0·6 |
| 25·5 | 7·64 | 2·0 | 6 | 3·2 | 1 |
| 34·8 | 7·80 | 3·0 | 2·5 | 2·8 | 2 |
| 44·4 | 7·96 | 4·9 | 0·9 | 2·7 | 4 |

At any rate, values of the order of $10^{-6}$ m indicate a weak adsorption of the product, roughly $10^{-8} - 10^{-7}$ mol/m$^2$. The results of the present work hence substantiate the assumption[1] that the measured data are influenced by adsorption of the electrode product. A direct comparison of our results with the earlier work[1], however, is not
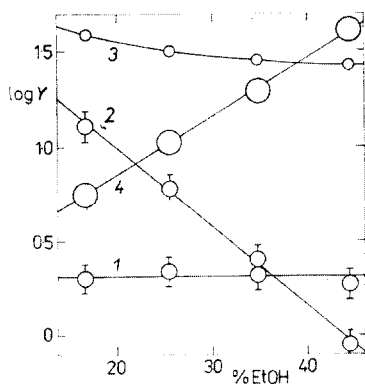


FIG. 7

Dependences of Calculated Parameters for Reduction of PDAB on Ethanol Concentration

The meaning of $Y$ is: $1$ $10^{-7}/ka_{H^+}$; $2\,a$; $3\,D \cdot 10^{11}$; $4\,B \cdot 10^7$.

possible since solutions of different ionic strength were used. The latter was kept as low as possible in the present work to enable a comparison of the pH* values at different alcohol concentrations according to ref.[8]. If the adsorption is taken into account, the rate constants are calculated higher than when it is neglected $(a \rightarrow \infty)$, as follows from a consideration and from the shift of the curves on the auxiliary theoretical diagrams. For a weak adsorption, such as was found with the electro-reduction product of PDAB, the mentioned increase is in the range of one half of an order of magnitude.

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