# THE NATURE OF THE DECREASE IN CURRENT ON POLAROGRAPHIC WAVES LIMITED BY A PRECEDING CHEMICAL REACTION

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## Abstract

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# THE NATURE OF THE DECREASE IN CURRENT ON POLAROGRAPHIC WAVES LIMITED BY A PRECEDING CHEMICAL REACTION

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Catalytic (and kinetic) currents in polarography, as was shown ([1,2]), are usually the sum of two currents; these components are limited by the rate of one and the same preceding chemical reaction, but in one case the reaction takes place in the bulk of the solution ( "bulk" current), and in the other—on the surface of the electrode ( "surface" current). The share of the "surface" current increases with increasing adsorption of the electrochemically inactive form of the depolarizer ([1]).

On a mercury dropping electrode, at the concentrations usually used in polarography, adsorption equilibrium is, as a rule, not attained ([3]). If adsorption obeys the Langmuir isotherm

$$\Gamma_e = \Gamma_\infty \frac{\beta C_k}{1 + \beta C_k}, \tag{1}$$

($\Gamma_e$ and $\Gamma_\infty$ are, respectively, the equilibrium and maximum amounts of adsorbed substance, $\beta$ is a constant, and $C_k$ is the concentration of the adsorbing substance in solution), then the amount of adsorbed substance at time $t$ is $\Gamma_t = y\Gamma_e$, where the completeness of establishment of equilibrium $y$ depends on the adsorption time, the rate of supply of the substance to the electrode, and the value of $\beta$ ([3]).

According to A. N. Frumkin ([4]), the quantity $\beta$ is a function of the electrode potential:

$$\beta = Be^{-\frac{1/2(c-c')}{RT\Gamma_\infty}\varphi^2} = Be^{-\alpha\varphi^2}, \tag{2}$$

where $c$ and $c'$ are the capacitances of the double layer of the electrode in the absence of the surface-active substance and at complete filling of it by molecules on the electrode surface, respectively; $\varphi = E - E_m$, $E_m$ is the potential at which adsorption is maximal; $B$ is a constant. With increasing $\varphi$, adsorption decreases

Figure 1. Catalytic hydrogen waves caused by anabasine in acetate buffer at pH 6.0; concentration of KCl in solution: 1–0; 2–0.1; 3–0.2; 4–0.5; 5–1.0 N.

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and, as a consequence, the share of the "surface"component in the total catalytic (or kinetic) current decreases. Thus, for example, in the second catalytic wave of quinine, observed at high negative potentials (about −1.9 V relative to the normal calomel electrode), the "surface" and "bulk" currents are comparable in order of magnitude ([1]). At less negative potentials the share of the "bulk" current becomes, as a rule, insignificant, and the observed catalytic current is practically purely "surface."

The dependence of the surface current on potential is determined, on the one hand, by its influence on the rate constant of the electrode process and, on the other, by the amount of adsorbed catalyst. In the case of an adsorbed catalyst the wave is irreversible ([5]). For the surface current, according to the mechanism of formation of the catalytic wave ([6]), one may write:

$$i = sF\{k_1[\mathrm{DH}^+]\Gamma - k_2[\mathrm{D}]\Gamma'\}, \tag{3}$$

$$i_{\mathrm{pr}} = sFk_1[\mathrm{DH}^+]\Gamma, \tag{4}$$

where $\Gamma$ and $\Gamma'$ are the adsorbed amounts of the basic and acidic—electrochemically active—forms of the catalyst; $k_1$ and $k_2$ are the rate constants for the interaction of the catalyst in the corresponding form with the proton donor $DH^+$ or the base $D$, respectively; $s$ is the electrode surface; $F$ is Faraday' s number.

According to A. N. Frumkin' s theory of slow discharge ([7])

$$i = sk_0\Gamma' e^{-\frac{\alpha FE}{RT}}. \tag{5}$$

If adsorption did not depend on the potential, then the equation of the catalytic wave, obtained by substituting the value of $\Gamma'$ (found by combining (3) and (4)) into (5), would have the form:

$$E = E_{1/2} - \frac{RT}{\alpha F}\ln\frac{i^0}{i'_{\mathrm{pr}} - i^0}, \tag{6}$$

where the superscript zero refers to quantities corresponding to adsorption at $E_{\mathrm{m}}$.

Figure 2. Dependence of the catalytic current in a 0.182 mM anabasine solution at $E = -1.84$ V on the concentration of acetic acid in acetate buffer, pH 6.0.

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**Fig. 1.** Catalytic hydrogen waves caused by anabasine in acetate buffer at pH 6.0; concentration of KCl in the solution: 1–0; 2–0.1; 3–0.2; 4–0.5; 5–1.0 N.

The adsorption of the catalyst as a whole depends on the adsorption of its basic and acidic forms, which are in protolytic equilibrium. The surface activity on mercury of the basic form, judging from Gouy' s data for organic bases obtained in neutral and acidic solutions ([8]), is considerably higher than that of the acidic form; moreover, on the negatively charged mercury surface the adsorption of the cationic form changes with the potential incomparably less than that of the basic form. Therefore the change in adsorption of the catalyst with potential is determined chiefly by the change in adsorption of its basic form, although the amount of adsorbed substance also depends on the ratio between the forms, i.e., on the pH of the solution.

**Fig. 2.** Dependence of the catalytic current in a 0.182 mM anabasine solution at $E = -1.84$ V on the concentration of acetic acid in acetate buffer, pH 6.0.

The catalytic current in an excess of proton donors is proportional to the concentration of catalyst at the electrode surface ([9]); consequently, the change in current with potential due solely to desorption of the catalyst may be expressed relative to the current $i^0$, determined from (6), in the following way:

$$\frac{i}{i^0} = \frac{\Gamma_t}{\Gamma_t^0} = \frac{y\beta}{1+\beta C_k} \cdot \frac{y^0\beta^0}{1+\beta^0 C_k}, \tag{7}$$

where, according to (2), $\beta^0 = B$.

Under the conditions of observing catalytic hydrogen waves, $C_k$ is usually small and the value of $y$, especially at low drop times, does not exceed 0.5 ([3]). At constant $C_k$ and $t$, the value of $y$, as follows from the data of Delahay and Fike ([3]), increases proportionally to $1+\beta C_k$, up to $y \approx 0.55$. Therefore, for $y < 0.55$, expression (7) may be represented as:

$$\frac{i}{i^0} = \frac{\beta}{B} = e^{-a\varphi^2}. \tag{8}$$

Thus the surface catalytic hydrogen wave is described by the set of equations (6) and (7) or (8). Its characteristic form is due to the change in adsorption of the catalyst with potential. The validity of the equations derived has been checked

using the example of catalytic hydrogen waves caused by anabasine, quinine, and the cysteine complex of cobalt.

The value of $\Gamma_\infty$ for anabasine, found [10] from Brdička's adsorption prewave [11], is $2.4 \cdot 10^{-10}$ mole/cm$^2$, which is close to the value $\Gamma_\infty = 3.2 \cdot 10^{-10}$, calculated from the area occupied by an anabasine molecule, 58 Å$^2$ (according to its model). If one assumes that $\Gamma_\infty = 3.2 \cdot 10^{-10}$, $c \approx 15$ and $c' \approx 5$ $\mu$F/cm$^2$, then from (2) for anabasine $a = 6.35$ V$^{-2}$.

As a result of desorption of the catalyst with increasing potential, the reciprocal value of the slope of the logarithmic plot of the initial segment [5] of the catalytic wave, $b_k = 2.3RT/\alpha_k F$, is greater than $b = 2.3RT/\alpha F$ of the wave determined by (6). If $b$ is known, then from the experimental value of $b_k$ one can find the potential $\varphi_\text{n}$ of the initial segment of the catalytic wave ($i = 0.1$—$0.2\, i_\text{max}$) relative to the potential of maximum adsorption $E_\text{m}$ and, consequently, estimate the value $E_\text{m} = E_\text{n} - \varphi_\text{n}$, where $E_\text{n}$ is the potential of the wave onset relative to the reference electrode. It is not difficult to show that

$$\varphi_\text{n} = \frac{2.3}{2a} \cdot \frac{b_k - b}{b_k \cdot b} = \frac{(a - \alpha_k)F}{2RTa}.$$

For catalytic waves caused by anabasine, $b_k = 0.10$ V [10], so that, taking for wave (6) $b = 0.080$ V ($\alpha = 0.738$), we find $E_\text{m} \approx -1.15$ V.

In Fig. 1, curve 1 was constructed from the values: $E_\text{m} = -1.143$ V (sat. cal. el.), $E_{1/2} = -1.718$ V, $i^0_\text{pr} = 97$ $\mu$A, and $b = 0.08$ V. The points on the curve are experimental values of the catalytic current (after subtraction of the anabasine pseudoreduction prewave [10]), obtained with an electrode having $m = 1.322$ mg/sec, $t = 0.24$ sec. As can be seen from Fig. 1, the calculated curve correctly describes the shape of the catalytic wave.

With all other conditions unchanged, introducing potassium chloride into the buffer solution somewhat lowers the height of the catalytic wave, apparently because of an increase in the capacitance $c$ [12]. Calculation shows that, for the observed decrease in current, the capacitance $c$ at $C_\text{KCl}$: 0.1; 0.2; 0.5 and 1.0 $N$ should have the following values, respectively: 15.5; 15.6; 15.9 and 16.4 $\mu$F/cm$^2$. In Fig. 1, curves 2-5 correspond to the calculated values; the points are experimental.

When the buffer capacity of the solution is decreased while keeping its pH and ionic strength constant, the catalytic current falls. Fig. 2 shows the dependence of the current in a 0.182 mM anabasine solution at $E = -1.84$ V (when $i^0$ reaches more than $0.95 i^0_\text{pr}$) on the concentration of undissociated $CH_3COOH$ in an acetate buffer with pH 6.0. From the slope of the straight line in Fig. 2, by (4), the rate constant was found for the interaction of the adsorbed base of anabasine with $CH_3COOH$ ($DH^+$): $k_1 = 2.9 \cdot 10^5$ L/mole $\cdot$ sec. The value $\Gamma_t = 2.4 \cdot 10^{-11}$ used in the calculation for $E = -1.84$ V was found from (1), with $\Gamma_\infty$, $y = 0.13$, and $\beta = 7.4$ mmole$^{-1}$ (at $E = -1.84$). The latter was found

Fig. 3. Catalytic waves of a $2.85 \cdot 10^{-6}\,M$ solution of quinine in citrate-phosphate buffer at pH 3.0 (1) and 4.0 (2).

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Fig. 4. Catalytic wave of the cysteine complex of $Co^{2+}$ in ammonia buffer.

Figure 4: Fig. 4. Catalytic wave of the cysteine complex of $Co^{2+}$ in ammonia buffer.

from (2), using $\beta \approx 100$ at $-1.42$ V, which, in turn, was found from (3) from $\Gamma_t/\Gamma_\infty = 0.62$, determined from the height of the anabasine prewave [(10)]. The intercept cut off by the straight line in Fig. 2 on the ordinate axis corresponds to the current limited by the rate of interaction of the anabasine base with water and hydrogen ions.

Fig. 3 gives experimental data (points) and calculated curves for catalytic waves caused by a $2.85 \cdot 10^{-6}$ solution of quinine in phosphate-citrate buffer with pH 3.0 (1) and 4.0 (2) (electrode with $m = 3.82$, $t = 0.26$ sec). For the calculation, the values $a = 4.6\ \mathrm{V}^{-2}$, $b = 85$ mV, $b_k = 100$ mV were used; for 1: $E_\mathrm{m} = -0.812$, $E_{1/2} = -1.325$, $i^0_\mathrm{pr} = 7.97\ \mu$A, for 2: $E_\mathrm{m} = -0.826$, $E_{1/2} = -1.426$, $i^0_\mathrm{pr} = 9.05\ \mu$A. Curve 2 is considerably

but it already satisfies the experimental data worse; apparently, for calculating curve 2 larger values of $a$ or $b$ should have been taken. It is interesting that in the present case an increase in pH has little effect on the magnitude of the catalytic current, since the decrease in the rate of protonation of the catalyst is compensated by an increase in its adsorbability owing to an increase in the fraction of the strongly adsorbing basic form of quinine in this pH region.

In Fig. 4, the points show the catalytic current caused by cysteine ($7.2 \cdot 10^{-6} M$) in the presence of $Co^{2+}$ ($2.9 \cdot 10^{-4} N$) in a buffer of $0.1\,N\,NH_4OH + 0.1\,N\,NH_4Cl$, with an electrode having $m = 1.19$ and $t = 0.13$ sec. For calculating the curves the following values were used: $b = 128$ mV, $b_k = 139$ mV, $E_{1/2} = -1.576$ V, $i^0_\mathrm{pr} = 4.67\,\mu$A, $E_\mathrm{M} = -0.976$, $a = 2.5\,\mathrm{V}^{-2}$, and $\Gamma_\infty = 6 \cdot 10^{-10}$, $c - c' = 7.45$.

**Fig. 3.** Catalytic waves of a $2.85 \cdot 10^{-6}\,M$ solution of quinine in citrate-phosphate buffer at pH 3.0 (1) and 4.0 (2)

**Fig. 4.** Catalytic wave of the cysteine complex of $Co^{2+}$ in ammonia buffer

Equations (7) and (8), strictly speaking, are valid only for cases in which adsorption obeys the Langmuir isotherm; in reality, however, the adsorption of many substances obeys the more complicated S-shaped isotherm of A. N. Frumkin[13]. Since under the conditions of polarographic investigations the surface coverage by the adsorbed substance is usually small, with a known approximation the portion of the A. N. Frumkin isotherm can be replaced by a portion of the Lang-

muir adsorption isotherm. It should also be borne in mind that the quantity $c$ is not constant; it changes with potential[12], but at not too negative potentials, over a comparatively narrow interval of their variation, $c$ may be regarded as constant.

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