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Abstract

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POLAROGRAPHIC CATALYTIC WAVES OF HYDROGEN AND ADSORPTION OF THE CATALYST

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In considering kinetic and catalytic currents in polarography it is necessary to take into account the influence of adsorption of substances participating in near-electrode chemical reactions, which, roughly speaking, leads to an increase in the concentrations of substances in the reaction space in comparison with their concentrations in the bulk of the solution. In this case, in addition to the usual kinetic or catalytic current, limited by the course of the chemical reaction in the volume of solution near the electrode, an additional kinetic current appears, caused by the course of the same reaction with the participation of the adsorbed substance. The observed kinetic current is evidently the sum of the currents of the "volume" and "surface" processes. Calculation from experimental data of the rate constants of preceding chemical reactions by equations for volume processes without allowance for adsorption leads to a considerable overestimation of their values.

In the present communication, using as an example the catalytic hydrogen wave caused by quinine, the influence of adsorption of the catalyst on the magnitude of the catalytic current and on the shape of the wave is shown. The experimental data presented in this work were obtained on a TsLA polarograph of Energochermet ([1]) at $25 \pm 0.1^{\circ}$ with a dropping electrode having forced detachment of drops ([2]). Its characteristics were: $m = 1.52$ mg/sec, $t = 0.23$ sec.

The catalyst causing the catalytic waves exists in solution in two forms: cationic —acidic—electrochemically active, and basic, not directly participating in the electrode process ([3]). Both forms are in protolytic equilibrium, and the ratio between them is determined by the ionization constant of the catalyst and by the pH of the medium.

The catalyst cations in solution and in the adsorbed state should in general differ in their depolarization properties ([4]), so that, in the case of surface-active catalysts, on waves under certain conditions one should expect the appearance of two steps corresponding to the discharge of adsorbed and nonadsorbed particles. Indeed, on the catalytic wave caused by quinine in a $0.1\,N$ borax solution, at a quinine concentration C_{quin} of about $4 \cdot 10^{-4}\,M$ (at $t = 0.23$ sec), an inflection appears, which with increasing C_{quin} turns into a separate peak (Fig. 1).

Fig. 1 and Fig. 2: polarographic curves

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Splitting of the catalytic quinine wave is also observed when a surface-active substance—tetraethylammonium benzenesulfonate (BSTE)—is added to the solution. Even at a comparatively low content of BSTE in the solution, the lower part of the catalytic wave, shifting somewhat toward negative potentials, sharply increases its steepness; with an increase in the concentration of BSTE and with C_{quin} and the pH of the solution kept constant, a decrease in the total height of the wave and its splitting are observed (Fig. 2). The lower, steeper step, while decreasing somewhat in height with increasing C_{BSTE} , almost does not change its $E_{1/2}$, whereas the upper—extended—step sharply decreases and shifts considerably toward negative potentials. The lower wave corresponds to the discharge of cations formed in the bulk of the solution. This "volume" wave has a reversible character ([3],[5]). The upper—extended wave with a characteristic maximum—is due to the irreversible discharge ([5]) of cations formed from the adsorbed catalyst (the "surface" wave).

With an increase of C_{BSTEA} above $0.07\,N$, owing to inhibition of the electrode process ([6]), the bulk wave also begins to decrease, becomes less steep, and shifts to negative potentials; at such high C_{BSTEA} the "surface" wave disappears completely.

It should be noted that in the absence of BSTEA the bulk wave, with increasing C_{quin}, becomes more negative (Fig. 1), i.e., the reversible discharge is, as it were, inhibited by adsorbed quinine. However, comparison of reversible and irreversible waves with close limiting currents shows that the reversible ("bulk")

Fig. 1. Catalytic waves of hydrogen caused by quinine in $0.1N$ borax solution. C_{quin} are, respectively (in $10^{-4}M$):
1—background; 2—0.34; 3—0.50; 4—0.79; 5—0.93; 6—1.04; 7—1.2; 8—1.4; 9—1.6; 10—1.8; 11—2.0.

Fig. 2. Change in the catalytic wave at $C_{\text{quin}} = \text{const} = 3.6 \cdot 10^{-5}M$ as a function of C_{BSTEA} (in $10^{-2}M$):
1—0; 2—0.92; 3—1.82; 4—2.61; 5—3.34; 6—4.62; 7—6.72; 8—7.9; 9—10; 10—background—$0.1N$ borax solution.

wave, separated from the total catalytic current by the action of BSTEA, is located at less negative potentials than the irreversible one ([5]).

Splitting of catalytic hydrogen waves is observed rather rarely. The necessary conditions for this are comparable heights of the "surface" and "bulk" waves and the location of $E_{1/2}$ of the latter within a certain narrow potential interval near the maximum of the "surface" wave. The scheme for the formation of a "double" catalytic wave is given in Fig. 3.

Fig. 3. Scheme of formation of two peaks on the catalytic wave.

Figure 2: Fig. 3. Scheme of formation of two peaks on the catalytic wave.

As a rule, separation of the catalytic waves does not occur, and the observed waves are the total current of the bulk and surface waves.

For catalytic currents close to the limiting current, i.e., when the reverse chemical reaction ([3]), leading to disappearance of the cationic form of the catalyst, has practically no effect, one may write

$$i_{\text{pr}} = i_{\text{bulk}} + i_{\text{surf}} = sFk_1\mu_1 C_0[\text{DH}^+]_s + sFk_1'\Gamma_1[\text{DH}^+]_s, \tag{1}$$

where s is the electrode surface; F is Faraday' s number; $[\text{DH}^+]_s$ and C are the concentrations at the electrode surface of the proton donor and catalyst (it is assumed that the equilibrium in the bulk is shifted strongly toward its basic–inactive–form); μ_1 is the thickness of the reaction layer in which the preceding bulk reaction proceeds ([7,8,3]); k_1 and

k^1–the rate constants for addition of a proton to the catalyst in solution and in the adsorbed state, respectively; Γ is the amount of adsorbed catalyst. The bulk catalytic current–the first term in (1)–is given by ([3]) on the basis of the reaction-layer concept ([7,3]); however, for the case considered here an exact calculation leads to practically the same expression (equation (49) in ([9])).

Fig. 3. Scheme of formation of two peaks on the catalytic wave. a–reversible ("bulk"), b– "adsorption," v–total wave. $E_{1/2}^{\text{obr}} - E_{\max}^{\text{neobr}}$ are equal, respectively (in mV): 1–+30; 2––30; 3––55; 4––75; 5––80; 6––95.

For the second catalytic wave of quinine (catalysis by the nitrogen atom of the quinuclidine nucleus) in a $0.1N$ borax solution, it was found from experimental data that

$$i_{\text{ob}}/C_{\text{quin}} = 43\ \mu\text{a/m}M.$$

Using (for the calculation of μ_1) the value of the diffusion coefficient of quinine

$$D = 5.4 \cdot 10^{-6}\ \text{cm}^2/\text{sec},$$

found from the diffusion current of its reduction ([10]), the ionization constants of quinine, $s_{\text{cp}} = 2.5 \cdot 10^{-3}$ cm^2, $[\text{OH}^-] = 1.7 \cdot 10^{-5}$, and the constant $K = 1.1 \cdot 10^{-6}$, assuming that $\text{DH}^+ = \text{H}_2\text{O}$, from (1) we found

$$k_1 = 1.6 \cdot 10^3\ \text{sec}^{-1}(\text{mol/l})^{-1}.$$

If it is assumed that the rate constants for interaction of the catalyst present in solution and in the adsorbed state with water molecules are close, i.e., $k_1 \approx k'_1$, then from the value of the maximum current of the total catalytic wave (6.2 μa) at $C_{\text{quin}} = 3.6 \cdot 10^{-5} M$, by (1) one obtains for Γ the value

$$2.1 \cdot 10^{-13} \text{ g} \cdot \text{mol/cm}^2.$$

The maximum value of Γ (Γ_∞), corresponding to saturation of the electrode surface, is $4.4 \cdot 10^{-10}$ ([11]), whereas Γ_∞, found from the maximum height of the adsorption pre-wave of Brdička ([12]) before the diffusion wave of quinine reduction, proved to be $1.3 \cdot 10^{-10}$ g $\cdot$ mol/cm^2. Taking $\Gamma_\infty = 4.4 \cdot 10^{-10}$, we find that the surface coverage under the indicated conditions ($E = 1.91$ V vs. sat. cal. el. and $C_{\text{quin}} = 3.6 \cdot 10^{-5} M$) is

$$\theta_{\text{op}} = \Gamma/\Gamma_\infty = 0.0018,$$

i.e., the surface is filled only by $\sim 0.2\%$. The adsorption process under consideration evidently occurs at potentials considerably more negative than the "desorption peak," which, as shown by A. N. Frumkin ([13]), corresponds to the maximum $d\theta/dE$.

It was established by special experiments that adsorption of the quinine reduction product (at the isoquinoline nucleus ([10])), i.e., the product that causes the catalytic wave under consideration, obeys the S-shaped adsorption isotherm of A. N. Frumkin ([14]). The magnitude of the attraction factor, however, is small in the present case, so that the Frumkin adsorption isotherm can be replaced by the Langmuir isotherm:

$$\theta_e = \Gamma_e/\Gamma_\infty = \frac{\beta C}{1 + \beta C}; \tag{2}$$

(where θ_e and Γ_e are equilibrium values), and for further calculations the results of the work of Delahay and Fike ([15]) can be used.

Taking, as a first approximation, that adsorption equilibrium is attained on the drop, i.e., $y' = \Gamma/\Gamma_e \approx 1$, we find from (2):

$$\beta' = 0.05 \text{ mmol}^{-1}$$

and $\beta' C$ (or C^0/a, in the notation of ([15])) $= 0.0018$. Using this value from Fig. 4 of ([15]), we find the value

$$y'_0 = \Gamma/\Gamma_e = 0.055$$

and, after introducing into it the correction for the larger than in ([15]) value of

Fig. 4. Catalytic wave at $C_{\text{quin}} = 1.4 \cdot 10^{-4}$ M and different h_{Hg} (cm): 1 –100; 2 –90; 3 –80; 4 –70; 5 –60; 6 –50; 7 –40 (uncorrected).

Figure 3: Fig. 4. Catalytic wave at $C_{\text{quin}} = 1.4 \cdot 10^{-4}$ M and different h_{Hg} (cm): 1 –100; 2 –90; 3 –80; 4 –70; 5 –60; 6 –50; 7 –40 (uncorrected).

D/T_∞ ($1.25 \cdot 10^4$ cm^4/s $\cdot$ mol), we obtain the second approximation $y'' = 0.069$ and $\theta_e'' = \theta_{\text{op}}/y'' = 0.026$. Substituting this value of θ_e'' into (2), finding β'', and again repeating the entire course of the calculations, we finally find: $\beta = 10.9$ mmol^{-1}, $y = 0.069$, and $\theta_e = 0.026$. These data show that, under the conditions considered, adsorption equilibrium is reached only by $\sim 7\%$ ($y \approx 0.07$)*.

With an increase in the adsorption time t, the value of y, and consequently also Γ, should increase, and according to (1) i_{pov} should increase as well. Indeed, as can be seen from Fig. 4, when the height of the mercury column is changed, a noticeable change in the adsorption catalytic wave is observed. The appearance and increase of i_{pov} can also explain the growth of waves with increasing t in catalysis by pyridine ([16,3]) and other substances ([17]).

The value of β, as A. N. Frumkin ([18]) showed, decreases sharply with increasing cathodic potential; therefore, for many substances whose catalytic waves are observed at less cathodic potentials than the second wave of quinine, one should expect considerably larger values of β, and consequently ([15]) of y and Γ, so that for their waves i_{pov} should exceed i_{ob} by several orders of magnitude. If, in this case, $y \approx 1$, then the catalytic waves do not depend on the height of the mercury column.

It should be noted that the change in β with potential ([18]) is the cause of the decrease in current on kinetic and catalytic ([5]) waves; ([19]).

Fig. 4. Catalytic wave at $C_{\text{quin}} = 1.4 \cdot 10^{-4}$ M and different h_{Hg} (cm): 1 –100; 2 –90; 3 –80; 4 –70; 5 –60; 6 –50; 7 –40 (uncorr.)

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* It should be kept in mind that the calculation given provides only an order of magnitude, since, generally speaking, $k_1 \neq k_1'$.

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