THE EFFECT OF THE STRUCTURE OF THE DOUBLE LAYER ON THE IRREVERSIBLE POLAROGRAPHIC REDUCTION WAVES OF ORGANIC SUBSTANCES HAVING PROTON CONSUMPTION IN THE POTENTIAL DETERMINING STAGE

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It follows from theoretical work by A. N. Frumkin [1-3] that the effect of the structure of the double layer on irreversible polarographic waves is, in the general case, governed by three factors: Change in the effective potential discontinuity between the electrode and the discharging particle, change in ion concentration at the electrode surface from the value in the volume of the solution, and change in adsorptivity of the substances involved. Using A. N. Frumkin's retarded discharge theory for the change in $E_{1/2}$ of waves independent of the pH, the following equation may be written when there is a change in structure of the double layer

$$\Delta E_{1/2} = \Delta \psi_1 \left(\frac{\alpha n_a - z}{\alpha n_a} \right), \tag{1}$$

where ψ_1 is the potential drop in the diffusional part of the double layer [3], α is the transfer coefficient ($0 < \alpha < 1$), n_a is the number of electrons being transferred in the potential determining stage (usually $n_a = 1$), z is the charge on the particle being discharged. If the concentration of indifferent electrolytes is increased, the absolute value of ψ_1 decreases, while for not too small values of ψ_1 in 1,1-charge electrolytes it is true [3] to a sufficient degree of accuracy that:

$$\psi_1 = \text{const} + \frac{RT}{F} \ln C - \frac{2RT}{F} \ln \varphi_a, \tag{2}$$

where C is the concentration of electrolyte, φ_a is the electrode potential, relative to electro-capillary zero. For aqueous solutions at 25°, if C is expressed in moles per liter, the constant in (2) is equal to ≈ -0.06 v. For the discharge of uncharged particles ($z = 0$), as follows from (1), $\Delta E_{1/2} = \Delta \psi_1$, i.e., the change in $E_{1/2}$ occurring during change in structure of the double layer is caused simply by the change in the effective potential discontinuity between the electrode and the particle being discharged, equal to $\varphi_a - \psi_1$. It should be noted that the influence of the change in the effective potential discontinuity on the value of $E_{1/2}$ for organic compound waves was first pointed out by E. S. Levin and Z. I. Fodiman [4].

The present paper discusses the effect of the structure of the double layer on the value of $E_{1/2}$ for irreversible waves for the case where proton consumption occurs in the potential determining stage of the reaction. Simultaneous transfer of an electron and a proton apparently has low probability; the actual electrochemical reaction is obviously preceded by protonation of the organic molecule. Actually protonation which precedes the reaction occurs in the reduction of nitro-compounds [5, 6] in acid medium, of derivatives with an azomethyl group [7], of nitrosoamines [8], of N-oxides [22] of various pyridine derivatives [9] of sidnones [10], and of many other organic compounds. It may therefore be assumed that the protonation which precedes the reaction occurs in all irreversible polarographic waves, which correspond with reactions having proton consumption in the potential determining stage

$$R + H^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} RH^+ \tag{I}$$

$$RH^+ + e^- \rightarrow RH^\cdot, \qquad (II)$$

where H^+ is a hydrogen ion or any other proton donor.

The chemical reaction which precedes the electron transfer can occur in the volume of the solution, – in the so-called reaction layer [11, 12], and on the surface of the electrode itself [13, 14] with adsorbed particles participating. Let us make a comparison between the quantity of the substance R, occurring in the reaction layer of μ, and in the adsorbed state on the electrode surface. We shall consider reactions occurring under conditions where no noticeable concentration polarization takes place. We shall assume that the thickness of the reaction layer is $\mu = 50$ A, while with the concentration of the substance R in the mass of the solution of the order 0.5 mM, the quantity in the reaction layer over against 1 cm^2 of electrode surface will be: $5 \cdot 10^{-7}$ cm × 1 cm^2 × $5 \cdot 10^{-7}$ mole/cm^3 = $2.5 \cdot 10^{-13}$ g-mole. On the other hand, if the filling of the electrode surface with adsorbed R amounts to only 0.5% altogether, then for $\Gamma_\infty = 5 \cdot 10^{-10}$ mole/cm^2 (Γ_∞ is the maximum amount of adsorbed substance on the surface when it is completely covered by a monolayer), the quantity of substance in the adsorbed state is $\Gamma = 2.5 \cdot 10^{-12}$ g/mole, i.e., an order of magnitude greater than in the volume reaction layer. We shall assume that the rate constant k_1 of the reaction (I) both in the volume and on the surface has one and the same order of magnitude, while even in the case considered above of relatively small adsorption, the process is determined principally by the reaction occurring on the electrode surface, i.e., by the "surface" reaction. If in addition we keep in mind that almost all organic substances at not very negative potentials have considerable surface activity [15] and further, that, as will be shown later on, the concentration of proton donors at the cathode surface is consideredably greater than in the volume of the solution, we can come to the conclusion that in the electrochemical reduction of organic substances the protonation preceding the reaction in acid solutions goes, as a rule, on the electrode surface.

The effect of structure of the double layer on the kinetics of the preceding chemical reactions involving ions depends on the relation between the thickness of the reaction layer and the extent of the diffusional part of the double layer [16]: With no change in the magnitude of the ψ_1-potential, the effect of the structure of the double layer will be greater, the smaller the thickness of the reaction layer [16]. The maximum effect of the double layer is obviously on the kinetics of the ionic reactions occurring on the electrode surface itself, i.e., on the "surface" kinetic currents [17, 23].

For any acid-base system

$$A^- + H^+ \rightleftarrows HA \quad \text{or} \quad B + H^+ \rightleftarrows BH^+, \qquad (III)$$

where A is any anion (including OH^-), B is an unchanged base (including water), and the charge of acidic components is always greater by unity than the charge of the bases conjugated with them, so that under the influence of the electrostatic field of the cathode, the acid-base equilibrium at the electrode surface is more shifted to the acid form side than in the volume of the solution [17, 23].

The change in ion concentration near the electrode surface with no specific adsorption obeys the Boltzmann distribution, so that for concentrations of cations $[BH^+]$ and anions $[A^-]$ we can write in the immediate vicinity of the electrode surface

$$[BH^+]_S = [BH^+]_0 e^{-\psi_1 F/RT} \text{ and } [A^-]_S = [A^-]_0 e^{\psi_1 F/RT}, \qquad (3)$$

where the indices S and 0 refer respectively to the concentrations at the electrode surface and in the body of the solution.

Assuming that the electrode field does not change the dissociation constant of the acids, and keeping in mind that in the absence of adsorption $[HA]_S = [HA]_0$ and $[B]_S = [B]_0$, we can write on the basis of (3):

$$\left(\frac{[HA]}{[A^-]}\right)_S : \left(\frac{[HA]}{[A^-]}\right)_0 = \left(\frac{[BH^+]}{[B]}\right)_S : \left(\frac{[BH^+]}{[B]}\right)_0 = \frac{[H^+]_S}{[H^+]_0} = e^{-\psi_1 F/RT}, \qquad (4)$$

from which it follows that under the influence of a field the pH at the cathode surface can be considerably lower than in the volume of the solution.

The value of $E_{1/2}$ for polarographic waves with preceding protonation becomes negative with increase in pH, giving usually $\partial E_{1/2}/\partial pH \approx (-40) - (-80)$ mv/pH unit. A change in pH at the electrode with change in structure of

the double layer ought to be reflected in the $E_{1/2}$ of such waves, the shift in $E_{1/2}$ from the change in $(pH)_S$ alone being, as is easily shown:

$$\Delta E_{1/2} = \frac{\partial E_{1/2}}{\partial pH} \frac{\Delta \psi_1 F}{2{,}3\,RT}. \qquad (5)$$

If in the processes with a preceding chemical reaction of first order with respect to R [for example (I)], the substance R is an ion, the change in concentration of R under the influence of a field will produce a proportional change in concentration of the electrochemically active product being formed, and, consequently, in the rate of the electrochemical reaction. Thus, even in the case of processes with a preceding chemical reaction, the initial reagent of which is provided by ions Eq. (1) is applicable, and $\underline{z}$ represents the charge of the original, electrochemically inactive particle R.

Bearing in mind what has been said, from Eqs. (1) and (5) we find the general expression for $E_{1/2}$ of the irreversible electrode process

$$\Delta E_{1/2} \approx \Delta \psi_1 \left(\frac{\alpha n_a - z}{\alpha n_a} + \frac{\partial E_{1/2}}{\partial pH} \cdot \frac{F}{2{,}3\,RT} \right). \qquad (6)$$

With no preceding protonation $\partial E_{1/2}/\partial$ pH = 0, and Eq. (6) goes over into Eq. (1).

For cations, $z > 0$, and so from (6) if the ionic strength of the solution is increased we should expect a shift of $E_{1/2}$ toward negative potentials. Actually, the $E_{1/2}$ values for the waves of the N-oxide of N-methylpiperidine [22] in acetate buffer with pH 4.65 at an ionic strength increased ten fold (addition of NaCl) become almost 200 mv more negative, which is in good agreement with (6): In the case mentioned $z = 1$ (pK_A of the N-oxide of N-methylpiperidine = 5.12), $\alpha n_a \approx 0.3$, $\partial E_{1/2}/\partial$ pH $\approx (-60)-(-70)$ mv/pH units.

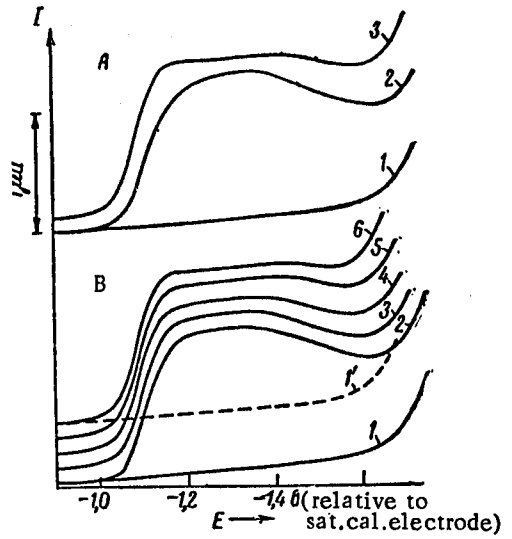
For the majority of organic substances $z = 0$. Bearing in mind that the magnitude of the second term in (6) is close to (−1), we can conclude from (6) that in the waves of uncharged substances with a preceding surface potential, $E_{1/2}$ should be only slightly dependent on ψ_1 or the ionic strength of the solution. Actually, as is shown by experiment, $E_{1/2}$ for the wave of the semicarbazone of 2-acetylthiophene is almost independent of the ionic strength of the solution. Very little change in $E_{1/2}$ with ionic strength is observed for some nitro compounds [18]. For the discharge of anions, $z < 0$, and, as is well known [2] an increase in the ionic strength of the solution, especially if it contains polyvalent cations, considerably facilitates reduction of the anions.

It should be noted that the effect of a change in the ψ_1-potential in processes preceded by protonation was first discussed by Z. Grabowski and E. Bartel [19], who found good quantitative agreement with theory thanks to the surface character of the process which they were studying.

The structure of the double layer affects not only the $E_{1/2}$ of the waves, but also the currents, which are limited by the preceding chemical reaction. Adsorption of components of the epi-electrode reaction, and the higher pH in the epi-electrode layer considerably accelerate the rate of epi-electrode chemical protonation reactions [17].

If we calculate the rate constants of the reactions from the polarographic data without taking account of these factors, the rate constants so found may be several orders of magnitude greater than their true values [13, 14]. Gradual desorption of material with increase in cathode potential [20] is a fundamental cause of the appearance of "drops" in the waves limited by a preceding reaction [21].

Figure 1 gives polarograms for the semicarbazone of 2-acetylthiophene in acetate buffer with pH = 4.65 with different buffer capacity of the solution (A) and different ionic strength (B). These waves are limited by the protonation rate of the semi-carbazone, which is in the adsorbed state. If the protonation rate is sufficiently high, the limiting current approaches the diffusion current (potential range (−1.2)−(−1.3) in figure). With increase in cathode potential, the adsorptivity of the semi-carbazone drops [20] as a result of which the rate of the preceding reaction is reduced [21], the limiting current becomes less than the diffusion current, and a characteristic drop (figure) appears on the wave. If the buffer capacity is reduced, the protonation rate falls off, as a result of which the depth of the drop is increased (fig. A). A similar phenomenon is observed also on increasing the ionic strength of the solution (fig. B), which, causes on the one hand, an increase in pH in the epi-electrode layer as given by (4), and, on the other hand, causes a reduction in adsorptivity of the semi-carbazone [20]: Either the one or the other reduces the rate of the protonation reaction, and, consequently, favors deepening of the drop on the polarogram.



Polarograms of semi-carbazone of 2-acetylthiophene ($4.0 \cdot 10^{-4}$ M) in acetate buffer solutions ($CH_3COOH + CH_3COOK + KCl$) with pH 4.65. Electrode characteristics (with forced drop separation), m = 1.02 mg/sec, t = 0.23 sec. A) Ionic strength constant = 0.5; 1) background; CH_3COOH concentration: 2) 0.1 M; 3) 0.4 M. B) CH_3COOH concentration constant (~0.1 M). Ionic strength: 2) 1.6; 3) 0.8; 4) 0.4; 5) 0.2; 6) 0.1 M. 1 and 1') Background at ionic strength 1.6 M and 0.1 M.

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