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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF THE STRUCTURE OF THE DOUBLE LAYER ON IRREVERSIBLE POLAROGRAPHIC WAVES OF REDUCTION OF ORGANIC SUBSTANCES WITH CONSUMPTION OF PROTONS IN THE POTENTIAL-DETERMINING STAGE

(Presented by Academician A. N. Frumkin on September 8, 1961)

From the theoretical works of A. N. Frumkin ($^{1-3}$) it follows that the influence of the structure of the double layer on irreversible polarographic waves is, in the general case, due to three factors: a change in the effective potential drop between the electrode and the discharging particle, a change in the concentration of ions at the electrode surface as compared with the bulk of the solution, and a change in the adsorbability of substances. On the basis of A. N. Frumkin' s theory of slow discharge, for the change in $E_{1/2}$ of waves that do not depend on pH, when the structure of the double layer is changed, one may write:

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

where ψ_1 is the potential drop in the diffuse part of the double layer (^{3}), α is the transfer coefficient ($0 < \alpha < 1$), n_a is the number of electrons transferred in the potential-determining stage (usually $n_a = 1$), and z is the charge of the discharging particle. With an increase in the concentration of indifferent electrolytes, the absolute value of ψ_1 decreases; moreover, for not too small ψ_1 in 1,1-valent electrolytes, the following relation holds with sufficient accuracy (^{3}):

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

where C is the electrolyte concentration and φ_a is the electrode potential relative to the electrocapillary zero. For aqueous solutions at 25°, if C is expressed in moles per liter, the constant in (2) is approximately −0.06 V. For discharge of uncharged particles ($z = 0$), it follows from (1) that $\Delta E_{1/2} = \Delta\psi_1$, i.e., the change in $E_{1/2}$ upon a change in the structure of the double layer is due only to the change in the effective potential drop between the electrode and the discharging particle, equal to $\varphi_a - \psi_1$. It should be noted that the influence of a change in the effective potential drop on $E_{1/2}$ of waves of organic compounds was first observed by E. S. Levin and Z. I. Fodiman (^{4}).

In the present work, the influence of the structure of the double layer on $E_{1/2}$ of irreversible waves is considered for the case when, in the potential-determining stage of the process, consumption of protons occurs. Simultaneous transfer of an electron and a proton is apparently unlikely; the electrochemical reaction proper is evidently preceded by protonation of the organic molecule. Indeed, preceding protonation occurs in the reduction in acid medium of nitro compounds (^{5,6}), derivatives with an azomethine group (^{7}), nitrosamines (^{8}), *N*-oxides (^{22}), various pyridine derivatives (^{9}), sidnones (^{10}), and many other organic compounds. It may therefore be assumed that preceding protonation occurs in all irreversible polarographic waves corresponding to processes with consumption of protons in the potential-determining stage:

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

$$\mathrm{RH}^+ + e^- \rightarrow \mathrm{RH}^{\cdot}, \tag{II}$$

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

The chemical reaction preceding electron transfer can proceed both in the bulk of the solution—in the so-called reaction layer (^{11,12})—and on the electrode surface itself (^{13,14}), with the participation of adsorbed particles. Let us compare the amount of substance R present in the reaction layer μ and in the adsorbed state on the electrode surface. We shall consider processes proceeding under conditions in which no appreciable concentration polarization occurs. Let us take the thickness of the reaction layer as $\mu = 50$ Å; then, at a concentration of substance R in the bulk of the solution of the order of 0.5 mM, its amount in the reaction layer opposite 1 cm^2 of electrode surface will be: $5 \cdot 10^{-7}$ cm $\times$ 1 cm^2 $\times$ $5 \cdot 10^{-7}$ mol/cm^3 $= 2.5 \cdot 10^{-13}$ g-mol. On the other hand, if the coverage of the electrode surface by adsorbed R is only 0.5%, then, at $\Gamma_\infty = 5 \cdot 10^{-10}$ mol/cm^2 (Γ_∞ is the maximum amount of adsorbed substance on the surface when it is fully covered by a monolayer), the amount of substance in the adsorbed state is $\Gamma = 2.5 \cdot 10^{-12}$ g-mol, i.e., an order of magnitude greater than in the bulk reaction layer. Suppose that the rate constant k_1 of reaction (I), both in the bulk and on the surface, has one and the same order of magnitude; then even in the case considered above of comparatively small adsorption, the process is determined mainly by the reaction occurring on the electrode surface, i.e., by the "surface" reaction. If, in addition, one takes into account that almost all organic substances at not very negative potentials possess considerable surface activity (^{15}), and bears in mind that, as will be shown below, the concentration of proton donors at the cathode surface is considerably higher than in the bulk of the solution, one may conclude that, in the electrochemical reduction of organic substances, the preceding protonation of them in acid solutions generally occurs on the electrode surface.

The influence of the structure of the double layer on the kinetics of preceding chemical reactions involving ions depends on the ratio between the thickness of the reaction layer and the extent of the diffuse part of the double layer ([16]): at a constant value of the ψ_1-potential, the influence of the structure of the double layer will be greater the smaller the thickness of the reaction layer ([16]). The double layer evidently exerts the maximum influence on the kinetics of ionic reactions occurring on the electrode surface itself, i.e., on "surface" kinetic currents ([17,23]).

For any acid-base system

$$\mathrm{A^- + H^+ \rightleftarrows HA} \quad \text{or} \quad \mathrm{B + H^+ \rightleftarrows BH^+}, \tag{III}$$

where A^- is some anion (including OH^-), B is an uncharged base (including water), the charge of the acidic components is always one unit higher than the charge of the conjugate bases; therefore, under the action of the electrostatic field of the cathode, the acid-base equilibrium at the electrode surface, in comparison with the bulk of the solution, is shifted toward the acidic form ([17,23]).

The change in the concentration of ions near the electrode surface in the absence of specific adsorption obeys the Boltzmann distribution; therefore, for the concentrations of cations $[BH^+]$ and anions $[A^-]$ directly at the electrode surface, one may write:

$$[\mathrm{BH^+}]_S = [\mathrm{BH^+}]_0 e^{-\psi_1 F/RT} \quad \text{and} \quad [\mathrm{A^-}]_S = [\mathrm{A^-}]_0 e^{\psi_1 F/RT}, \tag{3}$$

where the subscripts S and 0 refer, respectively, to concentrations at the electrode surface and in the bulk of the solution.

Assuming that the electrode field does not change the dissociation constants of acids, and taking into account that in the absence of adsorption $[\mathrm{HA}]_S =$ $= [\mathrm{HA}]_0$ and $[\mathrm{B}]_S = [\mathrm{B}]_0$, on the basis of (3) one may write:

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

whence it follows that, under the influence of the field, the pH at the cathode surface may be considerably lower than in the bulk of the solution.

The values of $E_{1/2}$ of polarographic waves with preceding protonation become more negative with increasing pH, and usually
$\partial E_{1/2}/\partial \text{pH} \simeq -40 \div -80$ mV/pH unit. A change in the pH at the electrode upon a change in the structure of the double layer should be reflected in $E_{1/2}$ of such waves; moreover, as is not difficult to show, the shift of $E_{1/2}$ due solely to the change in $(\text{pH})_S$ is:

$$\Delta E_{1/2} = \frac{\partial E_{1/2}}{\partial \text{pH}} \frac{\Delta\psi_1 F}{2.3\,RT}. \tag{5}$$

If, in processes with a preceding first-order chemical reaction with respect to R (for example, (I)), the substance R is an ion, then the change in the concentration of R under the action of the field will cause a proportional change in the concentration of the electrochemically active product formed, and, consequently, also in the rate of the electrochemical process. Thus, in the case of processes with a preceding chemical reaction in which ions serve as the initial reactant, expression (1) is applicable to them as well; in it the quantity z now denotes the charge of the initial, electrochemically inactive particle R.

Taking the above into account, on the basis of (1) and (5) we find the general expression for $E_{1/2}$ of an irreversible electrode process:

$$\Delta E_{1/2} \simeq \Delta\psi_1 \left(\frac{\alpha n_a - z}{\alpha n_a} + \frac{\partial E_{1/2}}{\partial \text{pH}} \cdot \frac{F}{2.3\,RT} \right). \tag{6}$$

In the absence of preceding protonation, $\partial E_{1/2}/\partial \text{pH} \simeq 0$, and expression (6) reduces to (1).

For cations $z > 0$; therefore, on the basis of (6), with increasing ionic strength of the solution one should expect a shift of $E_{1/2}$ toward negative potentials. Indeed, the $E_{1/2}$ of the waves of N-oxide of N-methylpiperidine ([22]) in acetate buffer with pH 4.65, when the ionic strength is increased 10-fold (addition of NaCl), becomes almost 200 mV more negative, which agrees well with (6): in the indicated case $z = 1$ (pK_A of N-oxide of N-methylpiperidine 5.12), $\alpha n_a \simeq 0.3$, $\partial E_{1/2}/\partial \text{pH} \simeq -60 \div 70$ mV/pH unit.

For most organic substances $z = 0$. Taking into account that the magnitude of the second term in parentheses in (6) is close to -1, on the basis of (6) one may conclude that, for waves of uncharged substances with preceding surface protonation, $E_{1/2}$ should depend only very weakly on ψ_1 or on the ionic strength of the solution. Indeed, as experience shows, $E_{1/2}$ of the wave of semicarbazone of 2-acetylthiophene depends almost not at all on the ionic strength of the solution. A very small change of $E_{1/2}$ with ionic strength was also observed for some nitro compounds ([18]). In the case of discharge of anions $z < 0$, and, as is well known ([2]), an increase in the ionic strength of the solution, especially the presence in it of polyvalent cations, markedly facilitates the reduction of anions.

It should be noted that the influence of a change in the ψ_1-potential on processes with preceding protonation was first considered by Z. Grabovsky and E. Bartel (^{19}), who obtained good quantitative agreement with theory owing to the surface character of the process they studied.

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

If rate constants of reactions are calculated from polarographic data without taking these factors into account, then the constants thus found

rates may exceed their true values by several orders of magnitude (^{13,14}). The gradual desorption of substances with increasing cathodic potential (^{20}) is the main reason for the appearance of "depressions" on waves limited by a preceding reaction (^{21}).

Figure 1 shows polarograms of 2-acetylthiophene semicarbazone in an acetate buffer with pH 4.65 at different buffer capacities of the solution (A) and different ionic strengths (B). These waves are limited by the rate of protonation of semicarbazone present in the adsorbed state. If the protonation rate is sufficiently high, then

Fig. 1. Polarograms of 2-acetylthiophene semicarbazone ($4.0 \cdot 10^{-4}$ M) in acetate buffer solutions ($CH_3COOH + CH_3COOK + KCl$) with pH 4.65. Electrode characteristics (with forced detachment of drops): $m = 1.02$ 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**: concentration of CH_3COOH 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 strengths 1.6 M and 0.1 M.

the limiting current approaches the diffusion current (potential region −1.2–−1.3 V in Fig. 1). With increasing cathodic potential, the adsorbability of semicarbazone decreases (^{20}), as a result of which the rate of the preceding reaction decreases (^{21}), the limiting current becomes lower than the diffusion current, and a characteristic depression appears on the wave (Fig. 1). When the buffer capacity is decreased, the protonation rate falls, as a result of which the depth of the depression increases (Fig. 1A). A similar phenomenon is also observed when the ionic strength of the solution is increased (Fig. 1B), which leads, on the one hand, to an increase in pH in the near-electrode layer according to (4), and, on the other, to a decrease in the adsorbability of semicarbazone (^{20}): both effects slow the rate of the preceding protonation reaction and, consequently, contribute to deepening the depression on the polarogram.

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