Physical Chemistry

S. G. Mairanovskii

1964

SovietRxiv

Abstract

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S. G. Mairanovskii

On Quasi-Diffusion Surface Waves in Polarography

(Presented by Academician A. N. Frumkin, 29 VIII 1963)

If a fast chemical reaction preceding the electrochemical stage proper of the electrode process takes place on the electrode surface with the participation of adsorbed substances, then the magnitude of the "surface" [^1] kinetic currents observed in this case is substantially influenced by the factors that determine adsorption of the components of the near-electrode chemical reactions. Thus, for example, a decrease in the adsorbability of substances[^2] as the cathode potential is shifted away from the potential of maximum adsorption $E_{\max}$ (which lies near the point of zero charge) leads to characteristic drops on the surface kinetic waves[^3].

Let i_d denote the diffusion current, and i_{pr} the observed or fictitious limiting kinetic current, which occurs (or would occur) at a sufficiently high rate of electron transfer. Let the adsorption of the components of the near-electrode reaction obey the Langmuir isotherm and let the surface coverage by these components be very small. In this case, provided that $i_d \geq i_{\text{pr}} > 0.55 i_d$, the form of the surface kinetic wave is expressed with sufficient accuracy by the following set of equations[^4]:

$$\lg \frac{i_{\text{pr}}}{i_d - i_{\text{pr}}} = A - 0.43 a \varphi^2, \tag{1}$$

$$E = E_{1/2} - \frac{bb'}{b' - b} \lg \frac{i}{i_{\text{pr}} - i}. \tag{2}$$

Here A is a constant, equal, for currents averaged over the dropping period, to

$$A = \lg 6.15 \cdot 10^{-3} m^{2/3} t^{1/6} n k_1 [\mathrm{DH}^+]_s \frac{\beta^0 c D}{i_d}, \tag{3}$$

$$b = \frac{2.3RT}{\alpha n_a F}, \qquad b' = -\frac{2.3}{2a(E_{1/2} - E_{\text{M}})}, \tag{4}$$

Figure 1

Figure 1: Figure 1

a is the factor of the Frumkin equation[^2], which determines the change in β —the coefficient of the Langmuir equation—with potential; β^0 is the value of β at $E = E_{\text{M}}$, $\varphi = E - E_{\text{M}}$ is the potential relative to the point of maximum adsorption, n and n_a are the numbers of electrons participating, respectively, in the entire electrode process and in its potential-determining stage, D is the diffusion coefficient of the reaction component, k_1 is the rate constant of the forward preceding chemical reaction, $[\text{DH}^+]_s$ is the near-electrode concentration of the 2nd reaction component (in the case of a protolytic preceding reaction, $\{\text{DH}^+\}_s$ is the concentration of proton donors). The potential $E_{1/2}$, at which $i = \frac{1}{2} i_d$, is equal to:

$$E_{1/2} = \frac{bb'}{b' - b} \left\{ \lg \frac{k_{\text{el}}}{k_2 [D]_s} + A - 0.43a \left[(E_{1/2} - E_{\text{M}})^2 - 2E_{\text{M}}(E_{1/2} - E_{\text{M}}) \right] \right\}, \tag{5}$$

k_{el} is the rate constant of electron transfer at $E = 0$, $k_2[D]_s$ is the rate of the reverse preceding reaction leading to deactivation of the electrochemically active particles.

The decrease in the limiting kinetic current with removal of the electrode potential from the point of maximum adsorption, due to the decrease in the adsorbability of the reaction components, is expressed by equation (1). The character of the dependence of i_{pr} on E is reflected by curve 1 in Fig. 1.

Fig. 1. The first reduction wave of 5-bromo-2-acetylthiophene ($C = 0.215$ mM) in a background of 0.1 N KCl + 0.1 N KOH at 25°. Points —experimental current values obtained with a dropping electrode ($m = 1.07$ mg/sec, $t = 0.26$ sec.); 1 —change of i_{pr} with potential (according to equation (1)); 2 —theoretical dependence i-E (according to equation (2) with $i_{\text{pr}} = i_d$); 3 —constructed according to equations (1) and (2); 4 —level of the diffusion current.

If the surface limiting kinetic current did not vary with potential, then the wave shape would correspond to curve 2 in Fig. 1, constructed from (2) under the assumption that $i_{\text{pr}} = \text{const} = i_d$. The combination of equations (1) and (2), thus taking into account the influence of a change in potential both on the adsorbability of the reaction components and on the rate of electron transfer, describes the shape of the surface kinetic wave. In Fig. 1 it is represented by curve 3. In the same place in Fig. 1, the experimental values of the reduction currents of 5-bromo-2-acetylthiophene proceeding with preliminary protonation of the molecule in the adsorbed state are shown by points.* As follows from Fig. 1, the experimental points fit the calculated curve well. The curves in Fig. 1 were constructed from the values: $a = 11.3$ V^{-2}, $A = 4.45$, $i_d = 0.68\,\mu$a,

Figure 2

Figure 2: Figure 2

$\frac{bb'}{b'-b} = 0.128$ V, $E_M = -0.45$ and $E_{1/2} = -1.20$ V (sat. cal. el.).

Good agreement between the experimental and the calculated curves according to (1) and (2) was also obtained for a number of other electrode processes with preceding surface protonation (4).

At a sufficiently high rate of the preceding surface reaction, the value of i_{pr} along the entire kinetic wave is close to i_d. In this case the wave has a distinct plateau of limiting current, and the wave height is determined by the Ilkovič equation; however, the shape of such a "quasidiffusion" surface wave and the dependence of its $E_{1/2}$ on various factors do not obey the regularities for ordinary irreversible polarographic waves. If the adsorption of the inactive form of the depolarizer obeys the Langmuir isotherm and the surface coverage is small, then the wave shape is described by equation (2), in which, instead of i_{pr}, there stands the practically equal value i_d (see curve 2 in Fig. 1). The half-wave potential is determined by expression (5). It follows from (2) that the slope of quasidiffusion surface waves in semilogarithmic coordinates is not equal to the value

Fig. 2. Dependence of $\lg \frac{i}{i_d - i}$ on E for a solution of bromoacetylthiophene at different pH values. 1–5.70; 2–6.16; 3–6.43; 4–7.08; 5–7.59; 6–8.25; 7–8.62; 8 –9.07; 9–0.1 N KOH + 0.1 N KCl

$$b = \frac{2.3RT}{\alpha n_a F},$$

characteristic of waves due to ordinary irreversible processes, but, as a rule, is appreciably greater than this latter value. As follows from (4), the quantity b'

* Presented in more detail in an article that will be printed in the journal *Izvestiya AN SSSR*, Chemical Series.

decreases as the $E_{1/2}$ of the wave moves away from E_{m}; therefore the slope of quasidiffusion waves $\frac{bb'}{b'-b}$ should increase when $E_{1/2}$ is shifted to more cathodic potentials (for example, when the pH of the solution is increased in the case of preceding protonation). This phenomenon, repeatedly observed experimentally (see, for example, [5–7]), has until now found no explanation.

The most active and widespread proton donor is the hydrogen ion; therefore, although other donors also exert some (small) influence on $E_{1/2}$ [8], for simplicity one may restrict consideration to the action of hydrogen ions alone and assume that only one proton participates in the potential-determining stage. In the case of waves with preceding bulk protonation, $\Delta E_{1/2}/\Delta\text{pH} = -b$, whereas the

value of $\Delta E_{1/2}/\Delta$pH for quasidiffusion waves, as the analysis of (5) shows [4], may differ somewhat from the slope of the semilogarithmic plot of the wave at a given pH.

It should be noted that, owing to the difference between the pH values in the bulk solution $(\mathrm{pH})_0$ and at the electrode surface $(\mathrm{pH})_S$, arising under the influence of the electrode field [9], when the pH is increased and $E_{1/2}$ is shifted to negative potentials, the inequality $\Delta(\mathrm{pH})_S < \Delta(\mathrm{pH})_0$ holds. This circumstance is the reason for a change in $E_{1/2}$ of surface waves with $(\mathrm{pH})_0$ smaller than that required by theory. Because of a certain change in ψ_1 (and consequently also in $(\mathrm{pH})_S$—see [9]) in the potential interval within the limits of the polarographic wave, the steepness of the wave corresponding to processes with preceding surface protonation may also increase (although, as a rule, only very slightly).

It follows from (3) and (5) that $E_{1/2}$ of quasidiffusion surface waves, with increasing t, as in the case of ordinary irreversible waves, becomes more positive; however, the magnitude of the shift of $E_{1/2}$ with $\lg t$ (which for a comparatively narrow interval of variation of t may approximately be regarded as linear) in the general case differs from half the slope of the semilogarithmic plot of the wave (the latter value is characteristic of the shift of $E_{1/2}$ with $\lg t$ for ordinary irreversible waves) [4].

Up to this point we have considered only cases in which the adsorption obeyed the Langmuir isotherm and the surface coverages were very small. However, under the conditions in which quasidiffusion waves are observed, the coverages may become quite appreciable, so that the S-shape of the A. N. Frumkin isotherms [10], characteristic of the adsorption of most substances, will begin to manifest itself. When the S-shape of the isotherm appears, equations (1)–(5) can no longer be used for quantitative calculations; however, the general character of the properties of quasidiffusion waves predicted by these equations is fully retained. In Fig. 2, as an example, plots are given of the dependence of $\lg \dfrac{i}{i_d - i}$ $-E$ for waves in a 0.102 mM solution of 5-bromo-2-acetylthiophene at different pH values in acetate-borate buffer mixtures with constant ionic strength $\mu = 0.2$ (in the final solution: 0.1 M CH_3COOK, 0.1 M KH_2BO_3, HCl to the required pH). Up to pH 7.0 the semilogarithmic plots are straight lines which, as the pH increases, shift toward negative potentials with some increase in slope (in qualitative agreement with (2)–(5)). At pH > 7.0 an inflection appears on the plots—the upper part of the waves has a larger slope than the lower part. At pH ≥ 8.3 a second inflection appears—the slope of the very upper part of the wave decreases in comparison with its value in the middle part. In a strongly alkaline solution the plot becomes nearly linear, with a slope close to that of the upper part of the wave at pH $\simeq 8.3$. This character of the change in the waves is explained by the S-shape of the adsorption isotherm of the unprotonated form of the depolarizer. In acidic solutions, where the potentials are close to E_{m}, very high adsorbability and high coverage occur, favored by the S-shape of the

isotherm. In this case, apparently, almost all are adsorbed

particles delivered to the electrode by diffusion. In weakly alkaline solutions, as the cathodic potential increases, adsorbability falls, and its maximum change with potential occurs on the rise of the S-shaped isotherm, which corresponds to the middle segment (with maximum slope) of curves 4-8 in Fig. 2. At still more cathodic potentials (and high pH), the surface coverage becomes so small that adsorption corresponds to the lower linear segment of the isotherm, and the slope of the wave is determined by equation (2).

Inflections in semilogarithmic plots of waves are encountered rather often. Thus, for example, Suzuki and Elving(11) observed an inflection on the waves of nitromethane in a strongly acidic medium, when the preceding protonation of the nitro compounds has a surface character(12). A picture very similar to that shown in Fig. 2 was observed by Elving and Olson in the polarography of solutions of aromatic N-nitrosohydroxylamines (see Fig. 3 in(13)).

It should be noted that quasidiffusion waves are a fairly widespread phenomenon in polarography. Thus, for example, all irreversible waves with preceding protonation (i.e., irreversible waves whose $E_{1/2}$ changes with pH), the height of which is close to the diffusion current, are quasidiffusion waves.

Changes in $E_{1/2}$ and in the slope of waves associated with a change in adsorption are observed not only for kinetic quasidiffusion surface waves, but also for irreversible waves with adsorption of the depolarizer. Thus, the appreciable shift of $E_{1/2}$ of the waves of α-bromocarboxylic acids(14) and their esters(14, 15), as well as of α-bromoaldehydes(16), toward less negative potentials with increasing length of the hydrocarbon chain and its branching was explained by Elving and co-workers by increased adsorbability of these compounds.

In the reduction of iodomethyltrialkylsilanes and bromoalkanes, which proceeds at very negative potentials, the adsorbability of these substances is practically not manifested; therefore, with increasing chain length and branching, $E_{1/2}$ of the waves (as a result of the inductive effect and steric hindrance) becomes somewhat more negative(17,18).

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
27 VII 1963

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