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Abstract

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THE INFLUENCE OF ADSORPTION OF ORGANIC SUBSTANCES ON THE KINETICS OF THEIR ELECTROREDUCTION

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A quantitative theory of the influence of the electric field on the adsorption of neutral molecules was proposed by A. N. Frumkin ([1,2]), who showed that, as the electric-field strength increases, the coverage of the electrode surface θ by adsorbed molecules decreases as a result of their displacement by solvent molecules, if the effective dielectric constant of the latter in the surface layer is greater than the effective dielectric constant of the adsorbate.

These ideas were used by S. G. Mairanovskii to construct a quantitative theory of "surface" catalytic waves of hydrogen ([3,4]). He showed that, with increasing negative potential, the rate of the process may pass through a maximum owing to the simultaneous acceleration of the process as a result of a decrease in the activation energy of the electrode reaction and its slowing as a result of a decrease in the coverage of the surface by molecules of the organic catalyst.

In the present work, on the basis of Frumkin' s theory, processes of irreversible reduction of adsorbed organic substances will be considered. It should be noted that L. I. Antropov ([5,6]) pointed out the connection between adsorption and desorption of organic substances, on the one hand, and the kinetics of their electroreduction, on the other.

For molecules with a complex structure, an important role in electrode reactions is played by their orientation relative to the electrode surface. Below we shall attempt to take the role of this factor into account as well. We shall confine ourselves to the case of low coverages, when the adsorption isotherm may be represented in the form

$$\theta = \beta c_s, \tag{1}$$

where c_s is the concentration of the reducible substance in the bulk of the solution near the electrode, and β is a function determined according to ([1]):

$$\beta = \beta_0 \exp[-a(\varphi')^2] = \beta_0' \exp\left[\frac{W_0 - a'(\varphi')^2}{RT}\right], \tag{2}$$

Fig. 1

Figure 1: Fig. 1

where φ' is the potential relative to the point of maximum adsorption, and W_0 is the adsorption energy without allowance for work against electrical forces.

The quantities W_0 and a' in equation (2) are determined by the structure of the molecules and by their orientation relative to the electrode. The value of a' increases with the area occupied by a molecule on the electrode surface ([1]); W_0 changes in the same way, since the adsorption energy will be the greater, the larger the part of the molecule in contact with the surface. Having calculated the values W_{0x} and a'_x for molecules with some definite orientation x, one can find, from formulas (1) and (2), the concentration of molecules with such an orientation in the adsorbed layer. As an approximation we shall consider the case in which the adsorbed molecules are found only in two limiting positions, namely, occupying the maximum or the minimum area on the electrode surface. The first position corresponds to the largest, and the second to the smallest, values of W_0 and a'. As follows from (2), the fraction of molecules of the first kind is especially large at small $|\varphi'|$ and falls sharply as $|\varphi'|$ increases. We shall denote the concentration of such molecules in the surface layer by c_{1a}.

Estimating c_{1a} by the formula

$$c_{1a} \approx 10^3 V^{-1} \theta_1, \tag{3}$$

where V is the molecular volume of the substance being reduced, we find for $c_s \leqslant 10^{-2}\, M$ that, even at $\theta \approx 0.01$, $c_{1a} \gg c_s$.* The fraction of molecules of the second kind, on the contrary, is insignificant at small $|\varphi'|$, but their number on the surface changes little with the potential. It is obvious that as long as $c_{1a} \gg c_s$, practically only molecules of the first kind are present in the surface layer.

Let us first consider the reduction of only such particles. Here and below it is assumed that the adsorption-desorption rate is much higher than the rate of the electrode reaction ([7]). In this case, in accordance with the theory of slow discharge ([8]), for the current density we have:

$$i = nFk_1 c_{1a} = nFk_{01} c_{1a} \exp\left[-\frac{\alpha n_{aF}}{RT}\varphi'\right], \tag{4}$$

where k_1 is the rate constant of the electrode reaction, α is the transfer coefficient of the electrode process, and n_a is the number of electrons participating in the slow stage.

Fig. 1. Polarization curves calculated for the following values of the constants: $a = 5$, $\chi = 10^{-5}$, $\sqrt{t/D} = 10^3$.

Fig. 2

Figure 2: Fig. 2

1 $-\alpha n_a = 0.35,\ k'_{01} = 1.0 \cdot 10^{-6}$; 2 $-\alpha n_a = 0.35,\ k'_{01} = 1.0 \cdot 10^{-7}$; 3 $-\alpha n_a = 0.23,\ k'_{01} = 1.5 \cdot 10^{-5}$

As was pointed out by A. N. Frumkin during discussion of the work, formula (4), which assumes proportionality between the concentration of the reacting substance in the activated-complex state and in the initial adsorbed state, is correct only at small θ. At large θ one should expect steric hindrance in the transition to the activated-complex state, and i may vary with θ nonmonotonically.

From (1), (2), (3), and (4) it follows that:

$$i = 10^8 V^{-1} n k'_{01} c'_s \exp\left[-a(\varphi')^2 - \frac{\alpha n_{aF}}{RT}\varphi'\right],$$

$$k'_{01} = \beta_{01} k_{01}, \tag{5}$$

$$-\frac{1}{i}\frac{\partial i}{\partial \varphi} = \frac{\alpha n_{aF}}{RT} + 2a\varphi'. \tag{6}$$

It follows from this that the quantity i passes through a maximum at the potential φ'_p:

$$\varphi'_p = -\alpha n_{aF}/2aRT. \tag{7}$$

The value of the current density at the maximum is i_p

$$i_p = 10^8 V^{-1} n k'_{01} c'_s \exp\left[a(\varphi')^2\right], \tag{8}$$

whence, denoting $\varphi' - \varphi'_p = \Delta\varphi$, we obtain:

$$i = i_p \exp\left[-a(\Delta\varphi)^2\right]. \tag{9}$$

Fig. 2. Difference between the potentials of the maximum and minimum on the λ, φ-curve. $\chi = 10^{-5}$

Let us now consider the case where c_{1a} is small, i.e., where "favorably" and "unfavorably" oriented molecules are present on the surface in comparable—

* The presence of an organic substance on the surface at such small θ does not affect the electrocapillary curves and practically does not reduce the capacitance of the double layer.

quantities. To the reduction of molecules with an orientation "unfavorable" for the formation of adsorption bonds we assign the rate constant of the electrode reaction k_{02} at $\varphi' = 0$. The rate constant depends on the orientation, which is explained by the influence of the latter both on the activation energy and on the value of the steric factor. In accordance with what was said above, the quantity β from (1) for the "unfavorable" orientation depends little on φ'. We shall regard it as approximately constant and denote it by β_{02}. Assuming that αn_a does not change upon reorientation, we have:

$$\begin{aligned} i &= nF\left(k_{01}c_{01} + k_{02}c_{02}\right)\exp\left[-\frac{\alpha n_{aF}}{RT}\varphi'\right] \\ &= 10^8 V^{-1} n k'_{01} c_s \{\chi + \exp[-a(\varphi')^2]\}\exp\left[-\frac{\alpha n_{aF}}{RT}\varphi'\right], \end{aligned} \tag{10}$$

where $\chi = \beta_{02}k_{02}/k'_{01}$,

$$-\frac{1}{i}\frac{di}{d\varphi} = \frac{\alpha n_{aF}}{RT} + 2a\varphi'\{1 + \chi\exp[a(\varphi')^2]\}^{-1}. \tag{11}$$

The potentials of the extremal points on the i, φ-curve are determined by the equation

$$\chi\exp[a(\varphi')^2] + \frac{2aRT}{\alpha n_{aF}}\varphi' + 1 = 0. \tag{12}$$

It is not difficult also to take into account the possible change of αn_a upon reorientation; however, in this case the kinetic equations become more cumbersome.

In the equations derived, concentration polarization is not taken into account. The problem with allowance for concentration polarization, without allowance for the consumption of substance associated with adsorption, was first solved for the case of nonstationary diffusion by N. N. Meiman ([9]). He showed that the density of the instantaneous current, controlled by diffusion and by the rate of a first-order electrode reaction at constant potential, is a function of the parameter λ:

$$i/i_d = F(\lambda), \qquad \lambda = t^{1/2}D^{-1/2}K = it^{1/2}/nFD^{1/2}c_s, \tag{13}$$

where i_d is the magnitude of the instantaneous diffusion current, and t is the time from the moment of birth of the mercury drop (the beginning of electrolysis).

Analogous equations were obtained for the mean current density over the lifetime of the drop $\bar{i}$:

$$\bar{i}/\bar{i}_d = F_1(\lambda), \qquad \lambda = \bar{i}t_1^{1/2}/nFD^{1/2}c_s. \tag{14}$$

Here t_1 is the drop time, and $\bar{i}_d$ is the value of the diffusion current averaged over the lifetime of the drop. Ya. Koutecký ([10]) tabulated the functions $F(\lambda)$ and $F_1(\lambda)$ and gave Meiman' s equation a form more convenient for calculations.

Equation (14) can be applied to the reduction of adsorbed substances if the amount of substance $\bar{i}t_1/nF$, reduced during the lifetime of the drop per unit surface, is much greater than its amount Γ, present per unit surface of the drop at the moment t_1:

$$nF\theta\Gamma_\infty/\bar{i}t_1 = y \ll 1, \qquad \text{where } \Gamma = \theta\Gamma_\infty.$$

Taking $\theta \leq 0.05$ and requiring $y \simeq 0.05$, we obtain the condition for applicability of equation (14) in the form

$$nF\Gamma_\infty \ll \bar{i}t_1. \tag{15}$$

If, for the case of reduction of adsorbed substances, equation (14) is valid at values of t_1 greater than a certain value τ, determined by (15), then equations (13) are all the more valid at $t \geq \tau$. Combining formulas (5) and (10) with (13), we obtain the equations of the λ, φ-curves for the corresponding cases. The potentials of the extremal points on these curves are determined by (7) and (12), and equations (6) and (11) remain valid after replacing in them the variable i by the new variable λ.

Analysis of the equations obtained leads to the conclusion that a change in adsorbability with potential affects the shape of the polarization curves for the reduction of organic substances, up to the appearance of extrema on them:

1. The reduction of an organic substance whose molecular orientation on the surface does not change over a sufficiently wide potential interval should correspond to a symmetric polarization curve with a maximum; in this case the function $\lg\lambda$ of $(\varphi' - \varphi'_p)^2$ is a straight line, the slope of which does not depend on an_a and is uniquely determined by the value of a.

2. Extremal points on the i, φ curve appear only if they are present on the λ, φ curve, and the value of the rate constant k'_{01} lies within certain narrow limits.

3. According to (12), on the λ, φ curve there may be two extremal points (Fig. 1, *3*), one (Fig. 1, *2*) or none (Fig. 1, *1*), which to a certain extent corresponds to the scheme of Fig. 3 in work ([3]).

4. The probability of the appearance of extremal points on the λ, φ curve passes through a maximum with increasing a (Fig. 2) and decreases with increasing χ and an_a.

5. In the general case, as follows from equation (11), $\dfrac{1}{\lambda}\dfrac{\partial\lambda}{\partial\varphi}$ is a linear function of the potential, so long as $\chi\exp[a(\varphi')^2] \ll 1$. This linear dependence,

like the nonlinearity of the plot $\lg \lambda - \varphi$, may serve as an indication of adsorption effects of the type considered.

Polarization curves of the form described in the present work have been observed experimentally by us and also, apparently, by W. Kemula and A. Cisak ([11]).

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