DETERMINATION OF THE DEGREE OF COVERING OF AN ELECTRODE BY A SURFACE-ACTIVE SUBSTANCE FROM THE LIMITING CURRENTS OF MODEL REACTIONS

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Determination of the degree of covering (θ) of an electrode by particles of surface-active substances, under the conditions of any given electrochemical process taking place at the electrode (for example, corrosion), is of considerable interest for an understanding of the mechanism of their inhibition.

One of the possible solutions of this problem consists in measuring the limiting current density in the absence and in the presence of surface-active substances and in comparing these values.

For the limiting currents in the absence (i_d) and in the presence (i_d') of surface-active substances, we can write

$$i_d = kc, \tag{1}$$

$$i_d' = (1-\theta)kc, \tag{2}$$

if the limiting current decreases linearly with θ.

From (1) and (2) it follows that

$$(1-\theta) = \frac{i_d'}{i_d} \tag{3}$$

or

$$\theta = \frac{i_d - i_d'}{i_d}. \tag{4}$$

However, under ordinary conditions, the thickness of the diffusion layer δ is incomparably greater than the height h of the adsorbed particles or agglomerates of surface-active substances. Under these conditions, there is a lateral supply of a depolarizer [1-4], and the values of i_d and i_d' practically coincide right up to a value of θ differing only slightly from unity. As a result of this, not $(1-\theta)$ but $f(1-\theta)$ enters into Eq. (2); here $f(1-\theta) > 1-\theta$, and differs only slightly from unity, i.e.,

$$i_d' = f(1-\theta)kc \approx i_d. \tag{5}$$

If the value of δ is decreased sharply, for example, by decreasing the thickness of the layer of electrolyte or by increasing the intensity of its circulation, then, in the final analysis, the probability of the lateral supply of inhibitor to the gaps in the film is also decreased, and $f(1-\theta)$ will approach $1-\theta$. It is most simple to attain this result using a rotating-disk electrode. The usual equation for the dependence of δ on the angular velocity ω,

$$\delta = \delta_0 \omega^{-1/2} \tag{6}$$

with large values of ω must be rewritten in the form

$$\delta = \delta_\infty + \delta_0 \omega^{-1/2}, \tag{7}$$

where δ_∞ corresponds to a limiting value of δ with $\omega \to \infty$, and reflects a sharp increase in the density (or viscosity) of the liquid in the immediate vicinity of the electrode. In the presence of adsorbed surface-active substances, the damping of the motion of the liquid should be most intense in the gaps between their

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surface agglomerates, i.e., $\delta \approx h$. Thus, measuring the limiting currents as a function of ω and extrapolating i_d and i_d' to $\omega = \infty$, with a sufficiently large rate of rotation, instead of (1) and (2), we can obtain, respectively

$$\lim i_{d_{\omega\to\infty}} = k_\infty c, \tag{8}$$

$$\lim i_{d'_{\omega\to\infty}} = (1-\theta) k_\infty c \tag{9}$$

and can determine $(1-\theta)$ and θ from the modified equations (3) and (4)

$$(1-\theta) = \lim \frac{i_d'}{i_{d_{\omega\to\infty}}} \tag{10}$$

and

$$\theta = \lim \frac{i_d - i_d'}{i_d}. \tag{11}$$

The use of the above-described method for finding the degree of covering demands the satisfaction of a number of conditions. The model equation serving to determine the limiting currents must take place under purely diffusion conditions, and only on that part of the surface of the electrode which is free of surface-active substances; the rate of the reaction on the screened surface must be equal or close to zero. The degree of covering must not depend on the mixing, and must be determined only by the adsorption equilibrium. The inhomogeneity of the surface must be due above all to the presence of adsorbed surface-active substances.

The plateau of the limiting current usually extends over tens of fractions of a volt or more. In the presence of surface-active substances, due to the dependence of the surface concentration and, consequently, also of the degree of covering on the potential, the plateau may not be parallel to the axis of potentials, and may have some profile depending on the character of the function $c'_{SAS} = f(\varepsilon)$. The value of θ, found from (11), therefore relates to a definite value of the potential of the electrode, and can serve as a basis for establishing the form of the dependence $\theta - \varepsilon$.

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