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Abstract

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STUDY OF ELECTRODE PROCESSES ON ZINC AMALGAM BY THE METHOD OF RADIOACTIVE INDICATORS

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The main difficulty encountered in the study of processes of anodic dissolution and electrodeposition of metals is connected with the fact that for many metals the rate of the actual electrochemical stage, namely the stage of discharge—ionization of the reacting particles, is so high that under ordinary conditions the rate of the whole process is, as a rule, limited by the stage of transfer of the reacting particles to the electrode surface or of the reaction products away from the electrode. Naturally, the stationary polarization curves obtained under these conditions do not directly reflect the kinetic regularities of the ionization and discharge stage. Therefore, for the study of the mechanism of fast electrode processes, measurement of one of the important parameters characterizing the ionization and discharge stage—namely, the exchange current—under conditions in which the influence of all other stages, except the electrochemical one proper, on the kinetics of the electrode process can be excluded, acquires special importance. Let us consider the kinetic regularities of the processes of ionization and discharge using as an example the reaction of anodic dissolution of a metal amalgam in a solution containing simple ions of the same metal: $\mathrm{Me} \to \mathrm{Me}^{n+} + ne$. On the basis of the theory of slow discharge (¹), the dependence of the current density on the potential under anodic polarization is expressed by the equation*

$$i = k' C_a e^{\beta F\varphi/RT} - k'' C_p e^{-\alpha F\varphi/RT}, \tag{1}$$

where C_a and C_p are the bulk concentrations of the amalgam and the solution, α and β are transfer coefficients, and it is assumed that $\alpha + \beta = n$. At the equilibrium potential φ_p, the rates of the anodic and cathodic processes are equal to the exchange current:

$$i_0 = k' C_a e^{\beta F\varphi_p/RT} = k'' C_p e^{-\alpha F\varphi_p/RT}. \tag{2}$$

If one takes into account the difference between the concentrations at the surface and the corresponding bulk values at large i, from equations (1) and (2) we obtain:

$$i = i_0 \left[(1 - i/i_d^a) e^{\beta F \Delta\varphi / RT} - (1 + i/i_d^k) e^{-\alpha F \Delta\varphi / RT} \right], \tag{3}$$

where i_d^a and i_d^k are the anodic and cathodic limiting currents, $\Delta\varphi = \varphi - \varphi_p$. By combining (2) with the Nernst equation, it is not difficult to obtain an expression for the dependence of the exchange current on the concentrations of the amalgam and the solution**

$$i_0 = k C_a^{\alpha/n} \cdot C_p^{\beta/n}. \tag{4}$$

As is evident from (4), by measuring i_0 at different concentrations of the amalgam and the solution, one can find the coefficients characterizing the slow stage –

coefficients α and β, which, in the case of a rapid electrode process, cannot be determined directly from ordinary polarization curves. In addition, determination of the parameters i_0, α, and β, in combination with measurement of limiting currents, makes it possible to calculate the complete polarization curve, expressed by equation (3), which takes into account not only the slowness of the discharge-ionization stage, but also concentration polarization.

For measuring exchange currents on amalgam electrodes, along with various nonstationary methods (alternating-current ([4,6–8]), galvanostatic ([9,10]), and potentiostatic ([11,12])), the radioactive-tracer method ([13,14]) is also used. The latter method is distinguished by the fact that measurements of the exchange current are carried out under conditions as close as possible to equilibrium.*

The aim of the present work is to measure exchange currents on zinc amalgam by the radioactive-tracer method in combination with polarization measurements

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* It is assumed that the overall electrode reaction consists of a series of consecutive one-electron stages, with the slowest of these stages limiting the rate of the whole reaction ([2,3]). It is also assumed that an excess of indifferent electrolyte is present in the solution, and therefore the presence of ψ_1-potential ([1]) can be neglected and the activity coefficients of the metal ions can be considered constant.

** An equation of this type was first obtained for the reaction of discharge of hydrogen ions and ionization of hydrogen atoms ([1]). Equation (4) differs from the expressions usually used for the dependence of the exchange current on the concentrations of amalgam and solution ([4,5]) in that the latter were derived under the assumption that the slow stage of the electrode process is the simultaneous detachment of n electrons and the normalization $\alpha + \beta = 1$ was adopted, whereas in the derivation given above it was assumed that $\alpha + \beta = n$. It is not difficult to see that the physical meaning of the coefficients α and β is different in the two cases ([2,3]).

and determination of the anodic and cathodic limiting currents. Such a combination makes it possible to clearly identify that interval of concentrations of the amalgam and solution in which the exchange rate is limited by the discharge-ionization stage and not by diffusion of the radioactive particles, and, in addition, makes it possible to compare experimental polarization curves with those calculated from equation (3) using the parameters i_0, α, β, and i_d, determined under identical experimental conditions.

We used the previously described procedure (^{2}) with certain improvements**. Exchange-current measurements were carried out in a nitrogen atmosphere at 25°C over the range of amalgam concentrations 0.00008-0.97 M, in 0.0001-0.20 M $ZnSO_4$ solutions acidified with H_2SO_4 (0.005 M), with $MgSO_4$ added to maintain a constant ionic strength (2 M). Preliminary measurements showed that the exchange current over a wide range of $ZnSO_4$ concentrations (0.01-0.20 M) depends little on the number of revolutions of the stirrer (200-500 rpm). The slight increase in exchange current observed with increasing stirring rate is apparently due to an increase in the surface of the amalgam. All experiments were carried out at a stirring rate of 400 rpm.

The results of measurements of the exchange current, as well as of the anodic and cathodic limiting currents, are presented in Figs. 1 and 2. The slopes of the straight lines $\lg i_d^{\mathrm{a}}$— $\lg C_{\mathrm{a}}$ and $\lg i_d^{\mathrm{k}}$— $\lg C_{\mathrm{p}}$ are respectively 0.96 and 0.97; i.e., the limiting currents are directly proportional to the corresponding concentrations. As can be seen from Figs. 1 and 2, the curves $\lg i_0$— $\lg C_{\mathrm{a}}$ and $\lg i_0$— $\lg C_{\mathrm{p}}$ consist of two sections with different slopes; moreover, in the region of low concentrations the slope coefficients are close to unity, and the corresponding sections are parallel to the straight lines for the limiting currents. Apparently, in this concentration region the rate of transfer of radioactive particles into the solution is limited not by the discharge-ionization stage but by diffusion of these particles, and the corresponding experimental values of i_0 are underestimated in comparison with the true exchange currents. At higher concentrations, a slower increase of the exchange current with concentration is observed: when the $ZnSO_4$ concentration is increased from 0.01 to 0.20 M (at $C_{\mathrm{a}} = 0.13$ M), the exchange current increases from 2.8 to 22.5 ma/cm^2; when the amalgam concentration is increased from 0.013

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* Of course, in the case of very high exchange currents, even with intensive stirring of the amalgam and solution, the uniform distribution of radioactive particles in both phases—which is the basic condition for correct measurement of the exchange current—may be disturbed; in this case it may turn out that the experimentally measured rate of transfer of radioactive particles across the phase boundary will be determined by the rate of diffusion of these particles within one of the phases (^{14}).

** A glass magnetic stirrer of the propeller type was introduced into the cell for stirring the amalgam and solution, as well as a burette with a device for

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

preliminary saturation with nitrogen of the added portions of solution. With a single portion of amalgam labeled with the radioactive isotope Zn^{65}, it was possible to measure several exchange-current values corresponding to different solution concentrations or different temperatures.

to 0.970 M (at $C_p = 0.025M$) the exchange current increases from 2.9 to 8.3 ma/cm^2. In this concentration region, from the slopes of the straight lines $\lg i_0 - \lg C_a$ and $\lg i_0 - \lg C_p$, using equation (4), we found the coefficients $\alpha = 0.52 \pm 0.04$ and $\beta = 1.40 \pm 0.05$.

Fig. 1. Dependence of the exchange current (a) and the anodic limiting current (b) on the amalgam concentration at a concentration $C_p = 0.025M$ $ZnSO_4$

Fig. 2. Dependence of the exchange current (a) and the cathodic limiting current (b) on the concentration of $ZnSO_4$ at a concentration $C_a = 0.13M$ Zn

Fig. 3. Dependence of the exchange current on temperature at $C_p = 0.025M$ $ZnSO_4$ and $C_a = 0.13M$ Zn

The values of the exchange currents obtained by us agree satisfactorily with the data of V. A. Pleskov and N. B. Miller (^{13}), although they are somewhat lower than the values found by other authors using nonstationary methods (^{4,6,9,10,11})*. The values of the transfer coefficients α and β agree well with Gerischer' s data (^{4}). The closeness of the sum of the experimental values of α and β to 2, as well as the independence of the value of i_0 from the stirring rate of the solution, indicate that in this concentration region the exchange rate is limited by the discharge-ionization stage, and not by diffusion of the radioactive particles. This conclusion is confirmed by the results of studying the temperature dependence of the exchange current for two amalgam concentrations (at $C_p = 0.025M$), corresponding to different portions of the curve $\lg i_0 - \lg C_a$ (Fig. 1). Figure 3 shows the dependence $\lg i_0 - 1/T$ for $C_a = 0.13M$ in the interval 3-45°. The activation energy calculated from the slope of this straight line is 7.4 kcal, whereas for the concentration $C_a = 0.00013M$, corresponding to the diffusion region, the activation energy is approximately 5 kcal.

Along with measurements of the exchange current, in the same cell and under the

Figure 3

Figure 3: Figure 3

same stirring conditions we recorded polarization curves. In Fig. 4 the results of these measurements are presented as circles and crosses, and in addition the exchange currents corresponding to these concentrations are plotted**; the solid lines show the theoretical polarization curves calculated from equation (3), using the values found by us for i_0, the coefficients α and β, and also the limiting currents***. As is seen from Fig. 4, the experimental points coincide well with the theoretical curves.

* It is possible that these discrepancies are due to differences in the anionic composition and ionic strength of the solutions used.

** The values of i_0 corresponding to dilute amalgams were determined by extrapolating that portion of the curve $\lg i_0 - \lg C_a$ (Fig. 1) which corresponds to the kinetic region.

*** For calculating the anodic curves, the following approximate equation, obtained from equation (3), was used:

$$i = i_d^a \frac{e^{\beta F \Delta\varphi/RT} - e^{-\alpha F \Delta\varphi/RT}}{i_d^a/i_0 + e^{\beta F \Delta\varphi/RT}}. \tag{5}$$

This is an additional confirmation that the values of i_0, α, and β used in the calculations (found by an independent radiochemical method) are reliable, i.e., they do indeed characterize the discharge–ionization stage and are not appreciably distorted by diffusion effects.

Analysis of equation (5) for the anodic polarization curves shows that, in the case of curve 3, $i_d^a/i_0 \sim 0.1$, and the first term in the denominator is small in comparison with the second (the rate of the anodic process is limited by diffusion), whereas for curve 1 $i_d^a/i_0 \sim 10$, and at not very high $\Delta\varphi$ the second term in the denominator may be neglected (the limiting stage is already discharge –ionization). Consequently, only as a result of increasing the concentration of the amalgam (approximately 200-fold), other conditions being equal, did a transition occur from the diffusion region to the kinetic region.

Fig. 4. Polarization curves for different concentrations of amalgam:
1—$C_a = 0.026\ M\ Zn$, 2—$C_a = 0.0029\ M\ Zn$, 3—$C_a = 0.00011\ M\ Zn$ ($C_p = 0.025\ M\ ZnSO_4$).
a –exchange current, b –points of the cathodic branch of the polarization curve, v –points of the anodic branch of the polarization curve. The solid curves are calculated from equation (3).

This effect is due to the different dependence of the exchange current and the anodic limiting current on the amalgam concentration C_a: while the limiting current depends linearly on C_a, the exchange current increases much more slowly with increasing C_a (equation (4) and Fig. 1)*. As is evident from the results we obtained, this effect can be used for such a selection of the concentrations of the reacting substances that it becomes possible substantially to reduce the influence of the diffusion stage on the rate of fast electrode processes, and in particular on the measurement of the exchange current.

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* A similar phenomenon may apparently lead to a transition from reversible waves to irreversible ones when recording anodic polarograms on amalgams ([15]).

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

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