Diethylamine m-nitrobenzoate	1.5 mass %
Benzotriazole	0.1 mass %

The selection of the molecular mass of the polyglycol is determined by the required viscosity of the particular hydraulic mechanism.

As shown by our investigations, these fluids can be used as preservative agents.

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AUTOMATIC COMPENSATION OF OHMIC POTENTIAL DROP BY THE INTERRUPTION METHOD IN POTENTIOSTATIC MEASUREMENTS

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UDC 620.193.01

The authors describe a method of automatic compensation and measurement of the ohmic potential drop in potentiostatic and potentiodynamic polarization by means of interruption by a controlled impedance in the polarization circuit. The method permits the elimination of certain errors (in particular, distortion of the polarization rate) due to the high resistance of the electrolyte or surface salt layers.

The precision of electrochemical polarization measurements is largely determined by the ohmic potential drop (OPD) which results from the passage of the polarization current through the ohmic resistance between the working (test) electrode and the reference electrode. This includes the resistances of the electrolyte, the layer coating the working electrode (WE), if any, and the WE itself with the current lead. If the measurements are made in a poorly conducting medium, or if a high-resistance coating forms on the WE, or if the currents passing are large, the OPD can reach quite high values in comparison with the measured (or rather, regulated) polarization voltage, and can thus distort the results.

To reduce the error due to the OPD, various methods are used; e.g., the Haber—Luggin capillary is brought close to the WE in order to reduce the electrolyte resistance, or the resistance of the current leads is eliminated by means of a differential amplifier during measurement of the potential. The OPD can also be compensated by positive current feedback in a potentiostatic automatic control system. Of course, it is usually assumed that the ohmic resistance remains constant during the experiment. Otherwise the OPD must be measured continuously throughout the polarization time. Another method is the ac or interruption method.

In this latter case, the polarization current is periodically briefly interrupted, mechanically or by means of an electronic switch. We can assume that after interruption of the current the OPD vanishes practically instantaneously. On the other hand, the polarization voltage of the WE falls much more slowly, so that during a brief interruption it can be regarded as constant. Thus it is possible to determine the OPD during the interruption period.

Several measuring devices based on the current interruption principle have been proposed. Even mechanical interruption systems have proved very effective and have been used

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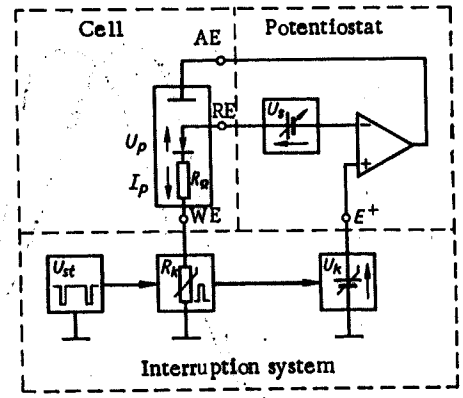

Fig. 1

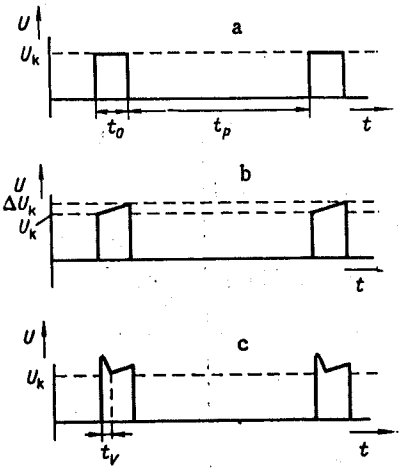

Fig. 2

Fig. 1. Circuit diagram of IR compensation by interruption method with controlled resistance R_K.

Fig. 2. Voltage pulses across R_k. a) Ideal voltage variation; b) voltage fall during interruption period; c) influence of rapid-acting potentiostat.

to investigate electrodes with passivating oxide or salt layers [1, 2]. With the development of electronics, electronic interruptors have been increasingly used [3-5], in particular to measure the resistance of gas films on electrodes [6] and in investigations of passivity [7].

Figure 1 illustrates the current interruption method in which the potentiostatic regulation scheme remains switched on during the interruption phase. The current is periodically interrupted by controlled resistance R_k connected in series with the measured ohmic resistance R_Ω. Master voltage pulse U_{St} periodically switches resistance R_k between the positions $R_{k_1} \ll R_\Omega$ and $R_{k_o} \gg R_\Omega$.

In the polarization phase, $R_{k_1} \ll R_\Omega$. The polarization current I_p is practically independent of the resistance R_{k_1}.

In the interruption phase $R_{k_o} \gg R_\Omega$ and the current is very small, $I_o \ll I_p$. The voltage drop now occurs directly across the external resistance R_{k_o} and can be measured by means of a high-resistance voltmeter or oscillograph. Assuming that the polarization voltage U_p remains constant during the interruption time, we get $I_o R_{k_o} = I_p R_\Omega$.

With automatic IR compensation the voltage $U_k = I_o R_{k_o}$ is measured in the interruption phase and stored, and in the polarization phase it is fed to the uninverted input of the potentiostatic amplifier. At low currents, if the accuracy requirements are not too stringent, we can use a controlled or field-effect transistor as the interrupting resistance R_k. However, it is more convenient to make R_k an operational amplifier with electronic switches in its feedback circuit. This permits interruption of polarizing currents of up to ±1 A in either direction without switching. In the polarization phase the voltage drop across R_{k_1} is less than 1 mV, but in the interruption phase $R_{k_o} > 10^8$ Ω.

The optimum interruption time t_o is found by means of oscillographic control of the interruption pulses at resistance R_k. Figure 2 shows typical pulse shapes for cathodic polarization. During the interruption period t_o there is a positive voltage pulse, the amplitude of which is equal to the OPD. In the ideal case the upper part of this pulse is horizontal (Fig. 2a). A rise in the voltage pulse during the interruption period t_o (Fig. 2b) indicates an appreciable fall in the polarization voltage of the WE during t_o. In OPD measurements this leads to an error ΔU_k, which is smaller when the interruption time t_o is shorter. On the other hand, t_o should be longer than the time t_v required for the interruption process (Fig. 2c). The value of t_v depends both on the speed of action of the potentiostat and on the properties of the electrochemical cell. For the minimum value of t_v the potentiostat must act quickly and the resistance of the cell between the reference electrode

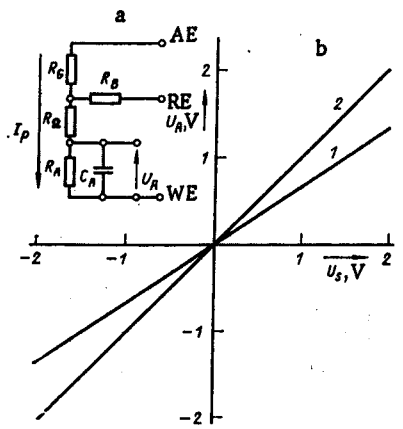

Fig. 3

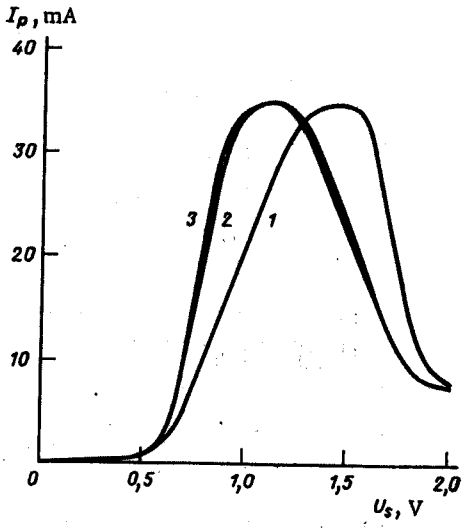

Fig. 4

Fig. 3. a) Electrical equivalent circuit for verifying interruption method; b) results of measurements with circuit in Fig. 3a: 1) without IR compensation, 2) with automatic IR compensation; $R_A = 200\ \Omega$, $C_A = 10\ \mu F$, $R_B = 10\ k\Omega$, $R_\Omega = 100\ \Omega$, $R_G = 70\ \Omega$, $t_o = 20\ \mu sec$.

Fig. 4. Results of measurements by means of circuit in Fig. 3a, with $R_A = dU_S/dI_P < 0$. 1) $R_\Omega = 10\ \Omega$ without IR compensation; 2) $R_\Omega = 0$ without IR compensation; 3) $R_\Omega = 10\ \Omega$ with automatic IR compensation; $R_B = 10\ k\Omega$, $C_A = 50\ \mu F$, $R_G = 7\ \Omega$, $t_o = 20\ \mu sec$.

and the auxiliary electrode must be very low to reduce the change of potential across the cell, ΔU_Z, when the current is interrupted.

The interruption circuit shown in Fig. 1 was tested quantitatively with an electrical equivalent circuit simulating the cell (Fig. 3a). The resistances R_A, R_B, R_G, R_Ω and the capacitance C_A can be varied over wide ranges. The voltage U_A was measured across a high ungrounded ohmic resistance R_A. The cell current I_p for automatic IR compensation was continuously regulated independently of R_Ω in such a way that U_A was equal to the nominal voltage U_S set by the potentiostat (Fig. 3b). On the other hand, in the absence of IR compensation, U_A forms part of the ohmic potential difference $I_p R_\Omega$. From this it also follows that in potentiodynamic measurements with automatic IR compensation the actual polarization rate is equal to the rate of change of potential set by the potential control. But in the

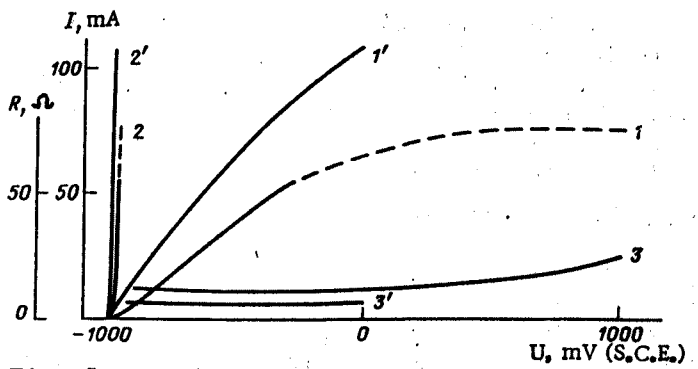

Fig. 5. Anodic behavior of zinc in 0.5 M solutions of $ZnSO_4$ (1-3) and $ZnCl_2$ (1'-3'). Polarization curves: 1, 1') not taking account of ohmic potential drop; 2, 2') taking account of ohmic potential drop; 3, 3') ohmic resistance vs nominal voltage.

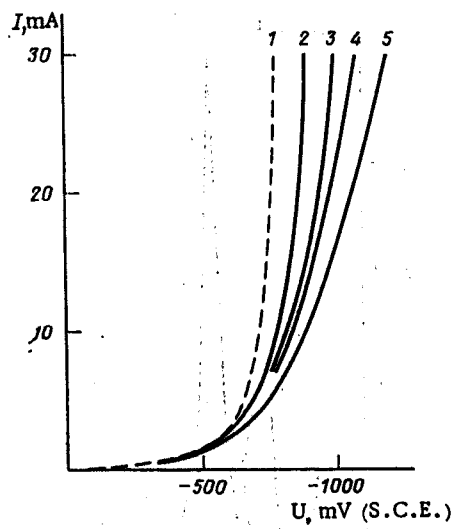

Fig. 6

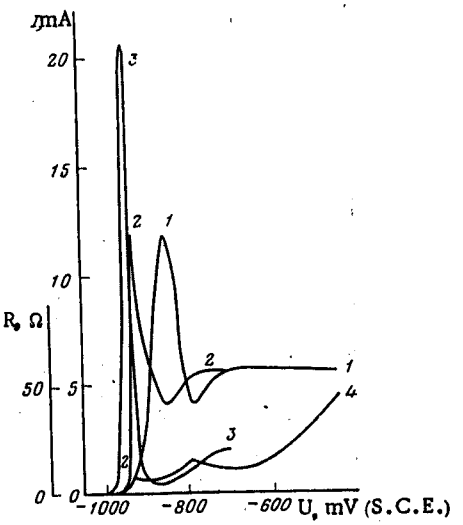

Fig. 7

Fig. 6. Influence of distance d of Haber—Luggin capillary from electrode surface on polarization curve of cathodic evolution of hydrogen (Pt/0.1 N H_2SO_4). 1) With automatic compensation of ohmic potential drop; 2-5) without allowance for IR error; values of d in millimeters: 2) 1; 3) 3; 4) 5; 5) 10.

Fig. 7. Anodic behavior of zinc in saturated $ZnSO_4$ solution. Potentiodynamic polarization curves (67 mV/min): 1) without allowance for ohmic potential drop; 2) with allowance for ohmic potential drop; 3) with automatic IR compensation; 4) ohmic resistance vs nominal potential.

absence of automatic IR compensation the true polarization rate depends on the OPD and in certain circumstances may become less than the set value.

The resistance R_A (Fig. 3a) can also be represented by electronic circuits which create a "falling section" on the (U_S, I_p) curve. Stability of control is also achieved in these sections (Fig. 4). The slight discrepancy between curves 2 and 3 in Fig. 4 can be explained by the influence of the resistances of the circuit and current leads.

In our electrochemical investigations we used both unpassivated and passivated electrodes, in order to elucidate the influence of the electrolyte and surface-layer resistances on the polarization curves. Polarization curves were recorded by two methods: 1) by the usual method, i.e., as the function $I = f(U_S)$ (where U_S is the nominal voltage regulated by the potentiostat), taking account of the measured OPD values (U_Ω) so as to plot corrected polarization curves not containing IR errors; 2) with automatic compensation of the OPD.

Influence of Electrolyte Resistance. If in an investigation of the anodic solution of zinc in 0.5 M $ZnSO_4$ solution (Fig. 5, curves 1-3) we do not pay attention to the OPD, the measured polarization is too high. Thus with a current strength of about 75 mA the apparent polarization, $U_S - U_0$ (where U_0 is the stationary potential) reached 2000 mV, whereas the true value is only about 50 mV. As expected, zinc dissolves without appreciable retardation. The OPD arises on the linear part of curve 1 and is due to the electrolyte resistance which

TABLE 1. Ohmic Resistance vs Distance of Haber—Luggin Capillary from Electrode Surface

d, mm	$\frac{U_\Omega}{I}$, Ω	$\frac{\rho d}{F}$, Ω
1	2	2
3	5	6
5	7	10
10	11	20

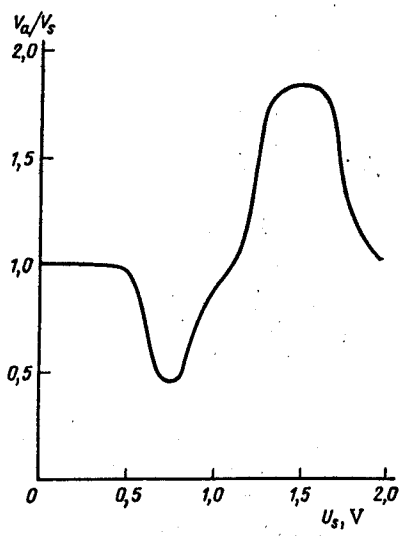

Fig. 8

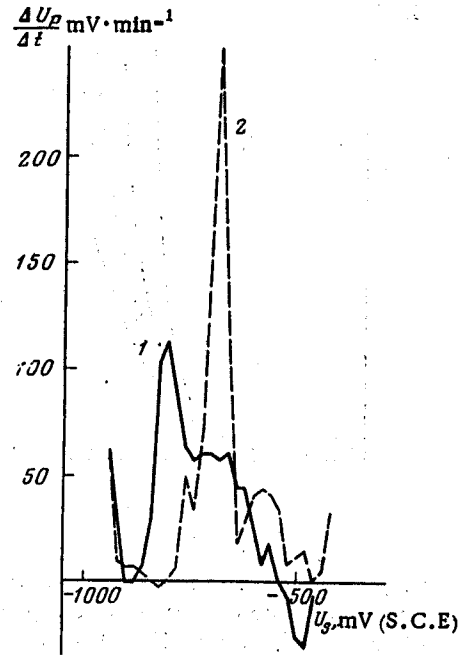

Fig. 9

Fig. 8. Ratio of "true" polarization rate v_A to nominal rate v_S measured in conditions of Fig. 4.

Fig. 9. Influence of ohmic potential drop on polarization rate dU_p/dt at given rate of change of nominal potential ($dU_S/dt = 67$ mV·min^{-1}). System Zn/sat. $ZnSO_4$. Distance between Haber—Luggin capillary and electrode surface, d = 1-1.2-5 mm (1).

is here constant (11-12 Ω). At high current strengths the resistance rises to 26 Ω, probably because a loose layer of $ZnSO_4$ is formed near the electrode surface owing to local supersaturation. This is evidently also responsible for the current fluctuations in the section (dashed part of curve 1). Similar phenomena were observed in anodic solution of zinc in 0.5 M $ZnCl_2$ solution (curves 1'-3', Fig. 5). However, in this case the electrolyte resistance is only about 7 Ω and is nearly constant even at high current strengths, evidently because no salt is precipitated near the electrode owing to the higher solubility of $ZnCl_2$. In both cases the curves obtained by correcting curves 1, 1' with allowance for U_Ω and the curves 2, 2' obtained with automatic OPD compensation coincide. This confirms the results in [2] obtained in galvanostatic conditions.

Since the electrode resistance determined from the OPD depends on the distance between the WE and the reference electrode, we also investigated the influence of the distance of the Haber—Luggin capillary from the WE surface on the polarization curves. Figure 6 shows polarization curves for the case of cathodic separation of hydrogen in the system Pt/0.1 N H_2SO_4 for various capillary distances, which were measured with a micrometer screw gage. We see that as the capillary distance increases, equal currents are attained at increasingly negative nominal voltages. Polarization curve 1, obtained with automatic OPD compensation, is shifted toward less negative potentials and is altogether independent of the capillary distance. The curves obtained from the (I, U_S) curves by correcting for OPD deviate from it by at most 20 mV.

When the current is increased from 1 to 30 mA, the ohmic resistance increases, according to the conditions, from 1 to 40 Ω, so that part of the electrode surface is clearly covered with gas bubbles. If we compare the resistances calculated from the equation $R = U_\Omega/I$ for small currents with those found from the expression $R = \rho d/F$ (where ρ is the resistivity of the electrolyte, d is the capillary distance, and F is the electrode surface area on the simplifying assumption that the cross section q of the electrolyte is equal to F), we find that these quantities are in satisfactory agreement for short distances (see Table 1). However, the effective resistance found from the values of U_Ω certainly increases less

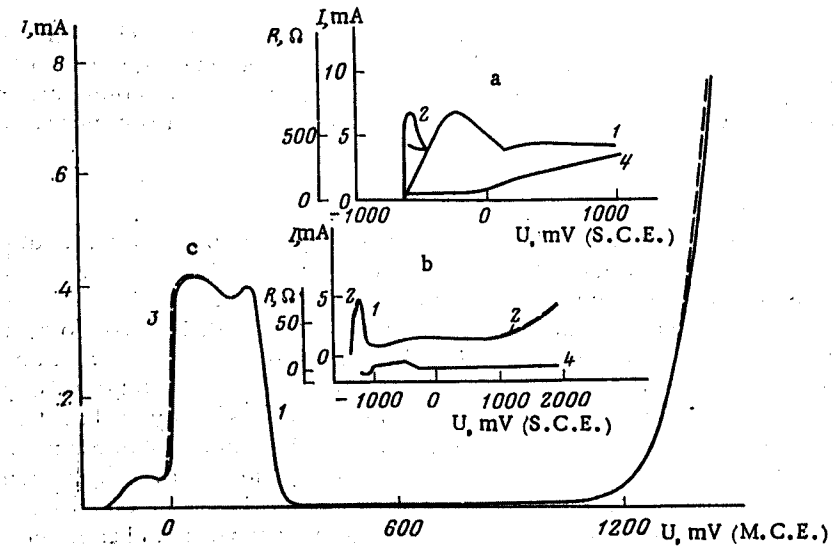

Fig. 10. Anodic behavior of zinc in saturated $ZnCl_2$ solution (a), zinc in 0.5 N NaOH (b), and nickel in 1 N H_2SO_4 (c). Potentiodynamic polarization curves (a and b, 50 mV·min^{-1}; c, 20 mV·min^{-1}): 1) Without allowance for ohmic potential drop; 2) with allowance for ohmic potential drop; 3) with automatic IR compensation; 4) ohmic resistance vs nominal voltage.

rapidly when d is larger. Although the working and auxiliary electrodes have the same dimensions and insulated nonworking surfaces (only the opposite front surfaces of these electrodes are effective), the geometry of the system is not sufficiently determinate to justify the simplifying assumption that q = F. The effective cross section of the electrolyte increases with the distance from the WE. The shapes of the lines of force can also be affected by the shape and position of the Haber—Luggin capillary, especially at short distances (owing to the screening effect).

Influence of Resistance of Coating Layer. Much more complicated relations appear when coating layers are formed on the electrode. As we see from Fig. 7, the ordinary potentiodynamic curve of anodic solution of zinc in saturated $ZnSO_4$ solution is shifted toward more positive voltages owing to OPD.

As also in dilute $ZnSO_4$ solution (Fig. 5), in these conditions at first zinc dissolves only with slight polarization. However, after the attainment of a current density which leads to the disappearance of the supersaturation, the electrode potential in the investigated region shifts about 250 mV toward the positive. This cannot be due to retardation of the transition or to concentration polarization. However, it is possible that on certain parts of the electrode surface $ZnSO_4$ can be formed by direct reaction between the metal and the sulfate ions. With a polarization of over 400 mV this reaction can occur over the whole surface and can lead to the formation of a layer of anhydrous $ZnSO_4$ with a marked occlusive effect [8].

By investigating the ohmic resistance we can obtain additional information concerning the formation of a layer. Thus, a slight rise in resistance to about 10 Ω in the passivation region indicates the formation of a comparatively conductive layer of $ZnSO_4 \cdot 7H_2O$ rather than a layer of anhydrous $ZnSO_4$ which has a resistivity of 10^{11} Ω·cm. The immediately following fall in resistance, which is due to a fresh rise in the current, is evidence of further destruction or solution of the initially formed layer. The linear rise in resistance in the limiting-current region, which is independent of the potential, again mainly reflects the growth of the coating layer. The high limiting-current density indicates that in these conditions there is no marked occlusive action which might be due to a layer of anhydrous $ZnSO_4$ formed directly by osmotic dehydration [8-11].

There is a marked difference between the polarization curves obtained with automatic OPD compensation (Fig. 7, curve 3) and with correction for U_Ω (Fig. 7, curve 2). Here we

must remember that the shapes of the polarization curves, especially in the case of electrode reactions involving formation of coating layers, depend on the polarization rate. In potentiodynamic measurements only the nominal voltage U_S varies at a constant rate; any changes in this quantity can be due either to a change in the polarization voltage U_p or to the OPD,

$$\frac{dU_s}{dt} = \frac{dU_p}{dt} + \frac{dU_\Omega}{dt}.$$

Since U_Ω depends on the current strength, the "true" polarization rate dU_p/dt has a different value even with constant resistance at each point on the polarization curve. For a polarization curve with a negative I—U characteristic there may be sharp changes in the polarization rate (Fig. 8). If the resistance also changes (e.g., owing to formation of a layer), we must expect additional variations in the polarization rate. As we see from curve 1 in Fig. 9, the true polarization rate during recording of a potentiodynamic polarization curve (Fig. 7, curve 1) varies extremely irregularly, and can take any value between zero and 125 mV/min. Since the change of resistance depends on such random phenomena as the formation of nuclei and the rate of their growth, this may be the cause of the poor reproducibility of such polarization curves. If, on the other hand, a polarization curve is recorded with automatic OPD compensation, the time dependence of the nominal voltage coincides with the true polarization rate. Thus, the two current—voltage curves (2, 3) in Fig. 7, free from ohmic errors, were in fact obtained in quite different conditions.

Since in potentiodynamic measurements the ohmic resistance influences the true polarization rate and thus also the time dependence of the electrode reaction, the shapes of the current—voltage curves also depend on the distance between the working electrode and the reference electrode. Therefore, if, in an investigation of the anodic behavior of zinc in a saturated $ZnSO_4$ solution, the distance between the Haber—Luggin capillary and the electrode surface is increased from 1 to 5 mm, the electrolyte resistance increases by 10 Ω, and the increased OPD leads not only to a shift in the ordinary polarization curve toward the positive, but also to a change in the curve corrected for IR error. The more gradual rise in the (I, U_S) curve at long capillary distances has the result that the "passivation" potential, corresponding to the current density at which the supersaturation at the electrode vanishes, is reached earlier. Correspondingly, the formation of a layer occurs at a higher polarization rate. Curve 2 in Fig. 9 shows that in this case the true polarization rate varies between zero and 250 $mV \cdot min^{-1}$ and that the entire polarization regime depends on the capillary distance. Thus, in potentiodynamic measurements the conditions of the electrode reaction can to a marked degree be governed by the distance from the capillary to the electrode surface.

From Fig. 9 we already see that during the recording of the potentiodynamic polarization curve even the direction of the polarization can change. This evidently happens when the OPD changes more rapidly than the nominal voltage. This effect is especially marked during the anodic solution of zinc in saturated $ZnCl_2$ solution. Thus, the polarization curves in Fig. 10a ($[dU_S/dt] = 50$ $mV \cdot min^{-1}$) reveal that after "passivation" and before attainment of the minimum on the curve, the electrode potential, regardless of the constant change in the nominal voltage towards the positive (curve 1), actually shifts toward the negative (curve 2). Since the cause of this is the rate of change of U_Ω, this effect becomes appreciable primarily at low sweep rates of the nominal voltage. Potentiostatic holding near the minimum of the polarization curve revealed that at constant nominal potential the OPD also rises with time, so that the electrode potential shifts correspondingly toward the negative. Thus, a constant nominal voltage certainly does not guarantee constant polarization conditions. The OPD rises monotonically for 10 min by about 100 mV and reaches a constant value, but in this period the ohmic resistance can even temporarily decrease. Thus, a monotonic rise in U_Ω is not always attributable to a rise in resistance, and can also be caused by layer formation, or by simultaneous changes in the electrode polarization. In potentiodynamic conditions layer formation is accompanied by a marked rise in ohmic resistance, reaching over 300 Ω.

Quite different conditions are realized when, e.g., oxide coatings are formed on zinc or nickel. Thus, in a study of the anodic behavior of zinc in 0.5 N NaOH it was found that the established nominal voltage (in other words, $U_S - U_o$) and the electrode polarization differ scarcely at all (Fig. 10b). Although the ohmic resistance of the electrolyte and coating layer after passivation reach values of up to 16 Ω, the current is so small that the OPD is about 15 mV, with a maximum of 35 mV. In contrast with zinc electrodes on which

salt layers form, in this case the resistance of the conductive ZnO layer does not increase throughout the passive region. Similar results were obtained in an investigation of the anodic solution and passivation of nickel in 1 N H_2SO_4 (Fig. 10c). In this case the polarization curves with and without automatic OPD compensation are practically the same, whereas in the active region the ohmic resistance can reach 4 Ω, while in the region beyond the transpassivation potential it is only 1-2 Ω. Owing to the low currents in the passive region ($U_\Omega < 1$ mV) the resistance of the passive layer cannot be measured, and is clearly very low.

Thus, the ohmic potential drop can exert a marked influence on the shape of the polarization curves. The use of polarization curves without allowance for this quantity can lead to large errors in the determination of the characteristic parameters, e.g., the potentials of passivation, activation, and pitting. If we may not ignore the ohmic potential drop, we must also reexamine electrochemical parameters found in the Tafel region without allowance for it, such as the transition coefficients, transition valence, exchange current density, and corrosion.

In 1973-1977, specialists from Hungary, East Germany, and the USSR, in a cooperative program — theme I ("Development of a Theory of Corrosion and Protection of Metals") of the COMECON project "Development of Means of Protecting Metals from Corrosion" — made joint tests of various methods of IR compensation, including that described above. The results of the joint tests will be published in this journal soon.

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