assumed that oxides on the surface of the investigated electrodes greatly accelerate the recombination of these radicals in comparison with the oxidation reaction. This leads to the appearance of measurable static photocurrents.

Let us express our gratitude to Yu. V. Pleskov for his discussion of this work.

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INVESTIGATION BY THE METHOD OF IMPEDANCE MEASUREMENT OF THE PROCESSES OCCURRING ON A ZINC ELECTRODE AT ITS STATIC POTENTIAL IN ALKALINE SOLUTIONS

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By a combination of impedance and polarization measurements, the system Zn—alkaline zincate solution was investigated at a static electrode potential in solutions with KOH concentration 0.6-3 M and zincate $6 \cdot 10^{-3}$-$2 \cdot 10^{-2}$ M. It was shown that simultaneously with the basic electrode process, for the Zn—Zn(II) in alkaline solutions, a process of insertion of the alkali metal occurs on the electrode; its rate is determined by the step of diffusion of K atoms into the electrode. The value of the exchange current in the system KZn_{13}—K^+ exceeds $2.5 \cdot 10^{-2}$ A/cm^2. The exchange currents of Zn in the investigated solutions are of the order of $3 \cdot 10^{-4}$ A/cm^2.

The system solid zinc electrode—alkaline zincate solution, of practical importance, has been studied by various modern methods over the last 15 years [1-8]. Despite this, the basic questions associated with the mechanism and kinetics of the electrode reactions in this system remain open. This can be seen from the contradictoriness of the experimental results and the conclusions of various researchers. At the static potential, the picture is distinguished by the fact that the cathodic and anodic processes of transport of zinc, the liberation of hydrogen, and also possibly the cathodic insertion and anodic extraction of the alkali metal occur simultaneously on the electrode [9, 10]. The use of the impedance method of studying the kinetics of electrode reactions permits a determination of the rates of parallel processes and successive steps of the electrode processes in a number of cases [6, 10, 11].

In the present work the method of impedance measurement, in conjunction with static polarization measurements, was used to determine the nature and rates of parallel processes and successive steps occurring on zinc in KOH solutions containing zincate, at the static electrode potential. The zinc used was TsO brand, KOH "special purity 18-3," ZnO "special purity 12-2," and the KF recrystallized twice. The solutions were prepared in double distilled water. The impedance and polarization measurements were conducted on wire

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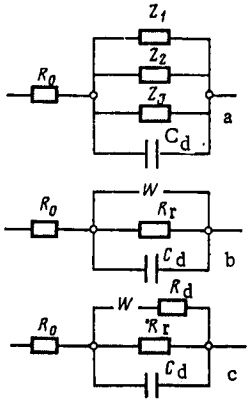

Fig. 1. Electrical circuits equivalent to electrochemical processes occurring at the static potential of a zinc electrode in an alkaline zincate electrolyte.

electrodes, pressed into a Teflon holder. The visible electrode surface did not exceed 0.01 cm^2. Before the measurements, the zinc electrode was subjected to anodic polishing in 50% phosphoric acid and cathodic reduction in 0.5 N sulfuric acid [12]. After thorough washing with double-distilled water, the electrode was kept for an hour in KOH solution free of zincate, at a constant potential approximately 100 mV more negative than the static potential, in an atmosphere of purified helium. The static cathodic polarization curve of the liberation of hydrogen in alkali was recorded on such an electrode. Then the frequency dependence of the impedance in pure alkali was measured at the static potential, after which the alkali solution was replaced by an alkaline zincate solution, free of oxygen.

The electrode potential was measured against a mercuric oxide electrode, in an alkali solution of the same concentration as the investigated solution. Measurements of the capacitance (C_1) and ohmic (R_1) components of the impedance were performed according to a series substitution circuit at alternating current frequencies 0.06-30 kHz with a P5021 bridge in KOH solutions with 0.6-3 M concentration, containing $6 \cdot 10^{-3}$-$2 \cdot 10^{-3}$ M ZnO. In a number of experiments the impedance measurements were performed in solutions with a constant ionic strength (3 M) against a background of KF. The alkali concentration was determined by titration with acid, while the zincate concentration was determined by titration with Trilon B. In certain experiments, after the impedance measurements, the static potentiostatic anodic curve was recorded on the same electrode in the given solution.

In accordance with the possibility that the processes indicated above may occur, an electrical circuit, in general consisting of the resistance of the solution R_0 and capacitance of the electrical double layer C_d, as well as two impedances connected in parallel, characterizing the processes of liberation of hydrogen Z_1, exchange in zinc Z_2 and alkali metal Z_3 (Fig. 1a), or simpler circuits, if one impedance or another is so large in comparison with the others that the conductivity of this pathway is negligible under our conditions, can be taken a priori as the electrical equivalent of the zinc/alkaline zincate solution boundary at the static potential. To make the scheme more concrete, we compared the experimentally determined frequency dependence of the components of the impedance with the calculated frequency dependence of several electrical circuits probable under the given conditions, as was done in [13].

Graphoanalytical treatment of the experimentally determined frequency dependence of the components of the impedance showed that in all the solutions studied, in the frequency region 0.12-2 kHz, the electrochemical processes that occur on zinc at the static potential are simulated, with the accuracy of the experimental determination of the components of the impedance R_1 and C_1, by the electrical circuit cited in Fig. 1b. Here W is the Warburg concentration impedance; R_r is the resistance of the reaction. The equivalence of this circuit to the investigated system is conveniently shown graphically (Fig. 2) [13]. Here R_2 and C_2 were obtained by recalculation of the measured values of R_1 and C_1 to a parallel substitution circuit after deduction of the resistance of the solution R_0, which was assumed equal to the value of R_1 at such high frequencies at which independence of R_1 from the frequency was observed. The experimental dependences of $1/R_2$ on $\sqrt{\omega}$ and C on $1/\sqrt{\omega}$ lie on straight lines, the slopes of which, equal to 1/2A (A is the Warburg impedance constant), coincide

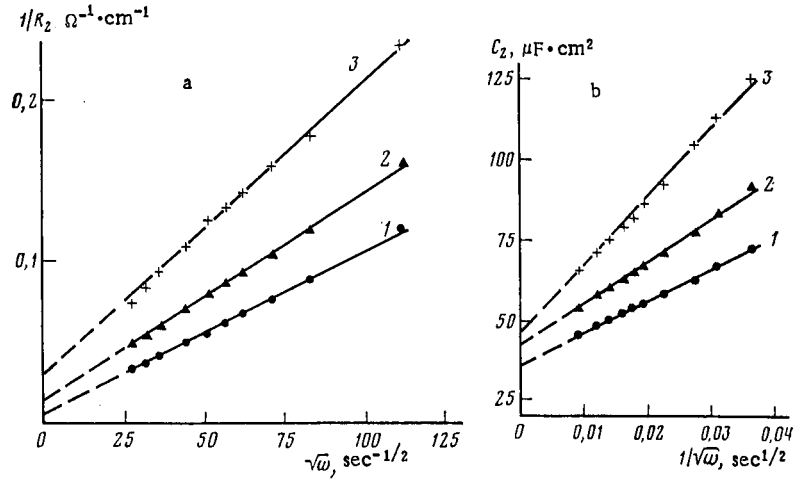

Fig. 2. Frequency dependences of the ohmic (a) and capacitance (b) components of a zinc electrode at the static potential in alkaline zincate solutions with composition: 1) 0.55 M KOH + $6.5 \cdot 10^{-3}$ M Zn(II); 2) 1.15 M KOH + $6.5 \cdot 10^{-3}$ M Zn(II); 3) 3.5 M KOH + $6.5 \cdot 10^{-3}$ M Zn(II).

TABLE 1. Comparison of the Values of the Active Resistance R_r, Determined from Impedance Measurements, with the Values of the Resistance of Probable Processes under the Investigated Conditions, Calculated from Direct Current Measurements

Solution	−E, V (n.h.e.)	R_{H_2}, Ω·cm²	R_r, Ω·cm²	R_t, Ω·cm²
0,60 *M* KOH; $6{,}2 \cdot 10^{-3}$ *M* ZnO	1,242	5000	65	40
1,16 *M* KOH; $6{,}2 \cdot 10^{-3}$ *M* ZnO	1,284	1500	30	30
1,25 *M* KOH; $7{,}3 \cdot 10^{-3}$ *M* ZnO	1,276	2600	80	40

with a maximum discrepancy of up to 15%. In this case, extrapolation of the first dependence to a zero frequency gives the value of $1/R_r$, while extrapolation of the second to an infinitely great frequency gives the value of C_d.

To establish which of the three proposed processes are simulated by circuit b (Fig. 1), we studied the dependence of the elements of the circuit on the composition of the solution. Measurements at different concentrations of one of the components of the solution were conducted on the same electrode. First of all, it should be mentioned that the resistance of the process (R_r) determined from impedance measurements is 1.5-2 orders of magnitude less than the polarization resistance of the process of liberation of hydrogen R_{H_2}, which we determined by extrapolation of the cathodic polarization curve of liberation of hydrogen in pure alkali to the static potential of a Zn electrode in an alkaline zincate solution (Table 1, columns 4 and 3). Thus, the impedance Z_1, characterizing the process of the liberation of hydrogen, in alkaline zincate solutions at the static potential of zinc is so great that it is not measured in practice. This agrees with the conclusions in [4, 8]. At the same time, the resistance R_r coincides in order of magnitude (with a maximum discrepancy of twofold) with the resistance of transport R_t, determined by extrapolation of the Tafel portion (beginning with overvoltage ≥ 25 mV) of the anodic curve of dissolution of zinc up to the static potential in the given solution (Table 1, columns 4 and 5). Thus, it can be considered that the element of the circuit R_r characterizes the exchange current of zinc in an alkaline zincate solution, i.e., the impedance Z_2.

Statistical treatment of our potentiometric data in solutions with various activities of the components showed that the static potential of the zinc−alkaline solution system in the region of alkali concentrations 0.5-3 M is determined by the Nernst equation $E = E_0 + (RT/2F) \ln (a_{Zn(II)}/a_{OH^-}^4)$ (Fig. 3), i.e., is the equilibrium potential and corresponds to the summary electrode reaction

$$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e. \quad (1)$$

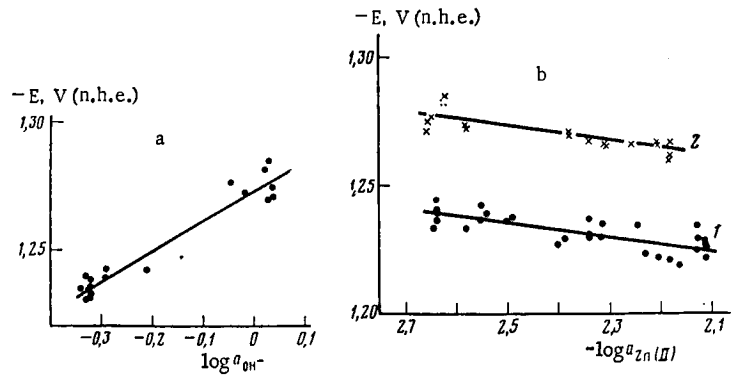

Fig. 3. Dependence of the static potential of a zinc electrode on the composition of alkaline zincate solutions: a) at constant activity of Zn(II) [(2-2.5)·10^{-3} mole/kg] on the activity of OH^-; b) at constant activity of OH^- [1) 0.48, 2) 1.09 moles/kg] on the activity of Zn(II). The points represent the experimental values of the static potential; the straight lines represent the calculation of the linear dependence of E on log a according to the method of least squares.

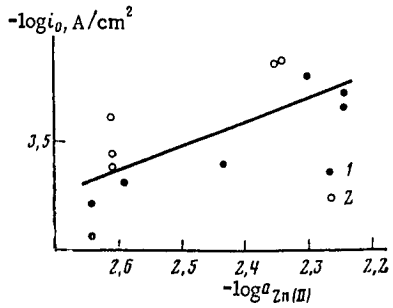

Fig. 4

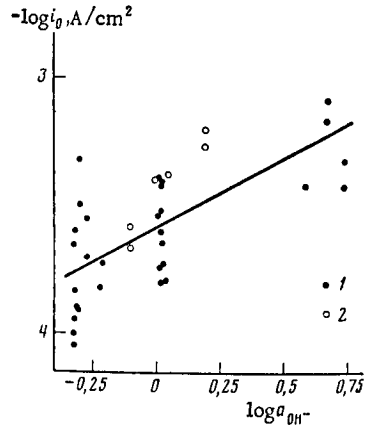

Fig. 5

Fig. 4. Dependence of the exchange current i_0 on the activity of Zn(II) at constant activity of OH^-: 1) 0.48-0.60, 2) 1.0-1.2 moles/kg. The point at the origin corresponds to a value of the logarithm on the y axis equal to −3.82.

Fig. 5. Dependence of the exchange current i_0 on the activity of OH^- at a constant activity of Zn(II) [(2.4-3)·10^{-3} mole/kg]. 1) Values of i_0 in solutions with variable ionic strength; 2) values of i_0 in solutions with ionic strength (3 M), supporting electrolyte KF.

This agrees with the existing concept of the composition of zinc complexes in alkaline solutions of the concentrations indicated above [14]. To calculate the activity of hydroxyl ions we used the data on the activity coefficients [15].

To confirm the hypothesis advanced above, that the resistance R_r characterizes the exchange current i_0 of the Zn−Zn(II) system, we determined the dependence of R_r on the concentration of zincate and hydroxyl ions. On each new electrode, a substantial time (from 1 to 3 h) was required to establish constancy of the value of R_r obtained from measurements of the impedance of zinc in alkaline zincate solutions at the static potential. In the case R_r dropped with time (i.e., the exchange current increased), which indicates an acceleration of the process of exchange of zinc, evidently associated with the effect of activation of the electrode surface, but not with an increase in its true surface (C_d and R_0 do not change with time). On account of the presence of the indicated time effect, which is of significance for an understanding of the kinetics of reactions of a zinc electrode in alkaline solutions, the frequency dependences of the impedance were recorded in a

TABLE 2. Comparison of the Values of the Exchange Current of the Zn−Zn(II) System, Obtained by Various Methods

Method	Solution	$i_0 \cdot 10^3$, A/cm^2	Source
Galvanostatic, one pulse, 15 μsec	3 *M* KOH; $1{,}5 \cdot 10^{-2}$ *M* ZnO	70	[3]
Galvanostatic, two pulse, second pulse 5 μsec	3 *M* KOH; $6 \cdot 10^{-3}$–$1{,}67 \cdot 10^{-1}$ *M* ZnO	190	[3]
Galvanostatic, one pulse, 5 μsec	3 *M* KOH; $2 \cdot 10^{-2}$ *M* ZnO	30	[4]
Chronopotentiometry	3 *M* KCl; $5 \cdot 10^{-3}$ *M* $ZnCl_2$; pH 3	1,25	[18]
Faraday impedance	3 *M* $NaClO_4$; $2{,}2 \cdot 10^{-2}$ *M* $Zn(ClO_4)_2$; pH 3,0–3,4	0,12	[19]
The same	3,2 *M* KOH; $6 \cdot 10^{-3}$ *M* ZnO	0,8	Data of this work

solution of the given composition several times until a constant value of R_r was established. The dependence of i_0 on the zincate concentration in the given frequency region cannot be established sufficiently accurately from impedance measurements. The partial coefficient $[\partial \log i_0/\partial \log c_{Zn(II)}]_{cOH^-}$ was determined considering the data of direct current measurements, by extrapolation of the anodic Tafel functions to the static values in solutions with constant OH^- activity and variable zincate activity, and a determination of the exchange currents. In Fig. 4 the currents correspond to the values of i_0 obtained by extrapolation, while the straight line represents a calculation of the linear relationship between $\log i_0$ and $\log a_{Zn(II)}$, obtained by the method of least squares. The slope of this function, i.e., $[\partial \log i_0/\partial \log a_{Zn(II)}]_{a_{OH^-}}$, is equal to 0.91. Figure 5 presents the dependence of the exchange current of zinc i_0 on the OH^- activity. Here the points correspond to values of i_0 obtained from impedance measurements (value of R_r) in solution with a constant concentration of Zn(II) ($6 \cdot 10^{-3}$ M). The straight line in Fig. 5 gives the results of a calculation of the linear relationship between $\log i_0$ and $\log a_{OH^-}$, obtained by the method of least squares. The slope of this function, i.e., the parameter $[\partial \log i_0/\partial \log a_{OH^-}]_{a_{Zn(II)}}$, is equal to 0.54. According to [16], the order of the summary anodic transition reaction $p_{a,m}$ and the cathodic transition reaction $p_{k,m}$, with respect to the component m can be determined according to the equation

$$\left[\frac{\partial \log i_0}{\partial \log a_m}\right]_{a_{j\neq m}} = p_{a,m} + \beta \nu_m \frac{z}{n} = p_{k,m} - (1-\beta)\nu_m \frac{z}{n}, \qquad (2)$$

where β is the transport coefficient of the anodic reaction; ν_m is the stoichiometric coefficient of the component m in the summary reaction; z is the valence of the transition; and n is the valence of the electrode reaction. For the equilibrium (1), n = 2, z = 2, $\nu_{Zn(II)} = 1$, $\nu_{OH^-} = -4$. The value of $\beta \simeq 0.80$ was determined from the slope of the Tafel function of the dissolution of zinc obtained experimentally (b = 0.036 V). Using Eq. (2) and the experimental values of the partial coefficients $[\partial \log i_0/\partial \log a_m]_{a_{j\neq m}}$, the following values were obtained for the orders of the electrochemical reaction with respect to Zn(II) ions and hydroxyl ions: $p_{a,Zn(II)} = 0.11 \simeq 0$; $p_{k,Zn(II)} = 1.11 \simeq 1$; $p_{a,OH^-} = 3.74 \simeq 4$; $p_{k,OH^-} = -0.26 \simeq 0$. The data obtained indicate that the reaction characterized by the quantity R_r is close to the summary electrode reaction according to Eq. (1).

According to the experimentally established scheme b (Fig. 1), on a Zn electrode at the static potentials, the exchange of zinc is paralleled by a certain reaction, the rate of which is controlled by the diffusion step (element of scheme W). The electrochemical step of this process proceeds at a higher rate, characterized by the value of R_d (scheme c, Fig. 1), while the summary impedance of this reaction within the investigated frequency region is commensurate with the impedance of the parallel reaction of dissolution and liberation of zinc. From the data obtained it follows that the exchange current, corresponding to the resistance R_d, is greater than 0.025 A/cm^2, since the value of R_d should be more than 50 times less than the impedance of diffusion in the frequency region used, in order for scheme c (Fig. 1) to turn into scheme b (Fig. 1), which we also determined experimentally. At the exchange currents that we found for the system zinc−alkaline zincate solution, the absence of a dependence of the value of A, characterizing the element W of the scheme, on the concentration of zincate and OH^- ions in solution indicates that the element W cannot be associated with diffusion of intermediate ions Zn(I) (along the electrode surface or in solution), as well, if we assume that the summary electrode reaction consists of two successive one-electron steps:

$$Zn+2OH^- \rightleftharpoons Zn(OH)_2^- + e, \quad (3)$$

$$Zn(OH)_2^- + 2OH^- \rightleftharpoons Zn(OH)_4^{2-} + e, \quad (4)$$

where i_0 of the first is much greater than i_0 of the second. With such a mechanism of the reaction, the quantity A, inversely proportional to the Zn(I) concentration, should be inversely proportional to the Zn(II) concentration and the square of the OH^- concentration in solution, which is not observed experimentally. And yet, the product of the diffusion coefficient D to the exponent 1/2 by the concentration of diffusing particles c (moles/cm^3), calculated from the coefficients A that we obtained experimentally according to the equation

$$2A = RT\sqrt{2}/n^2F^2c\sqrt{D}, \quad (5)$$

agrees in order of magnitude (10^{-10} mole · cm^{-2} · sec$^{-1/2}$) with the data of [17] on the reactive diffusion of alkali metal ions in the solid phase. Consequently it can be assumed that the element W simulates the process of diffusion of potassium in the solid phase of the electrode in the case of cathodic insertion and anodic extraction of potassium, corresponding to the impedance Z_3. The discrepancy that we observed in the values of R_d, A, and C_d, determined under the same experimental conditions but on different electrodes (a maximum for R_d – by an order of magnitude, A by half an order of magnitude, and C_d by twofold), is characteristic of the insertion of alkali metals and its influence on parallel reactions and is simultaneously explained by a vacancy mechanism of the insertion process.

The conclusion that a parallel process of insertion of an alkali metal occurs at the static potential of a zinc electrode in alkali is confirmed by the data of microanalytic measurements of the amount of potassium in the surface layer of the zinc electrode, performed by I. A. Astakhov on an analyzer of the JSM-50A type. These data will be published later.

From Table 2 it is evident that the value of the exchange current according to reaction (1) determined in this work is approximately two orders of magnitude less than the values obtained in [3, 4] by pulsed methods and coincides in order of magnitude with the values of the exchange current of the system Zn–Zn(II) in acidified solutions of Zn salts in solutions of alkali metal salts, obtained by the Faraday impedance method and by chronopotentiometry in [18, 19]. It can be assumed that the rates of the faster reaction of insertion of alkali metal ions into the zinc electrode were determined in [3, 4] instead of the exchange current of zinc. In [3] a decrease in the exchange current with increasing duration of the pulse was indicated, which, on the basis of the aforementioned, may be explained by the presence of diffusion impedance (scheme c, Fig. 1).

Thus, under the condition of detailed frequency analysis, the impedance method permits conclusions to be drawn on the ratios of the rates of successive steps and parallel pathways of complex reactions on zinc.

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