

CHANGES IN POLARIZATION RESISTANCE IN THE PROCESS OF FORMATION OF PROTECTIVE PHASE LAYERS WITH PARTICIPATION OF ORGANIC LIGANDS

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We study the principal kinetic regularities of the formation of protective metalloorganic films in acid media in the presence of complex-forming corrosion inhibitors and propose an equivalent scheme of the metal/electrolyte interface taking into account the polarization resistance of diffusion of the phase layer and intended for the analysis of the dynamics of its growth in the course of formation of protective layers with participation of inhibitors of the indicated kind. It is shown that the thickness of the film increases and protective properties improve with time according to the parabolic law obeying the regularities of diffusion kinetics.

Keywords: corrosion, complex-forming inhibitors, phase layers.

Contemporary methods of corrosion monitoring, diagnostics, and control enable one to significantly increase the efficiency of complex measures of corrosion protection, reduce the frequency of failures of the equipment, and prevent the occurrence of emergency situations. However, the reliability of the results of corrosion monitoring with the use of corrosion inhibitors is determined by the exactness of the models used to reflect the processes running in the investigated systems and serving as a basis for the creation of test and measurement installations and the development of methods aimed at the processing of accumulated results. The classical approaches to the analysis of the influence of inhibitors on the kinetics of electrode processes are based on the dominating concepts of adsorption nature of the protective action of corrosion inhibitors and require the calculation of isotherms and adsorption energies necessary for the determination of its type [1, 2]. At the same time, it was experimentally demonstrated that the decrease in the rate of corrosion fracture of steel in the presence of amino acids, guanidine derivatives, and a number of other ligands is caused by the formation of phase layers of difficultly soluble complex compounds of the inhibitor with cations of the corroded metal on its surface [3–5].

Thus, the investigation of the dynamics of formation of phase metalloorganic layers with the participation of organic ligands and the formalization of revealed regularities in the form of a generalized model would enable us to significantly increase the accuracy and representativeness of the results of corrosion monitoring in these systems.

Experimental Methods

The polarization resistance (PR) method is extensively used for the solution of the problems of corrosion monitoring because, in many cases, we observe an inversely proportional relation between the PR and corrosion

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rate. In finding the PR according to the two-electrode scheme, an electrochemical transducer (sensor) consisting of two identical electrodes fixed rigidly relative to one another is used. The equivalent electric scheme of this electrochemical system is represented as a combination of the resistance R_p with the corresponding polarization capacitance C_p and ohmic resistance of the electrolyte R_s .

To determine the polarization resistance, we used an R5126 instrument, which measures and compensates automatically the ohmic resistance of electrolyte and passivating films that can be formed on the surface, which enables us to isolate the polarization resistance of the corrosion system in pure form [6].

It was established in [5, 7] that, with increase in the time of holding of specimens in inhibited solutions, the degree of protection increases. Thus, the formation of the phase film is accompanied by an increase in its thickness and corrosion resistance, and the polarization resistance method enables us to obtain instantaneous values of the corrosion rate, which are necessary for the analysis of the dynamics of formation of protective layers.

In what follows, we analyze the dynamics of changes in the polarization resistance with time with the help of mathematical simulation modeling the laws and main quantitative relations characterizing the growth of phase films on the surface of metals [4, 8, 9].

Metalloorganic layers were formed in situ on the surface of specimens of 08kp and St20 steels in a 0.5 M H_2SO_4 solution with addition of organic ligands, namely, cysteine, acetylcysteine (ACC), methionine (Met), polyhexamethylene guanidine (PHMG), and polyhexamethylene biguanidine (PHMB).

The total polarization resistance was used as a parameter directly related to the thickness of the film.

Results and Their Discussion

The analysis of the dynamics of increase in the PR with time in the presence of amino acids and guanidine derivatives (Fig. 1) shows that the increase in the time of holding in inhibited solutions leads to a substantial increase in PR. This character of changes in PR for a long time cannot be explained by phenomena of physical (electrostatic) adsorption or chemisorption due to the rates of these processes.

It has been experimentally demonstrated in [4, 5, 10, 11] that, in the presence of ligands, a protective phase film forms on the metal surface from the products of interaction of the inhibitor with cations of the corroded metal and can play the role of a diffusion barrier. If the film forms from a nonconducting material, its resistance is determined by the ionic conductance of the electrolyte in the pores of the film. Thus, the value measured by the instrument includes not only the charge transfer resistance R_p , but also the resistance of diffusion R_d , which, under these conditions, will be determined by the diffusion resistance of the film. For this reason, in what follows, the measured quantity is called total polarization resistance (TPR) and denoted by $R_p + R_d$, and its increment with time is explained predominantly by the change in the parameters and properties of the formed films.

With increase in the thickness of the films, its resistance rises, and the total polarization resistance $R_p + R_d$ of the electrochemical system as a whole increases. Thus, under the condition $R_p + R_d \gg R_p$, in the first approximation, the character of changes in $R_p + R_d$ with time reflects the kinetics of growth of the protective film. Thus, the analysis of the character of changes in $R_p + R_d$ with time enables us to draw a number of conclusions on properties of the film (its density and permeability) and the nature of the limiting stage that determines its growth rate.

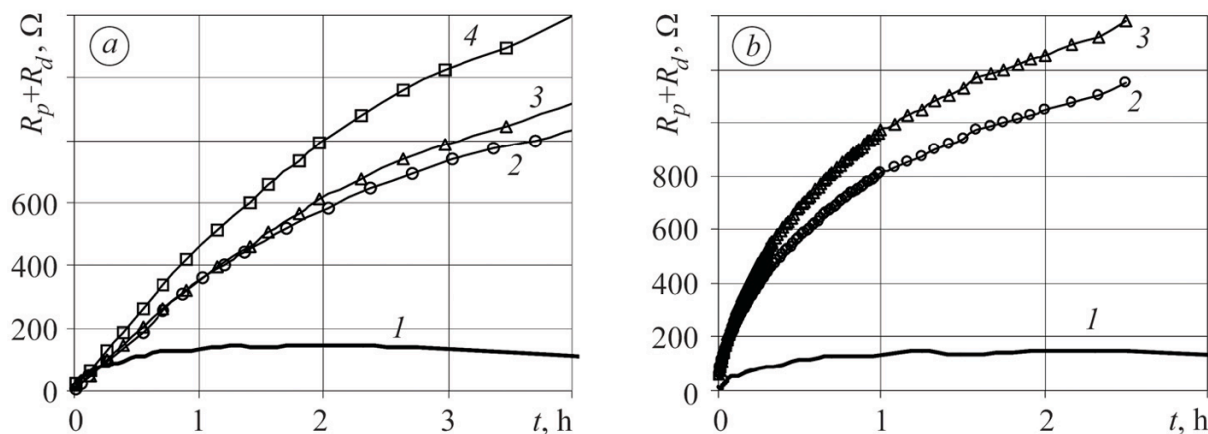


Fig. 1. Dependences of the total polarization resistance of steel electrode on the time of contact: (a): (1) 0.5 M H_2SO_4 ; (2) 0.5 M H_2SO_4 + 5 g/liter Met; (3) 0.5 M H_2SO_4 + 5 g/liter cysteine; (4) 0.5 M H_2SO_4 + 5 g/liter ACC; (b): (1) 0.5 M H_2SO_4 ; (2) 0.5 M H_2SO_4 + 5 g/liter PHMG; (3) 0.5 M H_2SO_4 + 5 g/liter PHMB.

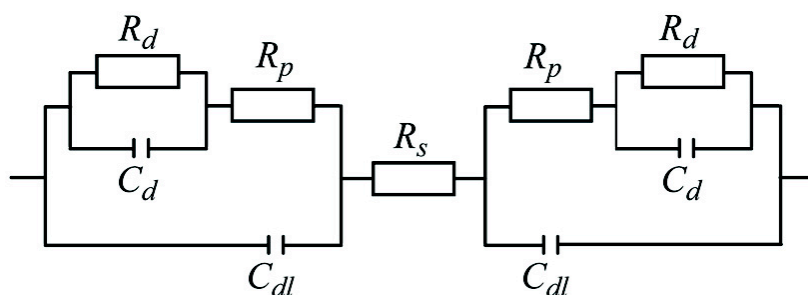


Fig. 2. Equivalent-circuit model of the electrochemical system in the presence of complex-forming inhibitors in the electrolyte.

In view of the arguments presented above, we propose an equivalent scheme of the electrochemical system which, parallel with the charge-transfer resistance R_p and the capacitance of the electric double layer C_{dl} , includes the diffusion resistance R_d and the capacitance C_d of the protective layer. This scheme is intended for the analysis of the dynamics of increase in the polarization resistance with time in the process of formation of phase metalloorganic layers involving organic ligands (Fig. 2).

It is known [8, 9] that the process of growth of a porous loose film that forms, e.g., during oxidation of some metals in an oxygen atmosphere, is described by the relation

$$h = kt, \quad (1)$$

in which h is the thickness of the film, t is time, and k is a constant coefficient.

It follows from Eq. (1) that there exists a linear relation between the thickness of the film h and the time t . In this case, the growth of the film is not accompanied by self-retarded processes, and the film has no protective properties.

In the case where a fairly dense film forms on the metal surface, the character of increase in the thickness of the film is described by a parabolic law [8, 9] described by the formula

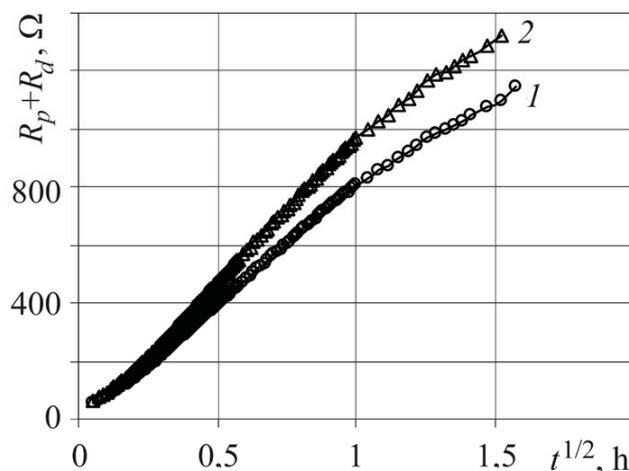


Fig. 3. Dependences of the total polarization resistance on the time of holding of steel electrode in the following solutions: (1) 0.5 M H_2SO_4 + 5 g/liter PHMG; (2) 0.5 M H_2SO_4 + 5 g/liter PHMB.

$$h^2 = kt = (2DC)t, \quad (2)$$

where D and C are, respectively, the diffusion coefficient and the concentration of particles participating in the process of growth of the film.

In the first approximation, we can assume that the quantity $R_p + R_d$ is linearly related to the thickness of the film. In this case, the polarization resistance of the electrochemical system also must change with time according to the parabolic law. It was established that, in the analyzed cases, the character of the changes in $R_p + R_d$ with time obeys the parabolic law and, hence, is described by the equation

$$R_p + R_d = (2DC)^{0.5} \rho t^{0.5}, \quad (3)$$

where ρ is the effective resistivity of the layer.

The graphic representation of the parabolic time dependence of the TPR on the $R_p + R_d - t^{1/2}$ coordinates for PHMG and PHMB is shown in Fig. 3. It is easy to see that, on these coordinates, the parabolic dependence is represented by straight lines. In [4, 8–11], it was shown that this parabolic dependence is typical of the cases where the growth rate of the film is limited by the diffusion rates of reagents or reaction products.

This enables us to postulate that, in the investigated systems, the film grows in a regime with diffusion control. Taking into account the small rate of diffusion processes in the solid phase, we see that the thickness of the film and, hence, the polarization resistance increase slowly with time and attain their limiting value within several hours [10]. Thus, the polarization resistance and, hence, the corrosion rate change for a long time according to a parabolic law, which indicates the presence of a retarded diffusion stage.

It should be noted that, according to the adsorption theory of inhibition, diffusion limitations in the monomolecular layers are completely excluded (except the Loshkarev effect, for which the selective permeability of the layer was observed). At the same time, we approximately calculated the intensity of the diffusion flow of the inhibitor to prevent the possibility of long-duration formation of a monolayer due to the retarded arrival of the inhibitor to the metal surface from the volume of the electrolyte.

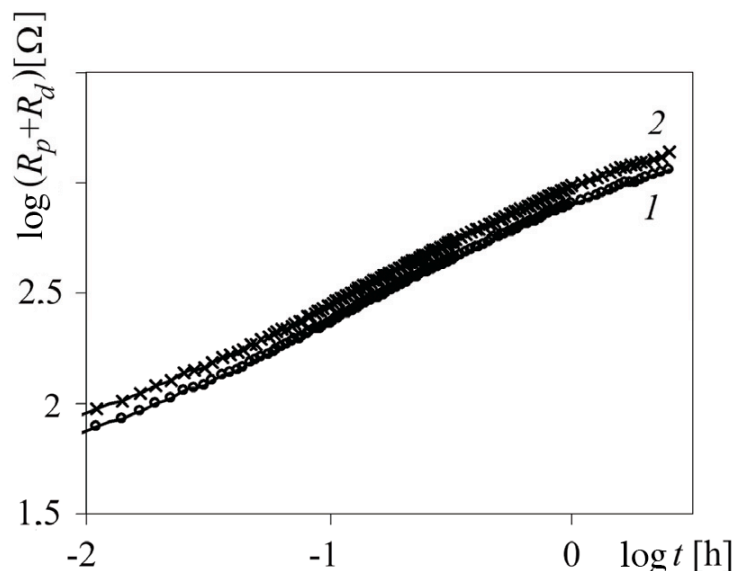


Fig. 4. Dependences of the polarization resistance of steel electrode on the time of holding in 0.5 M H_2SO_4 solutions containing 5 g/liter of the inhibitor on bilogarithmic coordinates: (1) 0.5 M H_2SO_4 + 5 g/liter PHMG; (2) 0.5 M H_2SO_4 + 5 g/liter PHMB.

According to Fick's first law, at a concentration of the ligand of 10^{-3} M/liter, diffusion coefficient of the inhibitor of $\approx 10^{-5}$ cm^2/sec , and a thickness of the diffusion layer $\delta = 10^{-2}$ cm [12], the flow of the inhibitor to 1 cm^2 of the surface of the electrode is $\Pi = (DC)/\delta = 10^9$ m/sec. At this rate of transfer of the inhibitor and a thickness of the layer of ≈ 10 nm, which accounts for the geometric parameters and conformation of molecules of the investigated polymeric ligands, the time required for the formation of a monolayer is ≈ 10 sec.

Thus, the diffusion control during formation of the protective layer is not connected with the retarded arrival of the inhibitor to the surface of the metal from the volume of the electrolyte.

Analysis of the experimental data in the coordinates $R_p + R_d - t^{1/2}$ shows that, with increase in the concentration of the inhibitor, the slope of the curves increases according to the equation

$$h = (2DC)^{0.5} t^{0.5}, \quad (4)$$

which proves its validity and indicates the retarded diffusion stage in the thickness of the protective layer.

The slope of the curves in the coordinates $\log(R_p + R_d) - \log t$ (Fig. 4) enables us to refine the exponent in Eq. (4).

As we can see, the experimental data for the guanidine derivatives in the bi-logarithmic coordinates are represented by straight lines with a slope $n = 0.51$, which is close to the exponent that corresponds to the equation for the purely diffusion regime of growth of the film ($n = 0.5$)

$$\log h = \log k + 0.5 \log t = 0.5 \log(2DC) + 0.5 \log t. \quad (5)$$

To justify the obtained relations, we also investigated the influence of the concentration of the ligands on the character of change of the total polarization resistance.

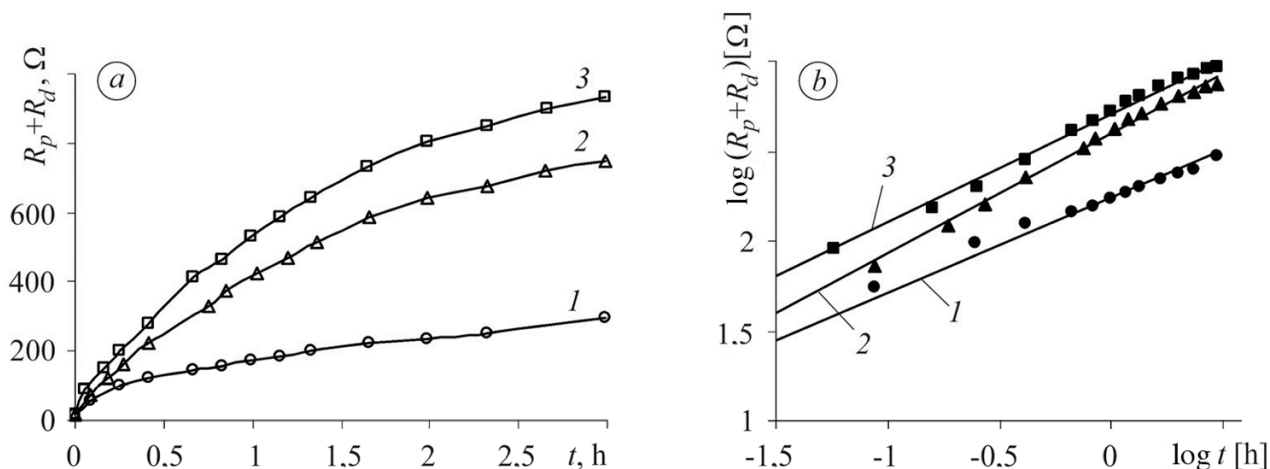


Fig. 5. Dependences of the polarization resistance of steel electrode on the time of holding in 0.5 M H_2SO_4 solutions containing methionine on the direct (a) and bilogarithmic coordinates (b): (1) 0.5 M H_2SO_4 + 0.5 g/liter Met; (2) 0.5 M H_2SO_4 + 2 g/liter Met; (3) 0.5 M H_2SO_4 + 5 g/liter Met.

It was established that, with increase in the concentration of methionine in the range 0.5–5 g/liter, the polarization resistance increases, and the slope of the curves in the coordinates $\log(R_p + R_d) - \log t$ hardly changes (Fig. 5).

The analysis of Eq. (5) indicates that, in the case of formation of the film in the mode with pure diffusion control, the plot of the function on the coordinates $\log(R_p + R_d) - \log t$ undergoes a parallel shift as the concentration increases and crosses the ordinate axis at the point $\log(2DC)^{0.5}$ corresponding to a new concentration.

As the concentration of the guanidine derivatives increases, the slope of the curves on the coordinates $\log(R_p + R_d) - \log t$ is also preserved and, hence, in the investigated systems, the increase in the concentration of ligands does not lead to changes in the mechanism of growth of the protective film.

Thus, using the polarization resistance method, we have investigated the kinetics of formation of metalloorganic layers with participation of the organic ligands and showed the validity of the application of the proposed generalized models for the analysis of the dynamics of growth of protective layers in the investigated systems.

CONCLUSIONS

The investigation of the dynamics of growth of phase layers by the methods of polarization resistance and mathematical simulation enable us to establish the principal kinetic regularities of formation of the protective metalloorganic films in acid media in the presence of complex-forming corrosion inhibitors.

We propose an equivalent scheme of the metal–electrolyte interface taking into account the polarization resistance of diffusion of the phase layer and intended for the analysis of the dynamics of its growth with time in the course of formation of protective layers with participation of complex-forming inhibitors.

It is shown that the thickness and protective properties of the film increase with time according to a parabolic law and obey the laws of diffusion kinetics. We also establish the regularities and deduce relations which enable us to increase the representativity of the results of corrosion monitoring of technological media by improv-

ing the test and measurement equipment and the methods aimed at data processing and their parameterization by using the refined models.

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