




# **An oversimplified corrosion inhibition experiment suitable for the development of the laboratory practice for undergraduate students**

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## **Supplementary Information**

The methodical instructions for the laboratory exercise concerning the study of the influence of inhibitors on the corrosion of mild steel in acidic environments.

The purpose of this work is to be introduced with gravimetric and electrochemical methods of studying the corrosion resistance of metals and alloys, and to study the effect of inhibitor addition on the corrosion behavior of mild steel in acidic environments.

There are four main groups of methods for protecting metals from electrochemical corrosion. The first group of methods includes the application of protective coatings (metallic, ceramic, polymeric, varnish, enamels, etc). The advantage of such coatings is an ease of application, but the disadvantage is a need to replace the coating if its integrity is damaged. The second group of methods includes the modification (i.e. alloying) of metals intended for work in aggressive conditions with components that enhance their corrosion resistance. The advantage of this approach is a low energy consumption, but the disadvantage is a high cost and complexity of manufacturing of special steels and alloys. The third group of methods includes an electrochemical protection, which can be cathodic or anodic in its nature. In the case of cathodic protection, a more electrochemically active metal is applied (or attached) to the metal acting as a “sacrificial anode”, and in the case of anodic protection, the metal is deliberately subjected to electrochemical passivation, as a result of which a protective film of oxides or other insoluble compounds is formed on its surface, preventing further dissolution. The advantages of this approach is a high autonomy of the system and an ability to preserve the protected metal for a long time, but the disadvantage is a need for periodic monitoring and replacement of anodes. Finally, the fourth group of methods includes a introduction of corrosion inhibitors into an aggressive environment, which, being adsorbed on the surface of the metal or on the surface of the oxide film formed on it, improve its protective properties and slow down the oxidation processes. The latter method is the easiest to use, but is applicable only for metal corrosion in closed containers, in which the composition of the medium can be easily controlled.

Both inorganic and organic compounds of various classes have inhibitory properties against corrosion of metals and alloys in aqueous environments. Among

inorganic compounds soluble cerium salts as well as phosphates, thiocyanates, and transition metal anions have inhibitory properties. Organic corrosion inhibitors include derivatives of aromatic and heterocyclic compounds, amines, organic acids, and surfactants.

Typically, the inhibitory properties of certain compounds are studied in acidic (hydrochloric, sulfuric, nitric, phosphoric acids), neutral (sodium chloride solution, sea water, solution simulating a cellular environment), or alkaline (alkali metal carbonates or hydroxides) environments. The simplest methods for studying the corrosion properties of alloys include gravimetric and electrochemical ones.

In gravimetric studies the prepared (cleaned and degreased) metal samples are weighed ( $m_0$ ), their geometric parameters are measured, and the samples are immersed in a corrosive environment for a certain period of time, then removed, dried, the corrosion products are removed from them, and the samples are weighed again ( $m$ ). Based on the difference in the masses of the samples before and after immersion ( $\Delta m = m_0 - m$ ), the corrosion rates are estimated:

$$\omega = \frac{\Delta m}{S \cdot t}, \quad (1)$$

where  $\omega$  is the corrosion rate (expressed in  $\frac{\text{mg}}{\text{cm}^2 \cdot \text{h}}$ ),  $S$  is the surface area of the sample that was in contact with the corrosive environment,  $\text{cm}^2$ ,  $t$  is the exposure time of the sample in the corrosive environment, hours. If the density of the sample is known, the corrosion rate can be expressed in  $\frac{\text{mm}}{\text{year}}$ . The inhibition efficiency ( $\eta$ ) is calculated based on the determined values of the corrosion rate in the absence ( $\omega_0$ ) and presence ( $\omega$ ) of the inhibitor:

$$\eta = \frac{\omega_0 - \omega}{\omega_0} \cdot 100\%. \quad (2)$$

Electrochemical measurements include the measurements of corrosion potential (open circuit potential), the recording of potentiodynamic polarization curves and the surface studies using an electrochemical impedance spectroscopy.

A corrosion potential ( $E_{\text{corr}}$ ) is a property of a surface, which characterizes its ability to donate electrons to a corrosive environment. The higher the corrosion potential value, the higher the corrosion resistance of the material. Accordingly, a change in the corrosion potential when an inhibitor is added to a corrosive environment qualitatively indicates its effect on the corrosion resistance of the material.

When an external current is passed through a corrosive electrochemical element, the potential of the metal deviates from its equilibrium value; this process is called polarization, and the dependence of the overvoltage (the difference between the potential of the metal when an external current is passed through it and the equilibrium value of the potential,  $\Delta E$ ) on the density of the transmitted current is called the polarization curve. For small deviations of the electrode potential from its

equilibrium value, this dependence is determined by the Tafel equation (named after the German chemist Julius Tafel):

$$\Delta E = A \cdot \ln \frac{i}{i_{\text{corr}}}, \quad (3)$$

in which  $\Delta E$  is the overvoltage, V,  $i = \frac{I}{S}$  is the current density equal to the ratio of the current to the surface area of the electrode,  $\frac{A}{\text{cm}^2}$ ,  $i_{\text{corr}}$  is the density of the corrosion current flowing through the corrosion element in the absence of external current,  $\frac{A}{\text{cm}^2}$ ,  $A$  is the proportionality coefficient, V. Therefore, if one represents the experimentally obtained dependence of the potential in the system on the transmitted current in the coordinates  $E = E(\lg i)$ , then in some area it will be a straight line, which can be approximated by the equation

$$E = a + b \cdot \lg i, \quad (4)$$

in which  $a$  and  $b$  are coefficients in the linear regression equation. A typical appearance of the polarization curve in coordinates  $E = E(\lg i)$ , and its linear sections are shown in Figure 1.

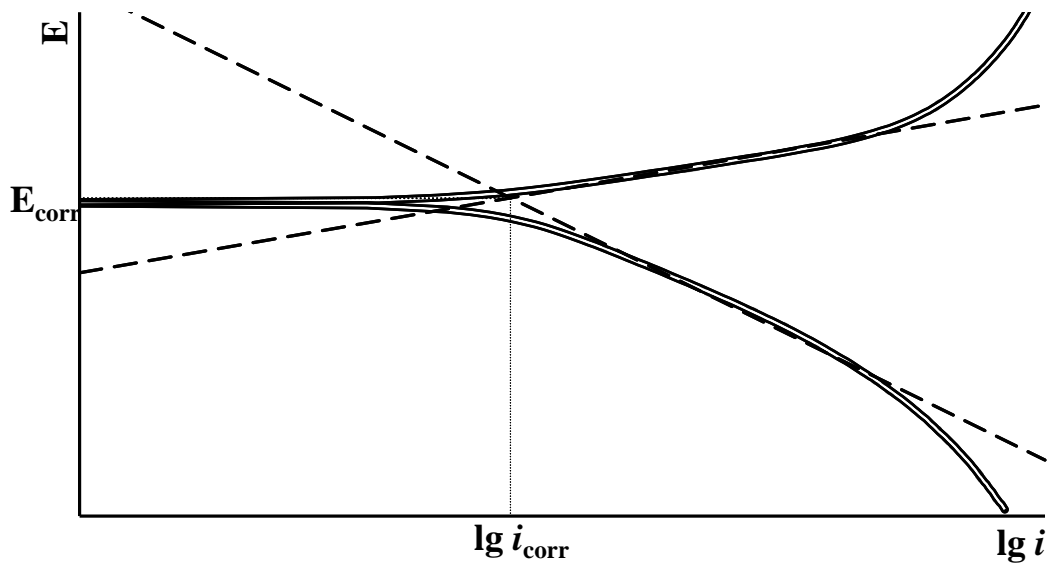


Figure 1. A polarization curve and its linear sections.

The part of the polarization curve located in the potential region above the corrosion potential is called the anodic branch of the polarization curve and is characterized by a coefficient in the Tafel equation  $b_a$ , and the other part located in the potential region below the corrosion potential is called the cathodic branch of the polarization curve and is characterized by a coefficient in the Tafel equation  $b_c$ . The intersection point of the approximating straight lines corresponds to the corrosion potential  $E_{\text{corr}}$ , and allows one to determine the logarithm of the corrosion current  $\lg i_{\text{corr}}$ .

The lower the corrosion current, the lower the corrosion rate of the sample. Thus by recording the polarization curves of the metal under study in the test

environment in the absence and in the presence of an inhibitor, identifying their linear sections, approximating them, determining the coefficients in the Tafel equation for the anodic and cathodic branches of the curves, and calculating the values of corrosion currents in the presence ( $i$ ) and in the absence ( $i_0$ ) of inhibitor, the effectiveness of the inhibitor under study can be quantitatively assessed:

$$\eta = \frac{i_0 - i}{i_0} \cdot 100\%. \quad (5)$$

Another important characteristics of the polarization curve is the polarization resistance ( $R_p$ ), which is a measure of the sample resistance to oxidation when an external current is passed through it, and is defined as the ratio of the overvoltage to the difference between the densities of the transmitted and corrosion currents:

$$R_p = \left( \frac{\Delta E}{\Delta i} \right)_{\Delta E \rightarrow 0} = \frac{\Delta E}{i - i_{\text{corr}}}. \quad (6)$$

Polarization resistance is expressed in  $\text{Ohms} \cdot \text{cm}^2$ . If one constructs a polarization curve in coordinates  $E = E(i)$ , then the polarization resistance can be determined as the tangent of the slope of the linear section of this curve for small deviations of the current density from the value of the corrosion current.

The relationship between polarization resistance, coefficients in the Tafel equation and corrosion current density is expressed by the Stern – Geary equation:

$$R_p = \frac{1}{\ln 10} \cdot \frac{1}{i_{\text{corr}}} \cdot \frac{b_a \cdot |b_c|}{b_a + |b_c|}. \quad (7)$$

From the values of polarization resistance in the absence ( $R_0$ ) and in the presence ( $R$ ) of the inhibitor, it is also possible to estimate the effectiveness of inhibition as:

$$\eta = \frac{R - R_0}{R} \cdot 100\%. \quad (8)$$

In the theory of electrical circuits an electrical impedance is the complex electrical resistance between two circuit nodes when a harmonic alternate current is applied to them. When an alternate current is applied to a circuit, the impedance of resistive elements is expressed by a real value, and the impedances of inductive and capacitive elements are expressed only by imaginary values, however, the relationships between the impedances of various elements when they are connected in series and in parallel are still determined by Ohm's and Kirchhoff's laws, as in the case of applying a direct current.

Each element of the electrical circuit that arises during the operation of electrochemical elements (namely, electrodes, an electrolyte solution, phase boundaries) can be associated with its corresponding resistive, inductive or capacitive circuit element. Thus such a circuit can be described by an equivalent electrical circuit consisting only of conductors of the first kind. For a corrosive electrochemical element, the simplest equivalent circuit that describes its operation is the simplified Randles circuit, named after the English electrochemist John Edward Brugh Randles and shown in Figure 2.

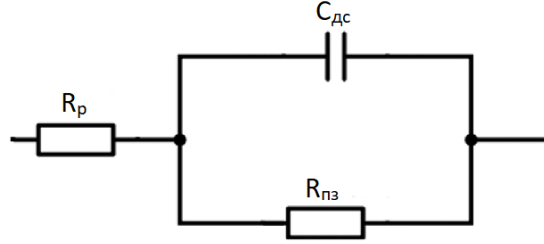


Figure 2. A simplified equivalent Randles circuit.

In this circuit, the resistor  $R_s$  determines the resistance of the electrolyte solution, the resistor  $R_{ct}$  determines the resistance caused by the charge transfer from the electrolyte to the metal through the protective passivating film on its surface, and the capacitor  $C_{dl}$  determines the capacitance of the double electrical layer formed at the “metal – solution” interface. The Randles' circuit describes the electrochemical elements corresponding to the corrosion of steels in acidic environments quite satisfactorily. The impedance of a capacitor is given by the equation:

$$Z_{C_{dl}} = \frac{1}{P \cdot (i \cdot \omega)^n}, \quad (9)$$

in which,  $\omega$  is the frequency of alternate current, Hz,  $i$  is the imaginary unit,  $P$  and  $n$  are parameters, and  $0 \leq n \leq 1$ . Accordingly, the impedance of the entire simplified equivalent Randles circuit is determined by the equation:

$$Z = R_s + \frac{1}{\frac{1}{R_{ct}} + P \cdot (i \cdot \omega)^n} = R_s + \frac{1}{\frac{1}{R_{ct}} + P \cdot \omega^n \cdot \left( \cos\left(\frac{\pi \cdot n}{2}\right) + i \cdot \sin\left(\frac{\pi \cdot n}{2}\right) \right)}. \quad (10)$$

It is convenient to display the impedance graphically using two types of diagrams. The first approach uses an algebraic representation of complex numbers in Cartesian coordinates, in which the abscissa is the real part of the impedance ( $Z_{Re}$ ), and the ordinate is the imaginary part, taken with the opposite sign ( $-Z_{Im}$ ). This dependence is called the amplitude-phase frequency response of an electrical circuit (or simply the “Nyquist diagram” named after the American-Swedish engineer Harry Nyquist). A typical Nyquist plot of a simplified Randles circuit is shown in Figure 3.

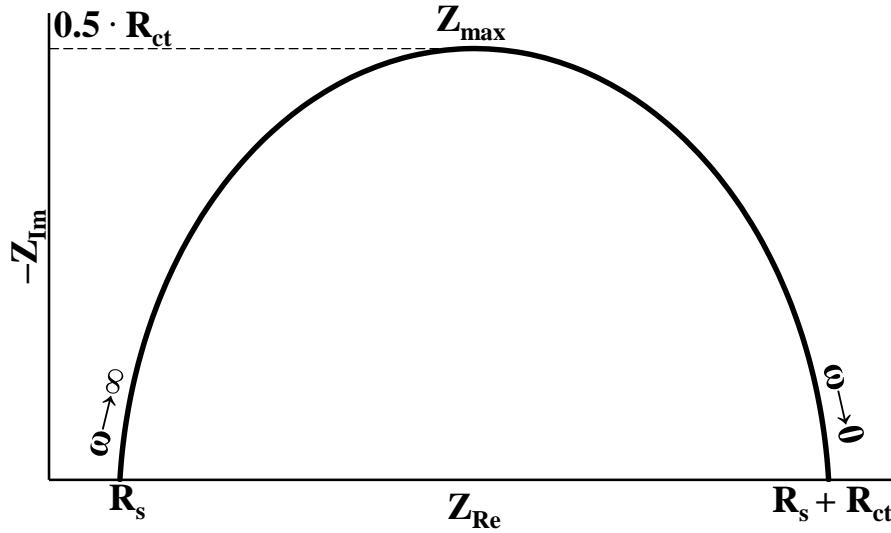


Figure 3. A typical Nyquist plot for a simplified equivalent Randles circuit.

As can be seen from Figure 3, it represents a semicircle intersecting the x-axis in diameter. From the equation (10) for the impedance of a simplified Randles circuit, it is clear that  $\lim_{\omega \rightarrow \infty} Z = R_s$  and  $\lim_{\omega \rightarrow 0} Z = R_s + R_{ct}$  therefore, the intersection points of the dependence  $Z_{Re} = Z_{Re}(Z_{Im})$  with the abscissa axis determine the values of  $R_s$  and  $R_s + R_{ct}$ , and the value of resistance  $R_{ct}$  can be determined straightforwardly as the diameter of a semicircle. In order to determine the capacitance of the capacitor  $C_{dl}$ , it is necessary to know the frequency of the alternate current  $\omega_{max}$  corresponding to the maximum ordinate value in the diagram (that is the minimum value of the imaginary part of the impedance):

$$C_{dl} = \frac{1}{2\pi \cdot R_{ct} \cdot \omega_{max}}, \quad (11)$$

and based on the formula for the capacitance of a flat capacitor:

$$C_{dl} = \frac{\varepsilon \cdot \varepsilon_0 \cdot S}{d}, \quad (12)$$

in which  $\varepsilon_0 = 8.854 \cdot 10^{-12}$  F/m is the electrical permittivity of vacuum,  $\varepsilon$  is the relative electrical permittivity of the medium,  $S$  is the surface area of the capacitor,  $m^2$ ,  $d$  is the distance between the plates of the capacitor, m, one can estimate the value of  $d$ , which would mean the thickness of the double electrical layer on the “electrode-solution” boundary and could be a measure of the thickness of the protective film formed on the metal surface.

The disadvantage of the Nyquist plot is that it does not contain data on the frequencies of the transmitted alternate current. Therefore, the second approach to plot the impedance uses a trigonometric representation of complex numbers in polar coordinates using the impedance modulus:

$$|Z| = \sqrt{Z_{Re}^2 + Z_{Im}^2}, \quad (13)$$

and the phase shift angle:

$$\theta = \arctg \left( \frac{-Z_{Im}}{Z_{Re}} \right). \quad (14)$$

The dependence  $|Z| = |Z|(\omega)$  is called the amplitude frequency response, and the dependence  $\theta = \theta(\omega)$  is called the phase frequency response. A diagram displaying both of the above dependencies in a single plot is called a “Bode diagram” named after the American engineer Hendrik Wade Bode. A typical Bode plot of a simplified Randles circuit is shown in Figure 4.

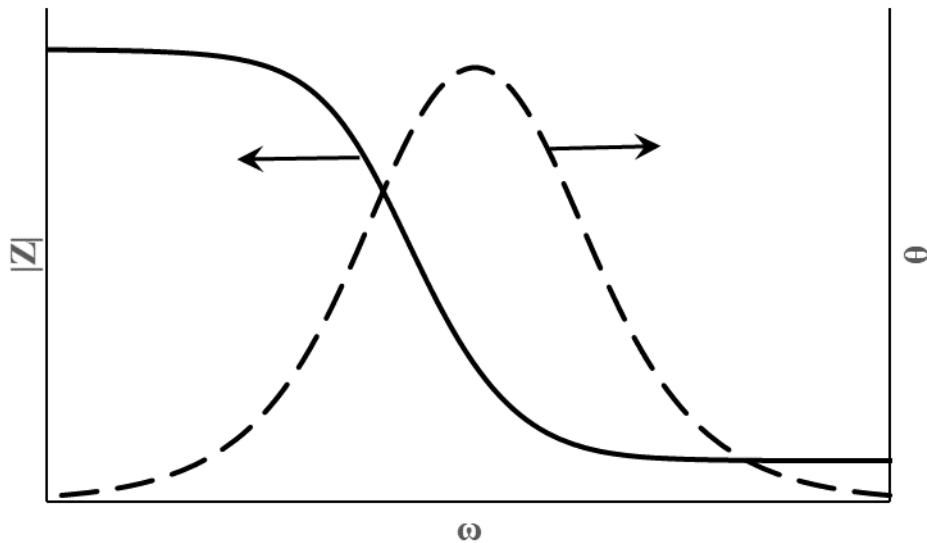


Figure 4. A typical Bode plot for a simplified equivalent Randles circuit.

When studying the effect of inhibitors on the metallic corrosion using the electrochemical impedance spectroscopy, the value of charge transfer resistance  $R_{ct}$  is of greatest importance. Knowing its values in the absence ( $R_0$ ) and in the presence ( $R$ ) of the inhibitor one can also evaluate the effectiveness of inhibition as:

$$\eta = \frac{R - R_0}{R} \cdot 100\%. \quad (15)$$

The protective effect of inhibitors is associated with their adsorption on the metal surface. By conducting corrosion experiments in a corrosive environment with different inhibitor additives and by determining the effectiveness of inhibition for various concentrations, it is possible to estimate the thermodynamic parameters of adsorption. Typically, the Langmuir adsorption model named after its founder the American chemist Irving Langmuir is used for this. In relation to the adsorption of an inhibitor on a metal surface, the Langmuir adsorption isotherm equation can be written as:

$$\eta = \frac{K_{ads} \cdot c_{inh}}{K_{ads} \cdot c_{inh} + 1}, \quad (16)$$

in which  $c_{inh}$  is the inhibitor concentration,  $K_{adc}$  is the equilibrium constant of the adsorption-desorption process,  $\eta$  is the fraction of the metal surface covered with the

inhibitor, assumed to be equal to the inhibition efficiency. The dimension of the adsorption-desorption constant will be inversely proportional to the dimension of the inhibitor concentration. This equation can be linearized as:

$$\frac{c_{inh}}{\eta} = \frac{1}{K_{ads}} + c_{inh} \quad (17)$$

By processing the experimentally obtained dependence  $\frac{c_{in}}{\eta} = \frac{c_{in}}{\eta}(c_{in})$  using the least squares method, one can determine the adsorption-desorption constant  $K_{ads}$  as the reciprocal of the intersect of the linear regression. Knowing this constant, one can estimate the Gibbs energy of adsorption process  $\Delta_{ads}G$ :

$$\Delta_{ads}G = -R \cdot T \cdot \ln(K_{ads} \cdot c_w), \quad (18)$$

in which  $R = 8,3145 \frac{J}{mol \cdot K}$  is the universal gas constant,  $T$  is the absolute temperature at which the experiment was carried out,  $K$ ,  $c_w$  is the concentration of the solvent (water) in the solution. In this case, the dimensions of the inhibitor concentrations  $c_{inh}$  and the water  $c_w$  in the solution must coincide.

An experimental electrochemical study of the inhibitory properties of substances is carried out using a potentiostat-galvanostat equipped with a frequency response analyzer for working with alternate current. Experiments are carried out in a standard three-electrode cell with a single compartment for the working, auxiliary and reference electrodes. The metal or alloy sample under study is used as a working electrode, a graphite rod is used as an auxiliary electrode, and a silver chloride, saturated calomel, or mercury sulfate electrode can serve as a reference electrode. The corrosive medium under study without additives or with additives of an inhibitor is used as an electrolyte. In this case, the surface of the working electrode immersed in the solution in all experiments should be as identical as possible.

Reagents and equipment:

Potentiostat-galvanostat with frequency response analyzer,

Personal computer with software for controlling the operation of a potentiostat-galvanostat,

Aquadistiller,

Analytical balance,

Connecting wires,

Laboratory stand and clamps for it,

Beakers, volumetric flasks, pipettes,

Concentrated acids i.e. HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>.

Inhibitors i.e. KSCN, Na<sub>2</sub>MoO<sub>4</sub>, Na<sub>2</sub>WO<sub>4</sub>, oxalic acid, benzoic acid, succinic acid, glycine,

Solution for filling the reference electrodes i.e. saturated KCl, saturated K<sub>2</sub>SO<sub>4</sub>,

Isopropyl alcohol,

Sandpaper,



Paper napkins,  
Steel wire,  
Steel plates with holes,  
Threads,  
Paraffin film,  
Ruler,  
Graphite rod,  
Reference electrode: silver chloride or mercury sulfate,  
Set of areometers,  
Watch,  
Cover for a beaker with holes for electrodes.

The experimental procedure.

Measure the density of concentrated acid, calculate its exact concentration and prepare a corrosive environment (the specific acid and its concentration are indicated by the instructor);

Prepare three inhibitor solutions in a corrosive environment (the specific inhibitor and solution concentrations are indicated by the instructor). When preparing inhibitor solutions, use a previously prepared corrosive medium as a solvent.

Prepare steel plates and steel wire: clean their surface with sandpaper, degrease with isopropyl alcohol, rinse with distilled water, dry, insulate part of the surface with paraffin film, measure the geometric parameters of the uninsulated surface, weigh the steel plates.

Hang the steel plates on threads and immerse them in a corrosive environment without additives or with inhibitor additives. Keep the plates in a corrosive environment for 2 hours.

At the end of the exposure, remove the plates from the solutions, rinse them with distilled water and dry. Carefully remove the formed corrosion products using sandpaper, rinse the plates again with distilled water, dry and weigh.

Assemble a three-electrode electrochemical cell. Fill the beaker with the corrosive medium without adding an inhibitor, and close the beaker with a lid. Place the working electrode (steel wire), auxiliary electrode (graphite rod) and reference electrode into the beaker. Make sure that the entire uninsulated surface area of the working electrode is immersed in a corrosive environment. Connect the electrodes to the potentiostat-galvanostat.

Run the control program, select the open circuit potential measurement and record the corrosion potential (open circuit potential) for 15 minutes.

Upon completion of the open circuit potential measurement, without removing the electrodes from the cell, select the impedance measurement mode and start the impedance measurement at the open circuit potential in the frequency range from 10 kHz to 100 mHz with a number of frequencies of 100 and a potential amplitude of 10 mV.

Upon completion of the impedance measurement, without removing the electrodes from the cell, select the linear sweep mode and start measuring the polarization curve in the potential range from  $-500$  to  $+500$  mV relative to the open circuit potential with a potential sweep rate of 10 mV.

Disassemble the electrochemical cell, rinse the beaker and electrodes with distilled water and dry. Clean the steel wire with sandpaper and remove the formed corrosion products.

Repeat electrochemical experiments in corrosive environments with different additions of inhibitors.

At the end of the work, thoroughly rinse the reference electrode with distilled water, close the hole and immerse it in the storage solution.

Processing of experimental results.

Calculate the areas of steel plates immersed in a corrosive environment. Calculate the mass loss of steel plates and the corresponding corrosion rates in the presence and absence of an inhibitor. Evaluate the effectiveness of inhibition based on gravimetric experiments.

Enter the data from gravimetric measurements into the table:

$c_{inh}$ , mg/l	$S$ , cm <sup>2</sup>	$m_0$ , g	$m$ , g	$\Delta m$ , g	$\omega$ , mg / (cm <sup>2</sup> · h)	$\omega$ , mm / year	$\eta$ , %

In a single graph plot the potential versus time for all experiments in the open circuit mode. Draw a conclusion about the change in corrosion potential when adding an inhibitor to a corrosive environment.

In a single graph plot the polarization curves in coordinates  $E = E(\lg i)$  for all experiments with linear potential sweep. For each of the polarization curves, determine the linear sections of its cathode and anode branches, process them using the least squares method and calculate the coefficients in the Tafel equation, corrosion current, and polarization resistance for each experiment. Evaluate the effectiveness of inhibition based on the data of electrochemical experiments.

Enter the data from electrochemical measurements into the table:

$c_{inh}$ , mg/l	$E_{cor}$ , mV	$b_a$ , mV/dec	$b_c$ , mV/dec	$i_{cor}$ , mA/cm <sup>2</sup>	$\eta$ , %	$R_p$ , Ohm · cm <sup>2</sup>	$\eta$ , %

In a single graph plot the Bode diagrams for all experiments with impedance, in the other graph plot all the Nyquist plots. Using the least squares method estimate the solution resistance, charge transfer resistance, as well as the parameters  $P$  and  $n$  for a simplified equivalent Randles circuit, calculate the capacitance of the capacitor and the thickness of the electrical double layer in each experiment. Evaluate the effectiveness of inhibition based on impedance experiments.

Enter the data from impedance measurements into the table:

$c_{inh}$ , mg/l	$R_p$ , Ohm	$P$ , s <sup>n</sup> / Ohm	$n$	$C_{dl}$ , $\mu F$	$d$ , nm	$R_{ct}$ , Ohm	$\eta$ , %

Enter data on the effectiveness of inhibition into the table:

$c_{inh}$ , mg/l	$\eta$	$c_{inh} / \eta$ , mg/l	$K_{ads}$ , l/mg	$\Delta_{ads}G$ , kJ / mol

Plot the data in the coordinates  $\frac{c_{inh}}{\eta} = \frac{c_{inh}}{\eta}(c_{inh})$ , process the resulting dependence using the least squares method, and use the regression equation to determine the equilibrium constant of the adsorption-desorption process and the Gibbs energy of adsorption. Draw a conclusion about the applicability of the Langmuir adsorption isotherm to the process of inhibitor adsorption on a metal surface.

Compare the experimental data obtained with the data available in the literature on the effectiveness of this inhibitor in relation to various alloys in various corrosive environments.

Draw the conclusions.

Topics for the self-study.

Corrosion of metals. Classification of corrosion processes.

Basic methods of protecting metals from corrosion.

Corrosion inhibitors and their mechanism of action.

Corrosive electrochemical cell.

Methods for assessing the inhibitory ability of compounds: gravimetric, electrochemical, and electrochemical impedance spectroscopy.

Corrosion potential, corrosion current and the Tafel equation. Polarization curves.

Electrochemical impedance spectroscopy. Simplified Randles equivalent circuit and the physical meaning of its elements.

Langmuir adsorption isotherm and its use in the evaluation of corrosion inhibitors.