Analysis of the properties and mechanisms of action of chamber corrosion inhibitors based on electrochemical impedance spectra

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Abstract

A methodology for analyzing the properties and mechanisms of action of chamber corrosion inhibitors using electrochemical impedance spectra, adequately described by the equivalent Mansfeld circuit, has been developed. The suggested approach makes it possible: to estimate the coefficient and degree of metal protection by the inhibitor; to estimate the degree of surface coverage with corrosion-blocking layers; to determine the predominant mechanism of corrosion inhibition. The informative value of the approach was illustrated by data on the effect on the electrochemical impedance spectra: of octadecylamine vapor pressure used in the chamber treatment of copper; of chamber treatment of steel with octadecylamine, benzotriazole and their mixtures with different ratios of the components; of time of zinc exposure in air after chamber treatment with ethylhexanoic acid.

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Introduction

The protection of metals and alloys from atmospheric corrosion remains an important technical challenge [1–8]. Various inhibitors, including vapor-phase ones, are widely used to solve it [1, 9–14]. Of these, volatile inhibitors are the most widespread in practice. Many publications [1, 10, 15–26] deal with the theory and practice of their action. Vapor-phase inhibitors of a relatively new type, chamber inhibitors (CIN), have been less studied so far.

Chamber treatment (CT) is a method of vapor-phase protection of metals that has been developing in the recent years. The method involves exposure of metal items to vapors of inhibitors with low volatility under normal conditions in a sealed chamber at elevated temperatures. During CT, nano-sized adsorption layers of chamber inhibitors are formed on a metal from the gas phase. These layers are able to prevent the atmospheric corrosion of the metal for a long time after removal of the metal items from the chamber [27–32].

As a rule, a set of methods is used in studies of the functional properties and mechanisms of CIN action, including corrosion tests (periodic moisture condensation, salt fog, outdoor tests), electrochemical (potentiodynamic polarization, electrochemical impedance spectroscopy), and physical methods (ellipsometry, X-ray photoelectron spectroscopy, atomic force microscopy, *etc.*). It should be noted that that electrochemical impedance (EI) spectroscopy plays a secondary role in these studies. Meanwhile, even in the *ex situ* variant, it is a powerful research tool capable of providing important information rather than just illustrating the conclusions obtained by other methods. Note that in all the experiments with various CINs, metals, and CT modes known to the authors, the EI spectra could be adequately described by the modified Mansfeld equivalent circuit [33–35] shown in Figure 1.

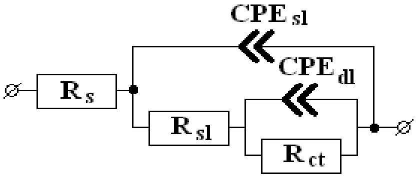

Figure 1. Modified Mansfeld equivalent circuit.

R_s – resistance of the bulk electrolyte between the auxiliary and working electrodes, which does not affect the electrode processes and depends on the conductivity of the medium and the geometry of the cell;
R_{sl} – resistance of the oxide-hydroxide and adsorption surface layers;
R_{ct} – charge transfer resistance of the Faraday reaction, which determines the kinetics of the corrosion process;
CPE_{sl} – constant phase element characterizing the capacitance of the surface layers;
CPE_{dl} – constant phase element reflecting the pseudo-capacitance of the Faraday reaction.

The goal of this work was to develop a methodology for analyzing the properties and mechanisms of action of CINs based on EI spectra described by the Mansfeld equivalent circuit.

Although this study is of predominantly theoretical character, the main points are illustrated by experimental results obtained previously. The experimental data describe the effect of the following on EI spectra:

- vapor pressure (p) of octadecylamine (ODA) in the CT of copper [31]. The p range studied was from $3.5 \cdot 10^{-10}$ to $3.5 \cdot 10^{-2}$ mmHg, the CT temperature was 100°C, the duration was 1 h, and the time exposure of electrodes to air after CT (τ_{exp}) was 24 h.
- CT of low-carbon steel with ODA, benzotriazole (BTA), and their mixtures with various ratios of the components [32]. The CT temperature was 120°C, duration 1 h, $\tau_{exp}=24$ h.
- τ_{exp} of zinc in air after CT with ethylhexanoic acid (EHA) [29]. The CT temperature was 100°C, duration 1 h.

All the EI spectra were obtained in borate buffer solution (pH 7.36) containing 0.001 M NaCl after 24 h of exposure.

Theoretical part

Let us first consider some concepts of the formal theory of action of corrosion inhibitors. The rate of metal corrosion (K) as a heterogeneous chemical process is described by the equation:

$$K = b \cdot S \exp\left(-\frac{W_{\mathrm{act}}}{RT}\right) \tag{1}$$

where b is a coefficient depending on the concentration of corrosive agents in the system, S is the active surface of the metal, W_{act} is the effective activation energy of corrosion, R is the universal gas constant, and T is the absolute temperature.

For a metal in the initial state ($^{\mathrm{is}}$) it can be written:

$$K^{\mathrm{is}} = b^{\mathrm{is}} S^{\mathrm{is}} \exp\left(-\frac{W_{\mathrm{act}}^{\mathrm{is}}}{RT}\right) \tag{2}$$

Let the metal be subjected to a treatment that increases its corrosion resistance, such as thermal treatment, inhibitor treatment, or some other. For the treated metal ($^{\mathrm{tr}}$):

$$K^{\mathrm{tr}} = b^{\mathrm{tr}} S^{\mathrm{tr}} \exp\left(-\frac{W_{\mathrm{act}}^{\mathrm{tr}}}{RT}\right) \tag{3}$$

Clearly, corrosion inhibition can occur due to:

- a decrease in b, *i.e.* the concentration of corrosive agents in the medium;
- a decrease in S, *i.e.* blocking at least a fraction of the surface (blocking action);
- an increase in W_{act} on the unblocked surface (effect on activation).

By dividing (2) by (3), we obtain:

$$\frac{K^{\mathrm{is}}}{K^{\mathrm{tr}}} = \left(\frac{b^{\mathrm{is}}}{b^{\mathrm{tr}}}\right) \cdot \left(\frac{S^{\mathrm{is}}}{S^{\mathrm{tr}}}\right) \cdot \left[\frac{\exp\left(-\frac{W_{\mathrm{act}}^{\mathrm{is}}}{RT}\right)}{\exp\left(-\frac{W_{\mathrm{act}}^{\mathrm{tr}}}{RT}\right)}\right] \tag{4}$$

Note that $K^{\mathrm{is}}/K^{\mathrm{tr}}$ is nothing else than the corrosion inhibition coefficient, often denoted in scientific literature by the letter γ. Moreover, $b^{\mathrm{is}}/b^{\mathrm{tr}}$ is the coefficient of corrosion rate K reduction due to changes in the concentration of corrosive compounds in the system. Let us denote this value by γ_{conc}. $S^{\mathrm{is}}/S^{\mathrm{tr}}$ is the coefficient of K reduction due to a change in the active surface of the metal, *i.e.* due to the blocking mechanism (γ_{block}). The

$\left(\exp\left(-W_{\mathrm{act}}^{\mathrm{is}} / RT\right) / \exp\left(-W_{\mathrm{act}}^{\mathrm{tr}} / RT\right)\right)$ ratio is the coefficient of K reduction due to an increase in the corrosion activation energy (γ_{act}).

Taking the above designations into account, we obtain:

$$\gamma = \gamma_{\mathrm{conc}} \cdot \gamma_{\mathrm{block}} \cdot \gamma_{\mathrm{act}} \tag{5}$$

It is important here that the total corrosion inhibition coefficient γ is determined by the product of partial inhibition coefficients γ_{conc}, γ_{block}, γ_{act}.

The above considerations do not claim to be something new. Equations of this type were first obtained by L.I. Antropov [12]. Since the works of this outstanding electrochemist and specialist in the field of inhibitor protection are not always available, we have given a simplified derivation of Equation (5), which will be used below.

By definition [36], addition of an inhibitor to a corrosive medium or treatment of a metal with an inhibitor do not affect the content of the main corrosive products and, consequently, the value of b. Thus, in the case of inhibitor protection, $\gamma_{\mathrm{conc}}=1$, so Equation (5) is simplified to the form:

$$\gamma = \gamma_{\mathrm{conc}} \cdot \gamma_{\mathrm{act}} \tag{6}$$

Let us consider the effect of a CIN on the metal. For systems whose EI spectra are described by the modified Mansfeld circuit, it was suggested [28] that the partial corrosion inhibition coefficients are characterized by the expressions:

$$\gamma_{\mathrm{block}} = \frac{R_{\mathrm{sl}}^{\mathrm{tr}}}{R_{\mathrm{sl}}^{\mathrm{is}}} \tag{7}$$

and

$$\gamma_{\mathrm{act}} = \frac{R_{\mathrm{ct}}^{\mathrm{tr}}}{R_{\mathrm{ct}}^{\mathrm{is}}} \tag{8}$$

This approximation is correct for γ_{block} and carries useful information about the mechanism of the protection process, first of all, about the degree of surface coverage with the layers that block it (Θ). Indeed, the following is true for surface blocking:

$$\Theta = 1 - \frac{1}{\gamma_{\mathrm{block}}} \tag{9}$$

Note that adsorption (mono- or polymolecular) and/or oxide-hydroxide layers formed during CT can block the surface. Hence, in general case, it is not correct to identify Θ with the surface coverage with the inhibitor.

Equation (9) is derived for the inhibitor protection process. However, it permits calculating Θ from γ_{block} for any corrosion systems whose EI spectra are described by the Mansfeld circuit. This equation also allows one to calculate the degree of blocking of the metal surface when the metal is treated not only by an inhibitor, but also using thermal or other kinds of treatment that do not affect the concentration of the main corrosive compounds.

Things are more complicated with the activation mechanism of corrosion inhibition. The γ_{act} value takes into account the change in the charge transfer resistance of the Faraday reaction on the entire surface. Thus, it already includes the change in the R_{ct} values of the equivalent circuit caused by blocking of a fraction of the surface by a CIN. Hence, a comparison of γ_{block} and γ_{act} values, contrary to the conclusions given in Ref. [28], does not allow us to draw an unambiguous conclusion about the dominance of the blocking or activation inhibition mechanism.

In order to assess more accurately the inhibition of the corrosion process by the activation mechanism, we introduce a new characteristic: γ_{act}^{*} – the true coefficient of corrosion inhibition by the activation mechanism, which takes into account the reduction of the active surface when it is blocked by the inhibitor. It can be calculated by comparing the specific resistances related to the surface where the Faraday process takes place:

$$\gamma_{\text{act}}^{*} = \frac{R_{\text{ct}}^{\text{tr}*}}{R_{\text{ct}}^{\text{is}}} \tag{10}$$

Here $R_{\text{ct}}^{\text{tr}*}$ is the charge transfer resistance on the treated sample taking into account its active surface (1–Θ), that is:

$$R_{\text{ct}}^{\text{tr}*} = \left(1-\Theta\right) R_{\text{ct}}^{\text{is}} \tag{11}$$

The $R_{\text{ct}}^{\text{is}}$ value refers to the complete geometric surface (no blocking), *i.e.*, no correction is required for it.

Substituting $R_{\text{ct}}^{\text{tr}*}$ into equation (10), we obtain:

$$\gamma_{\text{act}}^{*} = \left(1-\Theta\right)\frac{R_{\text{ct}}^{\text{tr}}}{R_{\text{ct}}^{\text{is}}} = \left(1-\Theta\right)\cdot\gamma_{\text{act}} \tag{12}$$

Combining equations (9) and (12) gives:

$$\gamma_{\text{act}}^{*} = \frac{\gamma_{\text{act}}}{\gamma_{\text{block}}} \tag{13}$$

The γ_{act}^{*} value characterizes corrosion inhibition on the surface that is not blocked due to metal surface treatment. In this regard, the comparison of γ_{block} and γ_{act}^{*} allows one to draw a conclusion about the mechanism of corrosion inhibition, which is more correct than the conclusion based on the comparison of γ_{block} and γ_{act} values calculated by equation (8).

If $\gamma_{\text{block}} > \gamma_{\text{act}}^{*}$, corrosion is mainly inhibited by the blocking mechanism, while if $\gamma_{\text{block}} < \gamma_{\text{act}}^{*}$, then by the activation mechanism. Comparable γ_{block} and γ_{act}^{*} values indicate a mixed mechanism of corrosion protection.

The overall corrosion inhibition coefficient should hence be carried out using the refined formula:

$$\gamma = \gamma_{\text{block}} \cdot \gamma^{*}_{\text{act}} = \gamma_{\text{block}} \frac{\gamma_{\text{act}}}{\gamma_{\text{block}}} = \gamma_{\text{act}} \tag{14}$$

Obviously, substituting equation (8) into (14) yields:

$$\gamma = \frac{R^{\text{tr}}_{\text{ct}}}{R^{\text{is}}_{\text{ct}}} \tag{15}$$

In other words, the overall protective coefficient of an inhibitor is determined by the ratio of the Faraday process resistances of the treated and original samples with the same area, directly calculated from the Mansfeld equivalent circuit.

The above considerations change the approach to the calculation of the degree of metal protection due to metal treatment, including inhibitor treatment (*Z*). In Refs. [27–30], *Z* was calculated in accordance with the recommendations given in Refs. [32–34] using the formula:

$$Z = \frac{\left(R^{\text{tr}}_{\text{ct}} + R^{\text{tr}}_{\text{sl}} - R^{\text{is}}_{\text{ct}} - R^{\text{is}}_{\text{sl}}\right)}{\left(R^{\text{tr}}_{\text{ct}} + R^{\text{tr}}_{\text{sl}}\right)} \tag{16}$$

The protection degrees calculated by this formula provide a general assessment of the anti-corrosion efficiency of a particular method of inhibitor treatment of a metal. However, comparison of the efficiency of various inhibitors, various treatment modes, *etc.* requires the use of a slightly different *Z* value, namely *Z**, which is determined as follows:

$$Z^{*} = 1 - \frac{1}{\gamma} = 1 - \frac{1}{\gamma_{\text{act}}} = \frac{\left(R^{\text{tr}}_{\text{ct}} - R^{\text{is}}_{\text{ct}}\right)}{R^{\text{tr}}_{\text{ct}}} \tag{17}$$

It is essential that the approach described above can be used to estimate the mutual effect of the components of mixed CINs. According to Refs. [28, 37], the main diagnostic criterion of additivity of the protective effect of the components in mixed inhibitors is determined by the relationship:

$$\gamma_{\Sigma} = \gamma_1 \cdot \gamma_2 \cdot \ldots \cdot \gamma_n \tag{18}$$

where the Σ index refers to a mixture of inhibitors 1, 2, … *n*.[1]

For binary mixtures the following is true:

$$\gamma_{\Sigma} = \gamma_1 \cdot \gamma_2 \tag{19}$$

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[1] Equation (18) was first derived by V.V. Ekilik [37]. Taking into account the importance of Equation (18) in the interpretation of inhibitor action mechanisms and the difficult accessibility of Ref. [37] for the English-speaking readers, the derivation of the equation was repeated by us in Ref. [28].

Considering Equation (14), Equation (19) can be transformed as:

$$\gamma_{\text{act},\Sigma} = \gamma_{\text{act},1} \cdot \gamma_{\text{act},2} \tag{20}$$

The fulfillment of inequalities $\gamma_{\text{act},\Sigma} > \gamma_{\text{act},1} \cdot \gamma_{\text{act},2}$ or $\gamma_{\text{act},\Sigma} < \gamma_{\text{act},1} \cdot \gamma_{\text{act},2}$ indicates the synergism or antagonism of the components, respectively. These inequalities allow one to make a conclusion about the mutual effects of the components of mixed inhibitors based on the impedance spectra if they are described by the Mansfeld equivalent circuit.

In some cases, it is more convenient to determine the mutual effects of the components of binary mixtures by the values of Z^*. Equation (17) can be transformed to the form:

$$\gamma_{\text{act}} = \frac{1}{\left(1 - Z^*\right)} \tag{21}$$

Combining Equations (20) and (21), we obtain the criterial equation based on the Z^* value:

$$Z^*_\Sigma = Z^*_1 + Z^*_2 - Z^*_1 Z^*_2 \tag{22}$$

that is similar to the expression suggested by K. Aramaki and N. Hackerman back in the 60s of the past century [38].

The inequality $Z^*_\Sigma > Z^*_1 + Z^*_2 - Z^*_1 Z^*_2$ makes it possible to make the decision that there is a synergism of the protective effects of components 1 and 2, while the inequality $Z^*_\Sigma < Z^*_1 + Z^*_2 - Z^*_1 Z^*_2$, that there is an antagonism.

Analysis of Equation (19) taking Equation (15) into account makes the following fact obvious: if the charge transfer resistances for components 1 and 2 of a binary mixture ($R^{\text{tr}}_{\text{ct1}}$, $R^{\text{tr}}_{\text{ct2}}$, respectively) are measured for samples with the same surface and compared to the same initial state $R^{\text{is}}_{\text{ct}}$, then:

$$\gamma_\Sigma = \gamma_1 \gamma_2 = \left(\frac{R^{\text{tr}}_{\text{ct1}}}{R^{\text{is}}_{\text{ct}}}\right) \cdot \left(\frac{R^{\text{tr}}_{\text{ct2}}}{R^{\text{is}}_{\text{ct}}}\right) = \frac{\left(R^{\text{tr}}_{\text{ct1}} \cdot R^{\text{tr}}_{\text{ct2}}\right)}{\left(R^{\text{is}}_{\text{ct}}\right)^2} \tag{23}$$

The above considerations determine the algorithm for analyzing the EI spectra in the studies of corrosion inhibitors. At the first step, one has to make sure that the spectra are adequately described by the modified Mansfeld circuit. Then one should calculate the equivalent circuit parameters (R_{sl} and R_{ct}) related to the geometric surface of a sample in the initial state and for inhibitor-treated samples.

Further analysis of experimental data should be continued as follows:

- estimate the partial corrosion inhibition coefficient due to the blocking mechanism (γ_{block}) based on $R^{\text{tr}}_{\text{sl}}$ and $R^{\text{is}}_{\text{sl}}$ values using Equation (7);
- determine the degree of blocking of the original surface (Θ) by the layers formed during metal treatment using the γ_{block} values and Equation (9);

- calculate the true coefficient of corrosion inhibition by the activation mechanism $\left(\gamma^{*}_{\mathrm{act}}\right)$ that takes into account the reduction in the active surface due to its blocking, using $R^{\mathrm{tr}}_{\mathrm{ct}}$, $R^{\mathrm{is}}_{\mathrm{ct}}$ and Θ values by Equation (10) and taking into consideration Equation (11);
- compare the γ_{block} and $\gamma^{*}_{\mathrm{act}}$ values and draw a conclusion about the mechanism of corrosion inhibition;
- calculate the degree of metal protection due to its treatment with the inhibitor (Z^*) by Equation (17) based on γ_{act} values;
- compare the γ_{act} values of the inhibitor mixture and the γ_{act} product of its components or (for binary mixtures of inhibitors 1 and 2) compare the Z^* values of the mixture with the expression $Z_1^* + Z_2^* - Z_1^* Z_2^*$ and draw a conclusion about the mutual effect of the components.

It should be noted that it is rational to use the developed approach for analyzing the EI spectra not only for chamber protection of metals. The method makes it possible:

- to estimate the degree of metal protection by an inhibitor,
- to estimate the degree of surface coverage with corrosion-blocking layers;
- to determine the predominant mechanism of corrosion inhibition based on EI spectra without and with addition of an inhibitor into the system almost for any corrosion objects. Impedance measurements in this case can be carried out both *ex situ* and *in situ*. A necessary and sufficient condition for the applicability of this approach is that adequate description of the EI spectra by the Mansfeld equivalent circuit has to be possible.

Returning to chamber inhibitors, let us illustrate the capabilities of the suggested algorithm for analyzing the EI spectra of copper after the CT with octadecylamine (ODA).

Analysis of the EI spectra of copper after the CT with octadecylamine

Let us omit the description of the Nyquist and Bode plots of copper treated with ODA at various vapor pressures of the inhibitor. We only note that all the EI spectra were adequately (with an accuracy of at least 97%) fitted by the modified Mansfeld circuit. The parameters obtained for various modes of electrode treatment are given in Table 1. The characteristic values of the protective effect of ODA calculated from the data in Table 1 are given in Table 2.

Note that the γ_{block} value upon heat treatment of copper is 3.39. Addition of ODA to the chamber results in a change in γ_{block}. With an increase in p_{ODA} in the chamber, this parameter first falls to 1.3 and then increases to 5606.

Table 1. Parameters of the equivalent circuit in various modes of copper electrode treatment.

Treatment conditions	R_s kΩ·cm^2	CPE_{sl}, S·s^n/cm^2	n_{sl}	R_{sl} kΩ·cm^2	CPE_{dl}, S·s^n/cm^2	n_{dl}	R_{ct} kΩ·cm^2
IS	0.51	$7.72 \cdot 10^{-6}$	0.87	2.69	$5.78 \cdot 10^{-5}$	0.83	3.03
Heat treatment without a CIN	0.47	$3.79 \cdot 10^{-6}$	0.85	9.11	$3.49 \cdot 10^{-5}$	0.72	24.37
$p_{ODA} = 3.5 \cdot 10^{-10}$ mmHg	0.43	$3.63 \cdot 10^{-6}$	0.86	11.52	$6.82 \cdot 10^{-5}$	0.58	38.27
$p_{ODA} = 3.5 \cdot 10^{-9}$ mmHg	0.45	$9.06 \cdot 10^{-6}$	0.82	3.50	$14.4 \cdot 10^{-5}$	0.64	17.77
$p_{ODA} = 3.5 \cdot 10^{-8}$ mmHg	0.27	$1.15 \cdot 10^{-5}$	0.68	4.89	$1.94 \cdot 10^{-7}$	1	4.52
$p_{ODA} = 3.5 \cdot 10^{-7}$ mmHg	0.36	$2.23 \cdot 10^{-6}$	0.90	7.60	$1.30 \cdot 10^{-5}$	0.79	6.64
$p_{ODA} = 3.5 \cdot 10^{-6}$ mmHg	0.46	$4.61 \cdot 10^{-6}$	0.77	20.85	$4.51 \cdot 10^{-5}$	1	28.09
$p_{ODA} = 3.5 \cdot 10^{-5}$ mmHg	0.41	$4.33 \cdot 10^{-6}$	0.76	24.76	$4.11 \cdot 10^{-5}$	1	19.20
$p_{ODA} = 3.5 \cdot 10^{-4}$ mmHg	0.43	$1.25 \cdot 10^{-6}$	0.81	92.70	$1.31 \cdot 10^{-5}$	1	69.30
$p_{ODA} = 3.5 \cdot 10^{-3}$ mmHg	0.56	$2.19 \cdot 10^{-7}$	0.93	794.75	$8.77 \cdot 10^{-7}$	1	1000
$p_{ODA} = 3.5 \cdot 10^{-2}$ mmHg (saturated vapors)	0.48	$2.09 \cdot 10^{-7}$	1	1506.41	$9.37 \cdot 10^{-7}$	1	11113

Table 2. Characteristic values of the protective effect of ODA calculated from the data in Table 1.

Treatment conditions	γ_{block}	γ_{act}	γ^*_{act}	Θ	Z^*
IS	–	–	–	–	–
Heat treatment without a CIN	3.39	8.03	2.37	0.70	0.87
$p_{ODA} = 3.5 \cdot 10^{-10}$ mmHg	4.29	12.61	2.94	0.76	0.92
$p_{ODA} = 3.5 \cdot 10^{-9}$ mmHg	1.30	5.85	4.50	0.23	0.82
$p_{ODA} = 3.5 \cdot 10^{-8}$ mmHg	1.82	1.49	0.82	0.45	0.33
$p_{ODA} = 3.5 \cdot 10^{-7}$ mmHg	2.83	2.19	0.77	0.65	0.54
$p_{ODA} = 3.5 \cdot 10^{-6}$ mmHg	7.76	9.26	1.19	0.87	0.89
$p_{ODA} = 3.5 \cdot 10^{-5}$ mmHg	9.21	6.33	0.69	0.89	0.84
$p_{ODA} = 3.5 \cdot 10^{-4}$ mmHg	34.45	22.84	0.66	0.97	0.96
$p_{ODA} = 3.5 \cdot 10^{-3}$ mmHg	295.78	359.60	1.22	0.997	0.997
$p_{ODA} = 3.5 \cdot 10^{-2}$ mmHg (saturated vapors)	5606.29	367.02	0.07	0.999	0.997

The Θ values also change depending on the CT mode. The data in Table 2 show that at p_{ODA} below $3.5\cdot10^{-10}$ mmHg, the Θ value is between 0.70 and 0.75. It should be assumed that this level of surface blocking is due to the formation of oxide-hydroxide layers on the surface. With an increase in p_{ODA}, the Θ values first decrease and then increase. Apparently, at p_{ODA} in the range from $3.5\cdot10^{-10}$ to $3.5\cdot10^{-9}$ mmHg, the ODA adsorbed on the surface does not yet form blocking layers, but already inhibits the thermal oxidation of copper. The ability of ODA to inhibit the thermal oxidation of copper was noted by us previously [39].

High concentrations of ODA in the chamber air ($p_{\mathrm{ODA}}>3.5\cdot10^{-9}$ mmHg) lead to a gradual increase in Θ due to the formation of adsorption layers. Vapor pressures at $p_{\mathrm{ODA}}>3.5\cdot10^{-3}$ mmHg provide blocking, in fact, of the entire surface, and the Θ value tends to unity.

The $\gamma^{*}_{\mathrm{act}}$ values did not exceed 4.5 for all the variants of copper treatment. It is important that the transition from the formal calculation of γ_{act} to the calculation of the $\gamma^{*}_{\mathrm{act}}$ value, taking into account the active surface, significantly changes the understanding of the mechanism of corrosion inhibition. In the first case, a mixed mechanism of inhibition could be erroneously assumed. Comparison of γ_{block} and true $\gamma^{*}_{\mathrm{act}}$ allows one to conclude that a pronounced blocking mechanism of corrosion inhibition of copper with ODA exists. The γ_{block} values significantly exceed $\gamma^{*}_{\mathrm{act}}$ at $p_{\mathrm{ODA}}>3.5\cdot10^{-8}$ mmHg.

The protection degrees Z^* increase symbatically with Θ, reaching a value of 0.997 at the same degree of surface blocking.

Thus, the analysis of the EI spectra of copper upon its treatment with ODA vapors indicates a purely blocking mechanism of protection. At $p_{\mathrm{ODA}}=3.5\cdot10^{-3}$ mmHg, the surface is completely filled with adsorption layers that prevent corrosion, and the mechanism of the Faraday reaction of metal oxidation on the unblocked part of the surface is not changed significantly.

Let us now use the same approach to analyze the EI spectra related to the CT of steel with octadecylamine, benzotriazole, and their mixtures [32].

Analysis of the EI spectra of steel upon chamber treatment with octadecylamine, benzotriazole, and their mixtures

Like in the case described above, all the EI spectra reported in Ref. [32] were adequately (with an accuracy of at least 96%) described by the modified Mansfeld circuit. Its parameters for various modes of electrode treatment are given in Table 3. The characteristic values of the protective effect of ODA, BTA and their mixtures calculated from the data of Table 3 are given in Table 4.

The γ_{block} value even upon heat treatment of copper without an inhibitor amounts to 9.79. Addition of BTA into the chamber leads to the increase in this value. At the same time, the value provided by ODA (26.79) is almost two times higher than the similar value for BTA (13.59). The highest value of γ_{block} is observed in the mixture containing 75% ODA (71.15). The γ_{block} value for the other mixtures was commensurate with the γ_{block} of ODA.

Table 3. Parameters of the equivalent circuit for various modes of steel electrode treatment.

Treatment conditions	R_s, kΩ·cm^2	CPE_{sl}, S·s^n/cm^2	n_{sl}	R_{sl} kΩ·cm^2	CPE_{dl}, S·s^n/cm^2	n_{dl}	R_{ct} kΩ·cm^2
IS	0.95	$3.41\cdot10^{-5}$	1.00	7.80	$4.39\cdot10^{-5}$	0.89	58.0
Heat treatment without CIN	0.46	$6.87\cdot10^{-6}$	0.88	76.4	$2.62\cdot10^{-5}$	1.00	76.0
BTA 100%	0.47	$9.02\cdot10^{-7}$	0.91	106	$6.87\cdot10^{-6}$	0.67	402
ODA 100%	0.59	$9.71\cdot10^{-7}$	0.85	209	$4.27\cdot10^{-6}$	1.00	441
ODA 25%+BTA 75%	0.57	$2.91\cdot10^{-6}$	0.91	179	$2.81\cdot10^{-6}$	0.92	588
ODA 50%+BTA 50%	0.59	$1.23\cdot10^{-6}$	0.92	207	$2.05\cdot10^{-6}$	0.98	926
ODA 75%+BTA 25%	0.96	$6.77\cdot10^{-7}$	0.93	555	$9.79\cdot10^{-7}$	0.64	2880

Table 4. Characteristic values of the protective effect of CINs calculated from the data of Table 3.

Treatment conditions	γ_{block}	γ_{act}	γ^*_{act}	Θ	Z^*
IS	–	–	–	–	–
Heat treatment without CIN	9.79	1.31	0.13	0.90	0.23
BTA 100%	13.59	6.93	0.51	0.92	0.86
ODA 100%	26.79	7.60	0.28	0.96	0.87
ODA 25%+BTA 75%	22.95	10.14	0.44	0.96	0.90
ODA 50%+BTA 50%	26.54	15.97	0.60	0.96	0.94
ODA 75%+BTA 25%	71.15	49.66	0.70	0.99	0.98

The Θ values also vary depending on the conditions of steel treatment. Note that the degree of surface blocking in all cases, including the heat treatment of the metal without inhibitors, exceeded 0.9. The maximum value of Θ (0.99) was observed for the ODA 75%+BTA 25% mixture.

The γ^*_{act} value both for individual compounds and their mixtures was below 1, *i.e.* all variants of steel treatment in fact slightly activated the Faraday reactions of metal oxidation, and it was only surface blocking with the inhibitor that provided corrosion protection. It is not surprising that comparison of γ_{block} and γ^*_{act} allowed us to make the conclusion about the existence of a purely blocking mechanism of steel corrosion inhibition by all CINs studied in this work. It should be noted that comparison of γ_{block} and γ^*_{act} values led the authors of work [31] to the erroneous conclusion about the mixed blocking-activation mechanism of inhibitor action.

The value of $Z^*_{\mathrm{ODA}} + Z^*_{\mathrm{BTA}} - Z^*_{\mathrm{ODA}} \cdot Z^*_{\mathrm{BTA}}$ calculated from the data of Table 4 is 0.98. Despite the fact that Z^* values of the mixtures studied are higher than the Z^* values of the components, the calculation indicates their antagonism for the inhibitors ODA 25%+BTA 75% (Z^*=0.90) and ODA 50%+BTA 50% (Z^*=0.94).[2] Only in the case of the (ODA 75%+BTA 25%) mixture (Z^*=0.98), the mutual effect of the components is small. The conclusion about the absence of synergetic interaction between ODA and BTA upon chamber protection of steel agrees with the previous data [31] obtained in prolonged and labor-consuming corrosion tests.

Summarizing the results given in this section, it is noteworthy that the EI data allowed us to make corrections to the data presented in [31] and state a purely blocking mechanism of corrosion inhibition. The possibility to quickly study the mutual effect of the components of mixed inhibitors is also important. Of course, the results of EI spectroscopy do not substitute direct corrosion studies, but they can reduce the amount of work significantly.

The same methodology was used by us to analyze the EI spectra for the CT of zinc with ethylhexanoic acid (EHA) [29].

Analysis of the EI spectra of zinc upon chamber treatment with ethylhexanoic acid

All the EI spectra reported in [29] were adequately (with an accuracy of at least 97%) described by the modified Mansfeld circuit. The parameters for various modes of electrode treatment are given in Table 5. The characteristic values of the protective effect of EHA calculated from the data of Table 5 are given in Table 6.

Table 5. Parameters of the equivalent circuit in various modes of zinc electrode treatment.

Treatment conditions	R_s, kΩ·cm^2	CPE_{sl}, S·s^n/cm^2	n_{sl}	R_{sl} kΩ·cm^2	CPE_{dl}, S·s^n/cm^2	n_{dl}	R_{ct} kΩ·cm^2
IS	0.1	$5.19\cdot10^{-6}$	1	0.99	$6.66\cdot10^{-5}$	1	0.68
Heat treatment without a CIN	0.1	$2.37\cdot10^{-6}$	0.92	1.13	$1.94\cdot10^{-5}$	0.8	0.77
EHA τ_{exp}=1 h	0.42	$3.51\cdot10^{-6}$	1	13.24	$2.19\cdot10^{-5}$	1	18.34
EHA τ_{exp}=5 h	0.42	$1.68\cdot10^{-6}$	1	30.37	$1.15\cdot10^{-5}$	1	20.99
EHA τ_{exp}=24 h	0.49	$1.10\cdot10^{-6}$	1	49.21	$6.88\cdot10^{-6}$	1	45.49
EHA τ_{exp}=72 h	0.37	$1.48\cdot10^{-6}$	1	48.99	$6.92\cdot10^{-6}$	1	45.31

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[2] We emphasize that there is no contradiction here. In Ref. [28] it is shown theoretically that the protective effect of mixed CINs in the absence of interactions between the components should exceed the protective effects of the components. In some cases, this is possible even in case of antagonism of the protective effects.

Table 6. Characteristic values of the protective effect of EHA calculated from the data in Table 5.

Treatment conditions	γ_{block}	γ_{act}	γ^{*}_{act}	Θ	Z^{*}
IS	–	–	–	–	–
Heat treatment without a CIN	1.14	1.13	0.99	0.12	0.11
EHA $\tau_{\text{exp}}=1$ h	13.4	27.0	2.00	0.92	0.963
EHA $\tau_{\text{exp}}=5$ h	30.7	30.8	1.00	0.97	0.967
EHA $\tau_{\text{exp}}=24$ h	49.7	67.5	1.36	0.98	0.985
EHA $\tau_{\text{exp}}=72$ h	49.5	56.6	1.14	0.99	0.982

Heat treatment of zinc in the absence of EHA was not accompanied by noticeable surface blocking: the γ_{block} values were close to 1. After CT of the electrode, corrosion inhibition due to the blocking effect enhanced. The γ_{block} values increased tens of times. During the first day of exposure of the electrode in air, the γ_{block} value increased to 49.7. Extension of the exposure time τ_{exp} to 3 days was not accompanied by strengthening of corrosion protection, including the corrosion inhibition due to the blocking mechanism.

The Θ values changed symbatically with those values of γ_{block}. Analysis of the effects of the specific "self-organization" of surface films observed in Ref. [29] indicates that an increase in corrosion protection is accompanied by an increase in the degree of surface blocking. At 1 h exposure time, the Θ value of was 0.92, while at exposure times of 5, 24, and 72 h, the degree of surface blocking reached 0.97, 0.98, and 0.99, respectively.

Exposure of zinc electrodes to air after CT was not accompanied by changes in γ^{*}_{act}. The calculated values of γ^{*}_{act} were in the range from 1 to 2, irrespective of the zinc treatment conditions.

Comparison of the γ_{block} and γ^{*}_{act} values allows us to draw the conclusion that the increase in corrosion protection upon electrode exposure to air after chamber treatment with EHA occurs due to a purely blocking mechanism rather than a mixed mechanism as it was assumed in the previous work [29]. It should be noted that Z^{*} increased from 0.96 ($\tau_{\text{exp}}=1$ h) to 0.98 ($\tau_{\text{exp}}=24$ h) upon such exposure.

The main conclusion of the present section, which complements the conclusions made earlier [29], is as follows: the chemical transformations in the adsorption layers of EHA during exposure of zinc electrodes in air after CT, accompanied by the increase in the corrosion resistance of the metal, are associated with an increase in the degree of surface blocking. At the same time, the kinetics of the corrosion process on the remaining active surface of the metal did not change much in comparison with the experiments without the inhibitor.

Conclusions

A methodology for analyzing the properties and mechanisms of action of corrosion inhibitors by electrochemical impedance spectra is suggested.

The approach developed makes it possible:

- to estimate the coefficient and degree of metal protection by the inhibitor;
- to estimate the degree of surface coverage with corrosion-blocking layers;
- to determine the predominant mechanism of corrosion inhibition for a wide range of corrosion objects using electrochemical impedance spectra without and with the addition of an inhibitor into the system.

A necessary and sufficient condition for the applicability of the suggested methodology is that the electrochemical impedance spectra should be adequately described by the equivalent Mansfeld circuit.

The capabilities of the approach are illustrated by the following data on the effect on the electrochemical impedance spectra:

- of copper chamber treatment with octadecylamine at various vapor pressures;
- of steel chamber treatment with octadecylamine, benzotriazole, and their mixtures with various ratios of the components;
- of the time of zinc exposure in air after chamber treatment with ethylhexanoic acid.

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