Study of steel corrosion inhibition in media containing H₂S and CO₂ by impedance spectroscopy and polarization resistance methods

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Summary

Inhibition of carbon steel corrosion by “INCORGAS” compositions in a NACE medium containing hydrogen sulfide and carbon dioxide was studied by electrochemical impedance spectroscopy and linear polarization resistance methods. Contribution of the inhibitor to the total protective effect of the “corrosion product film/inhibitor” system was calculated. Polarization measurements testify that the anodic process is hindered in the presence of the inhibitors. The same conclusion was made from the data of electrochemical impedance spectroscopy.

Key words: inhibitor, contribution, protective effect, impedance, polarization resistance.

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Introduction

The electrochemical impedance spectroscopy method is widely used in corrosion research [1]. The prospects of its application is conditioned by the fact that an electrode/solution boundary is studied without modification of its state and in a single experiment. Analysis of numeric values of the equivalent circuit parameters allows one to obtain information about the surface coverage by the inhibitor, its influence on diffusion of the depolarizer and charge transfer in the partial electrode reactions [2–4].

The linear polarization resistance (LPR) method, theoretically grounded by Stern, is used for estimation of the of media corrosivity and the inhibitor protective effect [5]. Its application in media containing hydrogen sulfide and carbon dioxide permits one to calculate the contributions of the corrosion product film and inhibitor to the protective effect in steel corrosion [6].

The aim of the present paper is to study the protective efficiency of new inhibitors of the “INCORGAS” series with respect to carbon steel in a NACE medium containing H₂S
and CO₂ by the electrochemical impedance spectroscopy and linear polarization resistance methods.

**Experimental**

St3 carbon steel with the following composition was used (mass %): C 0.20; Mn 0.50; Si 0.15; P 0.04; Cr 0.30; Ni 0.20; Cu 0.20; Fe balance. Corrosion tests of carbon steel samples were carried out by gravimetric method in a NACE medium (5 g/L NaCl + 0.25 g/L CH₃COOH) containing H₂S (400 mg/l) and CO₂ (1 atm) separately and in combination. The protective effect (Z, %) of an inhibitor is calculated according to the formula:

\[ Z = \left( K_0 - K_i \right) \cdot 100/K_0, \]

where \( K_0 \) and \( K_i \) are the corrosion rates in the uninhibited and inhibited solutions. The experiment duration was 24 h.

The linear polarization resistance (LPR) technique was used to achieve instant monitoring of variations in corrosion rates in the inhibited and uninhibited solutions. The “Expert-004” LPR device was developed at A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences [5].

Potentiodynamic polarization measurements were performed in a three-electrode cell (Pyrex) with divided anode and cathode spaces in solutions with free air access. The working electrode surface was polished with abrasive paper and degreased with acetone. A platinum counter electrode was used. The potentials were measured relative to an aqueous saturated silver/silver chloride electrode and were converted to the normal hydrogen scale.

Electrochemical impedance spectroscopy (EIS) measurements (Solartron 1255 FRA and 1287 potentiostat) were carried out in the frequency range of 10 kHz – 50 mHz. Processing of the results obtained was conducted using ZView 3.0 software.

The inhibitors studied, namely, INCORGAS 21T-A and INCORGAS 21T-B, are solutions of the active forms (20 mass%) in mixed organic solvents. The active form of the former is a mixture of tertiary amines and imidazolines based on polyethylene polyamine (PEPA) and naphthenic acids, while that of the latter is a mixture of imidazolines based on PEPA and C₁₀ – C₁₈ fatty acids and quaternary ammonium compounds.

**Results and discussion**

The impedance Nyquist plots represent a combination of semicircles whose diameter increases with the time of exposure of the steel electrodes in the NACE medium containing both H₂S and CO₂ (Fig. 1). This is caused by the formation of a film of corrosion products on the metal surface increasing the total resistance of the system and decreasing the corrosion rate.

The equivalent circuit shown in Fig. 2 was used as a model of steel electrode impedance at \( E_{\text{cor}} \). In this circuit, \( R_s \) is the solution resistance; \( R_1 \) and \( R_2 \) are the charge transfer resistances in the anodic and cathodic reactions, respectively; \( Z(D) \) is the generalized finite
diffusion impedance of the depolarizer; the $R_a - C_a$ chain is related to adsorption of intermediates in the anodic process; and $C_{dl}$ is the double layer capacity.

**Figure 1.** Nyquist plots of steel electrode at $E_{cor}$ in the NACE medium saturated with H$_2$S (400 mg/L). Duration of electrode exposure in the solution, h: 1 – 0.25; 2 – 2; 3 – 4; 4 – 6; 5 – 8; 6 – 24. The dots correspond to the experimental data, whereas the solid lines correspond to the impedance spectra fitted using the equivalent circuit.

**Figure 2.** Equivalent circuit for steel electrode at $E_{cor}$ in the NACE medium saturated by H$_2$S and CO$_2$.

The numerical values of the equivalent circuit elements in the solution with H$_2$S are shown in Table 1. Its analysis permits us to conclude that the charge transfer resistance in anodic and cathodic reactions increases with an increase in experiment duration. This is evidently due to the formation of an iron sulfide film on the metal surface. At that the double layer capacity nearly does not change (33–39 μF). Diffusion transfer resistance increases in time because of hindrance of cathodic depolarizer delivery through the surface sulfide film in accordance with [7, 8].
The charge transfer resistance in the anodic reaction, $R_1$, decreases with an increase in hydrogen sulfide concentration in the range of 100–1000 mg/l. This testifies that the steel corrosion rate increases and confirms the data about the stimulating action of H$_2$S. The $C_{dl}$ value nearly does not change, neither in time nor with a growth in H$_2$S concentration.

The formation of iron sulfide films on steel surface in H$_2$S-saturated media has been shown by a number of researchers [9–11]. Under our conditions, a decrease in the steel corrosion rate in H$_2$S-saturated media is observed in 24 h and in more prolonged tests (up to 30 days) [8, 12]. A similar picture is characteristic of CO$_2$ containing media, too.

Addition of the inhibitors under study to the corrosion media results in an increase in the diameter of the semicircles in the Nyquist plots. This indicates that the total resistance of the system increases and the corrosion rate decreases. The diameters of the semicircles increase with an increase in experiment duration, like in the uninhibited solutions (Fig. 3).

Addition of the inhibitors into the solution induces a decrease in the double layer capacity $C_{dl}$ because of their adsorption on the electrode surface (Fig. 4). This permits to calculate the surface coverage (Table 2) according to the formula:

$$\Theta = (C_0 - C)/(C_0 - C_1),$$

where $C_0$, $C$ and $C_1$ are the double layer capacities in the solution without an inhibitor, with an inhibitor and at maximum surface coverage with the inhibitor, respectively. The $C_1$ value is calculated from the intercept in Fig. 5.
Figure 3. Nyquist plots at $E_{cor}$ in the NACE medium saturated with CO$_2$ (1 atm) in the presence of INCORGAS 21T-A (200 mg/L). The test duration, h: 1 – 0.25; 2 – 2; 3 – 4; 4 – 6; 5 – 8; 6 – 24. (The dots correspond to the experimental data, whereas the solid lines show the data calculated from the equivalent circuit).

Figure 4. Plot of $C_{dl}$ on electrode exposure time in the solution saturated with H$_2$S (400 mg/L) in the presence of INCORGAS 21T-A, mg/L: 1 – without inhibitor, 2 – 25; 3 – 50; 4 – 100; 5 – 200.
Figure 5. Dependence of $C_{dl}$ on $1/C_{Inh}$ in the solution saturated with H$_2$S (400 mg/L) and CO$_2$ (1 atm) in the presence of INCORGAS 21T-A. Test duration: 1 – 15 min; 2 – 24 h.

Table 2. Surface coverage by the inhibitors in the NACE medium containing H$_2$S (100–1000 mg/l).

<table>
<thead>
<tr>
<th>$C$(H$_2$S), mg/L</th>
<th>Exposure time, $\tau$</th>
<th>INCORGAS 21T-A</th>
<th>INCORGAS 21T-B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>15 min</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>0.9</td>
<td>0.96</td>
</tr>
<tr>
<td>400</td>
<td>15 min</td>
<td>0.73</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>0.52</td>
<td>0.88</td>
</tr>
<tr>
<td>1000</td>
<td>15 min</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>0.82</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Analysis of the polarization curves of steel measured in the solutions containing H$_2$S and CO$_2$ shows that the inhibiting compositions essentially hinder the anodic process on steel and slightly hinder the cathodic process (Fig. 6).
Figure 6. Potentiodynamic polarization curves of carbon steel in the NACE medium (a) saturated with H₂S (400 mg/L) or (b) saturated with H₂S (400 mg/L) and CO₂ (1 atm) in combination, without an inhibitor (1) or with 200 mg/l of INCORGAS 21T-A (2) or INCORGAS 21T-B (3).

The decrease in the steel corrosion rate in the presence of an inhibitor is due to the joint effect of the corrosion surface products and the inhibitor. The contributions of the corrosion product film ($Z_{\text{film}}$) and the inhibitor ($Z_{\text{Inh}}$) to the total protective effect ($Z_{\Sigma}$) have been calculated on the basis of the method described in [6]. Measurements of the instantaneous corrosion rate by the LPR method in the inhibited and uninhibited solutions for 24 h (Fig. 7) permit the calculation of $Z_{\text{film}}$, $Z_{\Sigma}$ and $Z_{\text{Inh}}$ using the formulas:

$$Z_{\text{film}}, \% = 100\left(\frac{K_{\tau} = 0 - K_{\tau}}{K_{\tau} = 0}\right)$$

$$Z_{\Sigma}, \% = 100\left(\frac{K_{\tau} = 0 - K_{\tau, \text{Inh}}}{K_{\tau} = 0}\right)$$

$$Z_{\text{Inh}} = Z_{\Sigma} - Z_{\text{film}},$$

where $K_{\tau} = 0$, $K_{\tau}$, and $K_{\tau, \text{Inh}}$ are the corrosion rates in the initial moment and after exposure for 24 h in the uninhibited and inhibited solutions, respectively. The results of this calculation are given in Table 3 where one can see that the contribution of the corrosion product film to the total protective effect exceeds the inhibitor contribution for both inhibitor compositions under study. Analogous calculations have been previously conducted for other inhibitors [13].
As shown above, polarization measurements indicate that the anodic process is hindered in the presence of the inhibitors. The same conclusion can be made from the electrochemical impedance spectroscopy data ($R_1$ substantially increases in the presence of the
inhibitors). This fact allows one to calculate the inhibitor protective effect $Z$ using the formula:

$$Z, \% = 100(R_{1,\text{inh}} - R_{1,\text{without}})/R_{1,\text{inh}},$$


where $R_{1,\text{inh}}$ and $R_{1,\text{without}}$ are the charge transfer resistance in the anodic reaction in the presence of an inhibitor and in its absence, respectively.

Let us compare the $Z$ values of the inhibitors calculated by the EIS, weight loss measurements and LPR methods that are shown in Table 4. We can see that a qualitative correlation is observed.

**Table 4.** The $Z$ values of the inhibitors in media containing H$_2$S (400 mg/L) calculated by different methods.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$Z$, % at $C_{\text{inh}}$ (INCORGAS 21T-A), mg/L</th>
<th>$Z$, % at $C_{\text{inh}}$ (INCORGAS 21T-B), mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>$Z_{\text{EIS}}$ (τ = 15 min)</td>
<td>80</td>
<td>88</td>
</tr>
<tr>
<td>$Z_{\text{EIS}}$ (τ = 24 h)</td>
<td>66</td>
<td>81</td>
</tr>
<tr>
<td>$Z_{\text{weight}}$ (τ = 24 h)</td>
<td>69</td>
<td>68</td>
</tr>
<tr>
<td>$Z_{\text{LPR}}$ (τ = 15 min)</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>$Z_{\text{LPR}}$ (τ = 24 h)</td>
<td>70</td>
<td>79</td>
</tr>
</tbody>
</table>

The $\Theta = f(\log C_{\text{inh}})$ plot for the inhibition compositions under study has the form of curves approaching $\Theta = 1$ with a growth in the inhibitor concentration. It is characteristic of the Frumkin, Temkin, and a number of other adsorption isotherms [14]. But the additional criterion concerning the location of the minimum on the $d\log C_{\text{inh}}$ vs $\Theta$ plot at $\Theta = 0.5$ testifies that the inhibitor adsorption obeys the Frumkin adsorption isotherm [14]:

$$Bc = [\Theta/(1 - \Theta)]\exp(-2a\Theta), [14]$$

where $B$ is the constant of adsorptive equilibrium and $a$ is the attractive constant.

Calculation of the $a$ value for the INCORGAS 21T-B inhibitor adsorption in the solution containing 400 mg/l H$_2$S was carried out by the method described in [14]. The positive value of $a$ ($a = 0.79$) testifies about an attractive interaction between the adsorbate particles. Furthermore, the $B$ value and the adsorption energy were calculated.

The adsorption standard Gibbs energy was calculated according to the formula:

$$-\Delta G_{\text{ads}}^0 = RT \ln(55.5B) [14]$$

It is equal to $-24.09$ kJ/mol, testifying that physical adsorption occurs. Similar adsorption energies have been obtained for both inhibitors in other solutions under study.
Conclusions

Using the EIS method, it has been shown that inhibitor adsorption occurs on steel surface in the NACE medium containing H₂S and CO₂, both separately and in combination. The surface coverage by the inhibitors has been calculated. The inhibitor adsorption obeys the Frumkin adsorption isotherm. The standard Gibbs of adsorption energy is ca. –24 kJ/mol.

Measurements of the instantaneous corrosion rate by the LPR method permit a calculation of the contributions of the corrosion product film and inhibitor to the overall protective effect. The contribution of the inhibitors is smaller than that of the corrosion product film, but a protective efficiency of 90% or more is only reached in the presence of an inhibitor.

The Z values of the inhibitors calculated by the EIS, weight loss and LPR methods are in qualitative agreement.

References