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A STUDY ON THE CORROSION OF MILD STEEL IN A SOLUTION  
WITH ADDED ORGANIC COMPOUND

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*A study on the corrosion of mild steel in a solution with added organic compound: In the present work the inhibiting properties of an organic compound (D-5-isobutyl-mono-thiohydantoin), synthesized in laboratory conditions are investigated. The inhibitor's properties were studied on a low carbon Steel 10, using a gravimetric method and anodic polarization in 0.1 M aqueous solution of H<sub>2</sub>SO<sub>4</sub>. It was found that the organic compound acted as a mixed inhibitor of the low carbon steel's corrosion, reducing both cathodic and anodic reactions. The inhibitor efficiency was clearly pronounced only at concentrations above 10<sup>-4</sup> M and after a duration of 20 hours. The maximum value of 90% was reached at a concentration of 5.0 mol dm<sup>-3</sup>, at 45°C. The latter certainly allows to recommend D-5-isobutyl-mono-thiohydantoin for corrosion protection of low carbon steels at slightly elevated temperatures*

**Key words:** Corrosion protection: Corrosion inhibitors, Organic compounds, Gravimetric method, Anodic polarization, Steel 10

## INTRODUCTION

From the literature it is well known [1-4] that the introduction into the corrosive environment of a number of compounds alters the rate of electrochemical reactions, and sometimes their mechanism. In our previous studies [5-9] is shown the significantly better adsorption of various organic substances on low carbon steels in sulfuric acid environments. In the present work the influence of synthesized D-5-isobutyl-mono-thiohydantoin (CX1016) on the corrosion of low carbon steel in 0.1 M H<sub>2</sub>SO<sub>4</sub> is investigated and also the inhibitory effect by varying the concentration and temperature is estimated.

## EXPERIMENTAL

The inhibitory effect of CX1016 is studied on samples of Steel 10, having the following composition (0.07-0.14% C, 0.17-0.37% Si, 0.35-0.65% Mn, 0.15% Cr). Prior to all experiments the samples were subsequently mechanically and chemically polished and washed with distilled water. As a corrosive environment a 0.1 M aqueous solution of H<sub>2</sub>SO<sub>4</sub> (Merck) was used.

The synthesis of D-5-isobutyl-mono-thiohydantoin (CX1016) is carried out in laboratory conditions by classical methods, using components of the companies Fluka, Merck and Sigma-Aldrich. The structural formula of the synthesized compound is presented in Fig.1.

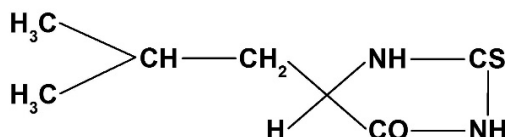


Fig. 1 Structural formula of the molecule of D-5-isobutyl-mono-thiohydantoin

The obtained compound was characterized by recording its IR-spectrum (tableted with KBr), using a spectrophotometer Perkin Elmer 1600. Furthermore, its elemental composition is determined (analyzer Carlo Erba 1106). Additionally the purity of the synthesized compound was controlled using thin-layer chromatography (TLC, Kieselgel 60, 0.2 mm, Merck), as well as its melting point.

The concentration of CX1016 in 0.1 M H<sub>2</sub>SO<sub>4</sub> was varied in the range from 10<sup>-4</sup> to 10<sup>-3</sup> mol dm<sup>-3</sup>. The experiments were conducted in a laboratory thermostatic bath at three temperatures (25°C, 35°C and 45°C). The pre-set temperature was maintained with a precision of ±1°C. For the assessment of the inhibitory effect of the synthesized organic compound two methods were used:

### 1) Weight loss method

The method measures the rate of corrosion, by immediately providing information for the amount of destroyed metal [10]:

$$k = \frac{m_0 - m}{St} \text{ (g m}^{-2} \text{ h}^{-1}\text{)},$$

where  $m_0$  and  $m$  is the mass of the samples before and after exposure to the corrosive environment, respectively,  $S$  is the surface of the sample and  $t$  is the exposition time.

To assess the inhibitor efficiency two variables were calculated:

*The protection degree (Z)*, which shows by how many percent the corrosion rate is reduced by the presence of an inhibitor:

$$Z = \frac{k_0 - k}{k_0} 100 \text{ (\%)}.$$

Here with  $k_0$  and  $k$  are denoted the metal corrosion rates in the corrosive environment with and without addition of inhibitor, respectively.

*Inhibitor activity coefficient (γ):*

$$\gamma = \frac{k_0}{k}.$$

### 2) Electrochemical method

In order to assess the inhibitor efficiency, the corrosion current density is measured ( $i_{cor}$ ), corresponding to the electrochemical corrosion rate.

By means of the measured current densities (m A cm<sup>-2</sup>) *the protection degree (Z)* can be calculated:

$$Z = \frac{i_0 - i_{cor}}{i_0} 100 \text{ (\%)}.$$

In this equation  $i_0$  and  $i_{cor}$  are the current densities of the corrosion current with and without the presence of inhibitor, respectively.

The *inhibitor activity coefficient (γ)* can be determined using the following expression:

$$\gamma = \frac{i_0}{i_{cor}}.$$

All electrochemical measurements were carried out in a three-electrode cell, using a saturated calomel electrode (SCE) as reference electrode. A Radelkis (OH-105) potentiostat, was used, connected to a PC (via NI USB-6008 controller). The surface area of the samples exposed to the corrosive environment was  $0.4 \text{ cm}^2$ . The corrosion current density and the corrosion potentials are determined by analysis of the  $i(E)$ -curves during sample polarization in the interval from  $-600 \text{ mV}$  to  $+1200 \text{ mV}$ . Prior to polarization the samples were immersed in the corrosive environment until a stationary value of the potential ( $E_{\text{eq}}$ ) was established, the times for reaching this value were also measured. All potential values are recalculated in relation to standard hydrogen electrode (SHE).

## RESULTS AND DISCUSSION

### Weight measurements

The conducted studies have shown that a fixed rate of corrosion was detected after 20 hours for  $0.1 \text{ M H}_2\text{SO}_4$ , as well as for the compositions containing the inhibitor. The results from the research on the corrosion rate are presented in Fig. 2.

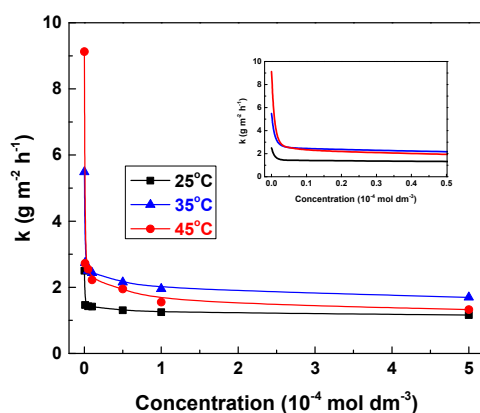


Fig. 2 Corrosion rate ( $k$ ) as a function of CX1016 concentration ( $C$ ) in  $0.1 \text{ M H}_2\text{SO}_4$  at three temperatures

It can be seen that at low inhibitor concentrations the increase in temperature leads to a significant raise of the corrosion rate ( $k$ ). With increase of the substance concentration (above  $0.5 \times 10^{-4} \text{ mol dm}^{-3}$ ), the corrosion rate's dependency on temperature slightly decreases. Upon reaching the highest concentration used ( $0.5 \times 10^{-4} \text{ mol dm}^{-3}$ ) the corrosion rate is practically independent of temperature. This indicates that the investigated substance is adsorbed well enough on the metal surface, thus preventing the dissolution of the metal substrate.

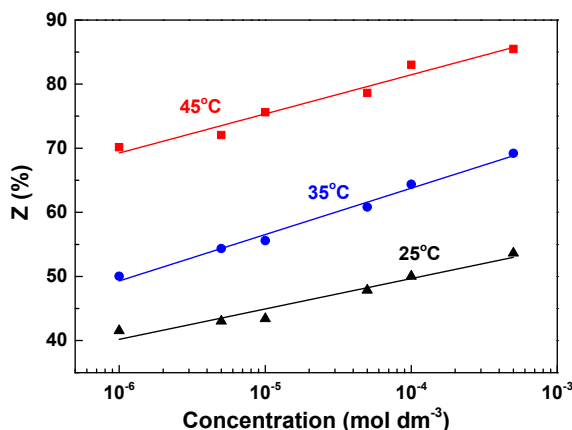


Fig. 3 Dependence of the protection degree ( $Z$ ) on the concentration of the investigated substance ( $C$ ) in  $0.1 \text{ M H}_2\text{SO}_4$  at different temperatures

The calculated values for the protection degree ( $Z$ ) confirm the fact that at concentrations above  $0.5 \times 10^{-4} \text{ mol dm}^{-3}$  the investigated inhibitor provides a good protection against corrosion even at the highest temperatures studied (Fig. 3). This result allows the synthesized organic substance to be recommended as a corrosion inhibitor of low carbon steel, designed to operate at higher temperatures.

### Electrochemical measurements

Due to the higher sensitivity of electrochemical measurements the polarization experiments were carried out in environments with different CX1016 concentrations. In Table 1 are presented the electrochemical characteristics of the investigated in solutions with different CX1016 concentrations specimens.

In the solution with the highest CX1016 concentration ( $10^{-3} \text{ M dm}^{-3}$ ) two types of experiments were carried out: without preliminary exposure and after a 24 hour exposure to the corrosive environment. The results presented in Fig. 4 indicate that the inhibitory action of CX1016 occurs after this 24 hour exposure. The polarization curves without and in the presence of the inhibitor (without prior exposure) practically coincide. This result clearly shows that the preliminary exposure of the samples in the corrosion environment allows the molecules of the inhibitor (CX1016) to be adsorbed on the metal surface, thus resulting in a decrease of the corrosion current density ( $i_{\text{cor}}$ ) by an entire order of magnitude.

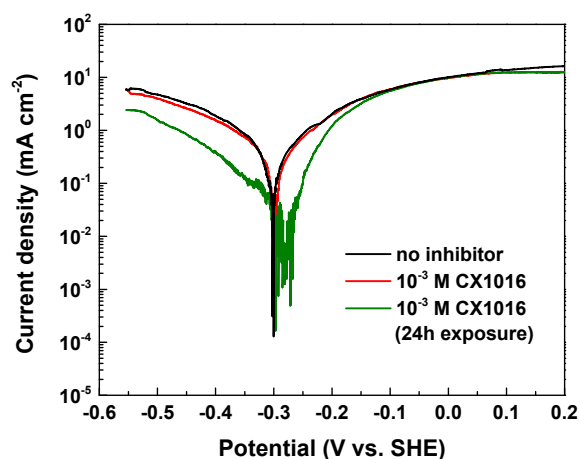


Fig. 4 Polarization curves of samples cut from Steel 10 in a 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution with and without inhibitor CX1016 ( $10^{-3} \text{ M}$ ), with no exposure and after a 24 hour exposure

Considering the above results, experiments were conducted at varying inhibitor concentrations, but with a preliminary stay of samples for 24 hours in the respective corrosion environment. The obtained polarization curves are presented in Fig. 5.

The obtained results show that with increasing inhibitor concentration, the corrosion potential shifts in a positive direction, but its value is only slightly influenced by the presence of the inhibitor and its concentration. However, the corrosion current density varies significantly. Such behavior is typical of mixed action inhibitors. At low CX1016 concentrations the steel corrosion accelerates, resulting in the shift of the equilibrium ( $E_{\text{eq}}$ ) and corrosion ( $E_{\text{cor}}$ ) potentials towards more negative values, compared to those estimated in a corrosion medium with no inhibitor.

The measured electrochemical characteristics of Steel 10 in H<sub>2</sub>SO<sub>4</sub> solution with and without the addition of inhibitor CX1016 and the efficiency of inhibitory protection are summarized in Table 1.

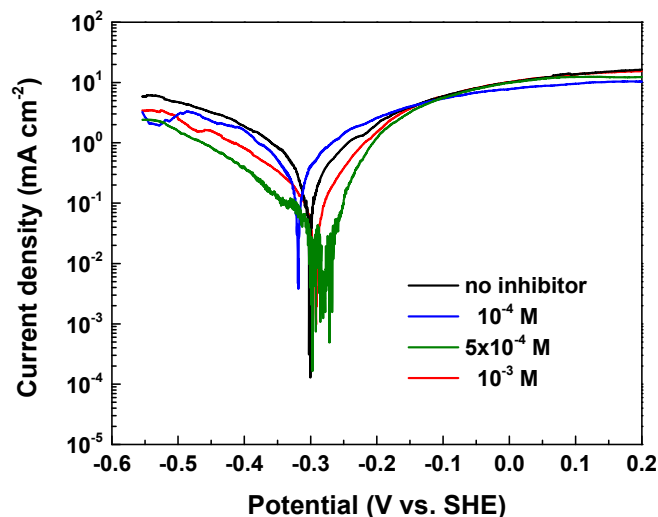


Fig. 5 Polarization curves of samples of Steel 10 in 0.1 M aqueous solutions of H<sub>2</sub>SO<sub>4</sub> with added corrosion inhibitor CX1016 with different concentrations, after a 24 hour preliminary exposure

Table 1. Electrochemical parameters

Concentration [mol dm <sup>-3</sup> ]	$E_{eq}$ [mV]	$E_{cor}$ [mV]	$i_{cor}$ [mA cm <sup>-2</sup> ]	$Z$ [%]	$\gamma$
0	-304.4	-300,3	0.25	-	-
10 <sup>-4</sup> M	-321.6	-319.1	0.5	-	-
5x10 <sup>-4</sup> M	-288.4	-300.1	0.1	64	2.5
10 <sup>-3</sup> M (no exposure)	-294.3	-276.3	0.6	-	-
10 <sup>-3</sup> M (24 h exposure)	-304.5	-280.5	0.04	84	6.25

It is worth noting that the obtained by the applied weight loss method experimental data are in good agreement with those, acquired from the performed electrochemical measurements.

## CONCLUSIONS

In laboratory conditions was synthesized and further characterized an organic compound (D-5-isobutyl-mono-thiohydantoin). This compound was then used as a corrosion inhibitor of the low-carbon Steel 10. The time for reaching a steady-state value for the corrosion rate of samples exposed to a sulfuric acid corrosive medium with and without the addition of inhibitor was experimentally determined. Further, it was found that the corrosion rate of the investigated steel decreases with increasing concentration of the organic additive. Moreover, the investigation, carried out in 0.1 M H<sub>2</sub>SO<sub>4</sub>, shows a good level of protection of the low-carbon Steel 10 at elevated temperatures of the corrosion environment. The studied substance (CX1016) exhibits inhibitory properties at concentrations above 10<sup>-4</sup> mol dm<sup>-3</sup>. The effective protection of the inhibitor occurs after a preliminary 24 hour exposure of the samples in the inhibiting solution. As an inhibitor D-5-isobutyl-mono-thiohydantoinat exhibits inhibitory action of mixed type.

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