The Inhibiting Corrosion Process of Carbon Steel in 15% Hydrochloride Solution by ETH

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Abstract: The aim of this investigation is to examine the inhibitory effect of ETH toward the corrosion of carbon steel corrosion in 15% hydrochloric acid solution. Weight loss and potentiodynamic polarization techniques were used in this work to evaluate the inhibition efficiency of the tested inhibitor. Also, Tafel method for determining of the kinetic parameters, scanning electron microscopy, all of them providing complete information about the mode of action of the inhibitors; simultaneously, has been studied, the ETH inhibiting efficiency with increasing temperature.

Keywords: ETH inhibitor, hydrochloride solution, corrosion inhibitor, inhibitor efficiency.

1. Introduction

Carbon steel is used as the constructional material in many industries because of its excellent mechanical properties and its low cost [1]. Carbon steel, the most widely used in engineering material, accounts for 85% of the annual steel production approximately worldwide [2]. Also, it is extensively used in chemical and allied industries for the manipulation of different acid, alkali and salt solutions [3]. Metals and alloys are exposed to the action of acids in many different ways and for many different reasons. One of the most commonly used acids in many industries is hydrochloric acid in some applications like: chemical cleaning and processing, acid treatment of oil wells [4]. This acid is very corrosive to most of the common metals and alloys [5]. The exposures can be severe to the properties of the carbon steel and thus leads to sudden failure of materials in service.

Corrosion is a fundamental process with an important role in economics and environmental protection, especially for metals and alloys. A number of ways such as material selection, cathodic or anodic protection, coatings and the use of corrosion inhibitors has been used to reduce corrosion of the installation industry [6,7]. The use of inhibitors is one of the most used methods for protection against corrosion, especially in acidic media [8]. Most inhibitors used in industry are primarily organic compounds which have in the molecular structure nitrogen, oxygen and sulphur atoms. Also, inhibitors containing double or triple bonds play an important role in the adsorption mechanism of these compounds onto metal surfaces [9]. The adsorption process depends on many factors such as: the nature and surface of the metal, the type of aggressive media, the structure of the inhibitor and the nature of its interaction with the metal surface [1]. Acid inhibitors are essentially used in metal finishing industries, acidizing of oil wells, cleaning of boilers and heat exchangers [10].

Stannine ETH is a commercial corrosion inhibitor. It is a blend of cationic surfactants in water to provide a

hydrochloric acid pickling inhibitor for ferrous metals [11]. This product is not recommended for use in other acids [12].

The objective of this work is to study the corrosion inhibition of carbon steel in 15% HCl solutions by ETH as corrosion inhibitors using weight loss and different electrochemical techniques.

2. Experimental

2.1. Materials

The working electrode was a cylindrical disc cut from a carbon steel sample. HCl reagent was used for the preparation of aggressive solutions. To determine the inhibitor effect of ETH on the corrosion rate of carbon steel in 15% HCl solution different concentrations of inhibitor, between 0.01 and 1%, have been used.

2.2.Methods

The cyclic voltammetry, linear polarization (Tafel polarization method) and weight loss methods were used in order to notice the inhibitive properties of ETH on the carbon steel corrosion process. The surface morphology of corrosion samples has been characterized by scanning electron microscopy (SEM) using a Quanta FEG 250 (FEI, The Netherlands) scanning electron microscope (SEM) equipped with EDAX analyzer, before and after corrosion tests.

The electrochemical studies were recorded using a SP150 BioLogic potentiostat/galvanostat, a typical glass cell consisting of the carbon steel specimen with 1 cm² exposed area as working electrode (WE), two graphite counter electrodes (CE), and a Ag/AgCl electrode as the reference electrode. All potentials were referred to the saturated Ag/AgCl reference electrode. The carbon steel electrode was abraded with different grit emery papers, cleaned in ultrasonic bath, washed with distilled water and finally dried. The electrode potential was allowed to stabilize 60 min before starting the measurements.

3. Results and Discussion

3.1. Cyclic voltammetry method

The information about how ETH can influence the corrosion process of carbon steel is pointed by its electrochemical behavior in the test solution. One of the most used method to investigate the electrochemical properties of various compounds is cyclic voltammetry. In Fig.1 (dE/dt = 5 mV s⁻¹) are shown the cyclic voltammograms recorded on Pt as working electrode, in 15% HCl solutions without and with highest concentrations (1%) of ETH used in corrosion tests. The base curve obtained in the absence of the inhibitor presents the characteristics of polarization curves drawn in hydrochloric acid solutions. On anodic branch of the voltammograms only the plateau characteristic for oxygen release, is observed.



Figure 1. Cyclic voltammograms on Pt electrode in 15% HCl in the absence/presence of ETH, scan rate 5 mV s⁻¹

In order to identify how ETH inhibitor influences the electrode processes, polarization curves were recorded separately, in cathodic domain as well as in anodic one. According to Fig. 2, the oxygen evolution reactions in 15% hydrochloric acid solution in the presence of ETH are inhibited due to adsorption on carbon steel surface of inhibitor molecules.

Also, as it is shown in Fig. 3, the hydrogen evolution reaction is not significantly inhibited by the existence of ETH molecules in corrosive test solutions.

3.2. Linear polarization method

The ETH inhibitor effect on corrosion of carbon steel was studied in 15% HCl corrosive environment by applying successive investigation methods presented above. These were applied after about 1 hour, sufficient time to install a electrode equilibrium or quasi-equilibrium state, as shown in Fig. 4.



Figure 2. Cyclic voltammograms on Pt electrode for anodic polarization in 15% HCl, in the absence/presence of ETH, scan rate 50 mV s⁻¹



Figure 3. Cyclic voltammograms on Pt electrode for anodic polarization in 15% HCl in the absence/presence of ETH, scan rate 50 mV s⁻¹



Figure 4. OCP for carbon steel electrode in 15% HCl in the absence/presence of ETH

In solutions with different concentrations of inhibitor, the OCP (open circuit potential) carbon steel electrode is shifted to more negative values, a phenomenon that can be attributed to adsorption of ETH molecules or corrosion products deposition on the electrode surface.

The temperature influence of the OCP has been studied for the case when in the test solution a 0.1% ETH was added. OCP versus time variation is shown in Fig. 5. As expected, it can be observed the OCP displacement towards more positive values, reflecting a corrosion rate increase with temperature.

The manner in which ETH can be a corrosion inhibitor for carbon steel in 15% HCl solution and its effect on corrosion rate can be estimated by various experimental procedures. The Tafel curves recorded without and with various ETH concentrations are shown comparatively in Fig. 6.

The polarization curves presented in Fig. 7 show that ETH significantly influences both processes: the cathodic process of hydrogen evolution reaction and the anodic process of dissolution/passivation of the metal. As the concentration of inhibitor is higher, the diminution of the cathodic current is more pronounced, suggesting that ETH acts by blocking the electrode surface through the adsorbed inhibitor molecules mechanism.

To investigate how temperature affects the carbon steel corrosion process in 15% HCl, Tafel curves were determined at various temperatures in the range 298 - 338 K, using different concentrations of ETH inhibitor. The results obtained are shown in Fig. 7 a-c.

The numerical values of the corrosion current density (i_{corr}) , the corrosion potential (E_{corr}) , the anodic (b_a) and the cathodic (b_c) Tafel slopes, the polarization resistance (R_p) and the corrosion rate (v_{corr}) , with various concentrations of the ETH inhibitor at various temperatures were obtained from polarization profiles by extrapolating potentiodynamic curves using BioLogics software. All obtained values are presented in Table 1.



Figure 5. OCP for carbon steel electrode in 15% HCl in the presence of 0.1% ETH at different temperatures



Figure 6. Linear polarization curves on carbon steel electrode in 15% HCl in the absence/presence of ETH, scan rate 2 mV s⁻¹

TABLE 1. Polarization parameters for carbon steel corrosion in 15% HCl in the absence/presence of ETH inhibitor

Electrolyte		Т	i _{corr}	E_{corr}	- <i>b</i> _c	b_{a}	R_p	Vcorr
		[K]	$[mA cm^{-2}]$	[V]	$[V dec^{-1}]$	$[V dec^{-1}]$	[Ω]	$[mm an^{-1}]$
SB	(HCl 15%)	298	4,23	-329,33	115,6	142,3	10,2	14,93
		308	8,97	-322,79	152,5	171,9	5,31	31,67
		318	13,47	-316,74	180,5	192,9	2,23	47,59
		298	0,32	-311,35	65,9	122,2	42,8	1,62
SB + 0.1% ETH		308	1,00	-309,86	80,7	119,5	22,6	3,54
		318	2,97	-287,87	86,7	118	8,83	10,47
		328	5,51	-261,22	89,6	117	2,65	19,45
		338	7,52	-253,6	97,2	113,8	1,51	26,56
		298	0,23	-394,97	188,1	151,1	117	0,94
SD -		308	0,38	-379,88	191,3	150,3	73,7	1,33
	30 T 1% FTH	318	0,61	-359,73	200,8	135,8	40,7	2,14
	170 L111	328	1,20	-342,89	211,6	130,4	24,8	4,25
		338	2,14	-334,61	222,8	117,4	9,18	7,57



Figure 7. Linear polarization curves on carbon steel electrode for anodic polarization in 15% HCl in the absence (a) and presence of 0.1% (b), 1% (c) ETH at different temperatures, scan rate 2 mV s⁻¹

Inspection of dates from Table 1 reveals that the corrosion rate decreases with the increasing of the inhibitor amount added in corrosive media. Also, corrosion rate increases with temperature in experimental range (298 - 338 K). When using the ETH inhibitor, it can be concluded that it impedes the corrosion by merely blocking the reaction sites on carbon steel surface interfering especially with the anodic dissolution reaction. This inhibitor causes significant changes in the anodic Tafel slopes. The influence of inhibitor addition on cathodic process is not so pronounced. This suggests that ETH behaves as an anodic-type inhibitor.

The inhibition efficiency (*IE*) and surface coverage (θ) have been calculated with equations (1) and (2). The obtained values are presented in Table 2 depending on concentration and temperature.

$$\begin{split} lE(\%) &= \left(\frac{i_{corr}^{o} - i_{corr}^{inh}}{i_{corr}^{o}}\right) \times 100 \quad (1) \\ \theta &= \frac{i_{corr}^{o} - i_{corr}^{inh}}{i_{corr}^{o}} \quad (2) \end{split}$$

where *icorr* and *icorr* are the uninhibited and inhibited corrosion current densities, respectively.

TABLE 2. The inhibition efficiency (IE) and surface coverage (θ) for carbon steel corrosion in 15% HCl, in the presence of ETH

Electrolyte	T [K]	<i>IE</i> [%]	θ
SB +	298	86.81	0.87
0.1% ETH	308	81.56	0.82
0.170 2111	318	77.95	0.78
SB	298	95.79	0.96
3D + 1% FTH	308	95.47	0.95
170 EIII	318	94.58	0.95

From the results shown in Table 2, it can be seen that by increasing the inhibitor concentration the inhibition efficiency increased. Also, ETH inhibition efficiency had almost the same high values on the entire temperature range in which have been performed experimental studies.

3.3. Weight loss method

The gravimetric measurements of carbon steel discs samples immersed in 15% HCl, in the absence and presence of different concentrations of ETH inhibitor, were investigated and determined after 240 hours of immersion, at 298 K. The weight loss of carbon steel samples decreased with the increase of ETH concentration. This means that ETH acts as an inhibitor. The corrosion rate of carbon steel (W_L) was determined using the relation (3) and the inhibition efficiency (*IE*) and surface coverage (θ) with equations (4) and (5):

$$W_{corr} = \frac{W_1 - W_2}{S \times t} \tag{3}$$

where W_1 and W_2 are the initial and final mass of the samples in mg, S is total surface area in cm² and t is the exposure time in h.

$$lE(\%) = \left(1 - \frac{W_{corr}}{W_{corr}^0}\right) \times 100$$

$$\theta = 1 - \frac{W_{corr}}{W_{corr}^0}$$
(4)

where W_{corr} and W_{corr}^{0} are the weight loss in the presence and absence of inhibitor, respectively.

TABLE 3. The inhibition efficiency and surface coverage obtained by weight loss method

ETH conc. [%]	$\frac{W_{\rm corr}}{[\rm mg~cm^{-2}h^{-1}]}$	IE [%]	θ
SB	0.039	-	-
0.01	0.011	70.93	0.71
0.1	0.006	84.58	0.85
1	0.001	95.45	0.95

The inhibition efficiency and the obtained surface coverage values using this method are comparable to those calculated on the basis of Tafel polarization curves. The data presented in Table 3 show that inhibitor efficiency reaches to appreciable values for concentrations of ETH bigger than 1% in 15% HCl solution.

3.4. Surface analysis

SEM analysis was performed to investigate the surface morphology of the carbon steel after immersion in 15% HCl, in the absence (Fig.8) and presence of 1% ETH (Fig.9) for 240 h, at 298K. Damaged surface was observed in the absence of inhibitor due to high dissolution rate of iron in test solution.

The EDX spectrum of the powder is presented in Fig. 10 and confirms the chemical composition of samples, the identified elements being carbon, iron, oxygen and chlorine. The presence of chlorine is only visible in sample without inhibitor introduced in corrosive media.

The sample surface was protected by adsorption of inhibitor molecules that form a protective film, or due to complex compounds between iron and ETH molecules. The comparing of micrographs recorded at the same magnification for both samples suggests that the corrosion process of carbon steel is inhibited. This is confirmed by the weight loss measurement, cyclic voltammetry and polarization results.





Figure 8. SEM images obtained on carbon steel after 10 days of immersion in HCl 15%, at different magnification





Figure 9. SEM images obtained on carbon steel after 10 days of immersion in HCl 15% with 1% ETH



Figure 10. EDX on carbon steel samples after 10 days of immersion in HCl 15% without (a) and with 1% ETH (b)

4. Conclusions

Stannine ETH inhibition efficiency has been studied by two different methods: weight loss and linear polarization, both giving comparable values. This compound exhibited excellent inhibition performance as an especially anodic-type inhibitor for carbon steel in hydrochloride solutions, at concentrations bigger than 1%.

ETH acts as an efficient corrosion inhibitors in 15% HCl solution and it exhibits a maximum inhibition efficiency of 95%. SEM micrographs showed that the inhibitor molecules form a good protective film on the carbon steel surface.

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