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Research Article

A Corrosion Study: Use of Thionine dye having structurally metachromatic influence

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ABSTRACT

In the present study, it was examined the inhibition performance of Thionine, which has metachromatic properties and is generally used as a vital dye for different staining of nucleus and cytoplasm, on mild steel in acidic medium as a different application area which is not existed in the literature. In order to understand how Thionine interacts with the mild steel surface, different types of adsorption isotherms were plotted and it was seen obeyed the Langmuir isotherm. The test results revealed that as the inhibitor concentration increased at each temperature, the corrosion current density (i_{corr}) values diminished and accordingly, the inhibition efficiencies ($\eta\%$) increased slightly. The results indicated that the Thionine molecules continued to be adsorbed onto the metal surface to some extent, even when elevated to high temperatures. Thermodynamic adsorption parameters revealed a strong and chemical interaction between Thionine and mild steel. It was determined that the Thionine acted as a mixed-type inhibitor on the mild steel surface. Finally, field emission scanning electron (FESEM) and atomic force microscopy (AFM) analyses were performed to determine the surface characteristics.

Keywords: Thionine, adsorption, acidic corrosion, FESEM.

Bir korozyon çalışması: Yapısal olarak metakromatik etkiye sahip olan tiyonin boyasının kullanılması

ÖZ

Bu çalışmada, genellikle nükleus ve sitoplazmanın farklı şekillerde boyanması için metakromatik özelliğe sahip ve hayati bir boya olarak kullanılan Tiyonin'in, farklı bir kullanım alanı olarak literatürde mevcut olmayan asidik ortamdaki yumuşak çelik üzerine inhibisyon performansı incelendi. Yumuşak çelik yüzeyi ile Tiyonin'in ne şekilde etkileştiğini anlamak için farklı tür adsorpsiyon izotermleri çizildi ve Langmuir izotermine uyduğu görüldü. Deney sonuçları, her sıcaklıkta inhibitör derişimi arttıkça korozyon akım yoğunluğu (i_{corr}) değerlerinin düştüğünü ve buna bağlı olarak da inhibisyon etkinliği değerlerinin ($\%\ \eta$) de bir miktar yükseldiğini göstermiştir. Sonuçlar, Tiyonin moleküllerinin yüksek sıcaklıklara çıkıldığında bile, bir dereceye kadar metal yüzeyine adsorplanmaya devam ettiğini göstermiştir. Termodinamik adsorpsiyon parametreleri, Tiyonin ile yumuşak çelik arasında güçlü ve kimyasal bir etkileşimin olduğunu ortaya çıkarmıştır. Tiyoninin, yumuşak çelik yüzeyinde karma tip bir inhibitör görevi gördüğü tespit edildi. Son olarak, yüzey karakteristiklerinin belirlenmesi için alan emisyon taramalı elektron mikroskobu (FESEM) ve atomik kuvvet mikroskobu (AFM) analizleri yapıldı.

Anahtar Kelimeler: Tiyonin, adsorpsiyon, asidik korozyon, FESEM.

1. INTRODUCTION

The first thing that comes to mind when matter is mentioned is metals, polymers and ceramics. Metals can be classified as ferrous and non-ferrous. In this study, ferrous material is used as a priority. Ferrous materials are both steel and cast iron.[1] Mild steel and its alloys are mainly made of iron and carbon, and certain properties can be achieved by adding further alloying elements.[2] There are more than 3500 diverse steel grades covering unique physical, chemical and environmental characteristics, according to the World Steel Association.[3] Mild steel is one of the most preferred materials in terms of usage and processability in industry. Mild steels have advantages compared to other materials due to the fact that they are easily accessible and not expensive. In addition to being preferred in most applications, mild steels are also highly sensitive to aggressive environments such as acidic media. The primary purpose of reducing sensitivity in acidic environments is to thoroughly isolate the metal from the medium.[4,5]

Among the most commonly used metal isolation methods, there is the application of organic inhibitors. Organic inhibitors exhibit high corrosion resistance due to their non-toxicity, having a large molecular structure and their including of heteroatoms with unpaired electron pairs such as nitrogen, sulphur and oxygen.[6,7] These unpaired electrons facilitate the adsorption of inhibitors to the metal surface. When the inhibitors are added generally an acidic solution, they prevent from the dissolution of the metal. Dyes are also used as corrosion inhibitors such as compounds of organic origin. Dye solutions are also used as corrosion inhibitors in the corrosion process and their discharges to the environment are prevented.[8,9] In one of recent studies done, the potential of being a good corrosion inhibitor for metals in acidic solutions as an additional usage field of dyes has been investigated.[10–14]

Thionine has been often utilized as a sensitizer in photographic processes, laser components and chemotherapy. Thionine is also used to stain the nucleus and cytoplasm in different ways and is called as a vital dye. Thionine chloride is a powerful metachromatic dye greatly utilized for biological staining[15] is acknowledged as an electron-shuttling for bioelectricity production.[16] The term of metachromatic was expressed to portray the colour alterations passed through certain substances when the temperature is elevated by Ackroyd in 1876.[17] The first application in the biological circumstances was realized in the mast cell staining by Ehrlich in 1879.[18] Metachromatic dyes are divided into two types as cationic and anionic. Thionine chloride is among the most widely used cationic metachromatic dye classes. Anionic ones are used less than cationic dyes.[19] Thionine related molecules chemically possess abilities to intervene electron transport. Thionine chloride (*3,7-diaminophenothiazin-5-ium chloride*), shown in Figure 1, is a type of phenothiazine dye that has been thoroughly explored due to their quirky physicochemical properties. A wide range of studies and applications area of Thionine have been encountered,[15,20,21] but no study has been observed which will report the influence of inhibitor performance for mild steel in 1.0 M HCl solution. Therefore, this paper is an original study. This current study was designed to survey a dye whether will act as inhibitor that does not contain azo group in its structure and has a metachromatic effect. In other words,

Thionine's inhibitor performance was evaluated with potentiodynamic polarization measurement technique at a temperature range of 298 K–328 K in hydrochloride acid solution and a different perspective was provided to be used as an alternative commercial inhibitor in industrial applications. The effect of temperature on the adsorption behaviour of the Thionine molecule was also clarified by some thermodynamic parameters such as adsorption free energy (ΔG°_{ads}), adsorption equilibrium constant (K_{ads}), corrosion activation energy (E_a^*). In the last step of the study, inhibitor behaviour on metal surface was investigated by FESEM and AFM techniques.

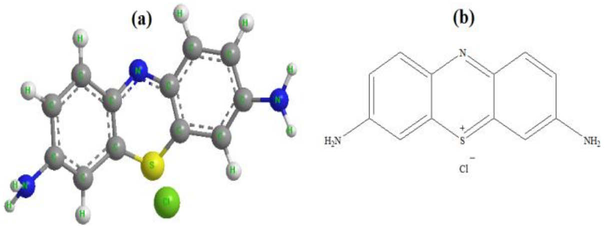

Figure 1. Three-dimensional ball & stick model (a) and chemical structure (b) of Thionine chloride inhibitor.

2. EXPERIMENTAL DETAILS

Corrosion tests were conducted on the surface of the mild steel whose chemical composition was 0.01040 Mo; 0.01900 S; 0.00222 Nb; 0.21700 Cu; 0.40900 Mn; 0.00198 Co; 0.07890 Ni; 0.08400 C; 0.01620 Sn; % 0.01100 P; 0.06030 Cr; 0.10200 Si; 0.01100 V and the rest was Fe (wt.%). The surface area of the mild steel electrode is 0.5024 cm^2. The surface areas of the working electrodes that will come into contact with the solution were left exposed, the entire surface was first covered with epoxy and then with polyester. Prior to all electrochemical measurements, the mild mild steel electrodes were sanded with 600 and 1000 grids of emery paper respectively, polished with alumina solution, and then cleaned in acetone and distilled water to immerse in test solutions. Experimental measurements were carried out using the classical three electrode technique by the CHI 660B model electrochemical analyser. Mild steel, whose chemical composition is given above, has been used as working electrode. Platinum (Pt), which is used as counter electrode in the study, was cut 1 x 1 cm in size from the pure platinum plate and after it was attached with Pt-wire, only the Pt plate was left out and connected with a copper wire in a glass tube. Finally, Ag/AgCl was used as the reference electrode for potentiodynamic polarization measurements. All electrochemical measurements were performed in the representative experimental set-up (see Figure 2).

The system was allowed to equilibrate for 1 hour before each measurement and then the test measurements were carried out. The electrochemical behaviour of mild steel was evaluated by Tafel extrapolation method for five different concentrations (1.0 x 10^{-5} M – 1.0 x 10^{-3} M) of 1.0 M HCl solution in the 298 K – 328 K temperature range. Corrosion current density (i_{corr}) values were determined by plotting the semi-logarithmic current-potential curves against the potential (V) after measuring the open circuit potential (E_{corr}) of the mild steel with the reference electrode (Ag/AgCl). For this purpose, at the scanning rate of 1 mV/s, first to the cathodic direction (-350 mV) and then to the anodic direction (+350 mV) were scanned.

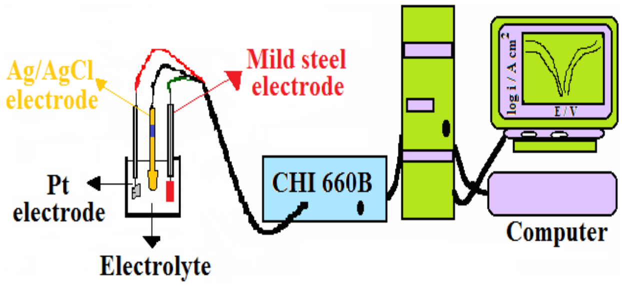

Figure 2. Representative experimental set-up obtained of potentiodynamic polarization spectra.

To obtain information about surface morphologies, surface roughness and surface elasticities of mild steel electrodes immersed into 1.0 M HCl media without and with 1.0 x 10^{-3} M Thionine for 120 h, the detailed surface images with FESEM (ZEISS GeminiSEM 500 model with computer controlled) and AFM (Veeco Multimode 8 Nanoscope 3D model) analyses were examined.

3. RESULTS AND DISCUSSION

3.1. Evaluation of potentiodynamic polarization tests

Potentiodynamic polarization curves in the absence and the presence of the Thionine with various concentrations (1.0 x 10^{-5} M – 1.0 x 10^{-3} M) for mild steel electrode are given in Figure 3. These curves are only for 298 K and 328 K. In addition, potentiodynamic polarization parameters obtained from these curves are given in Table 1.

The values of η% were calculated from the potentiodynamic polarization curves according to the following equation.[22]

$$\eta\ (\%) = \left(\frac{i_{corr} - i'_{corr}}{i_{corr}}\right) \times 100 \qquad (1)$$

Where i_{corr} and i'_{corr} are uninhibited and inhibited corrosion current density values, respectively. The E_{corr} values were measured as -0.475 V and -0.484 V in 1.0 M HCl solution and i_{corr} values were calculated as 265 and 2536 µA cm^{-2} at 298 K and 328 K, respectively (see Figure 3, Table 1). As the inhibitor was added to the anodic potentials except for a few values and ranged from -0.460 V to -0.479 V. The values of i_{corr} in the acidic medium, the corrosion potentials shifted to more inhibited media decreased for each temperature compared to the values in the uninhibited solution.

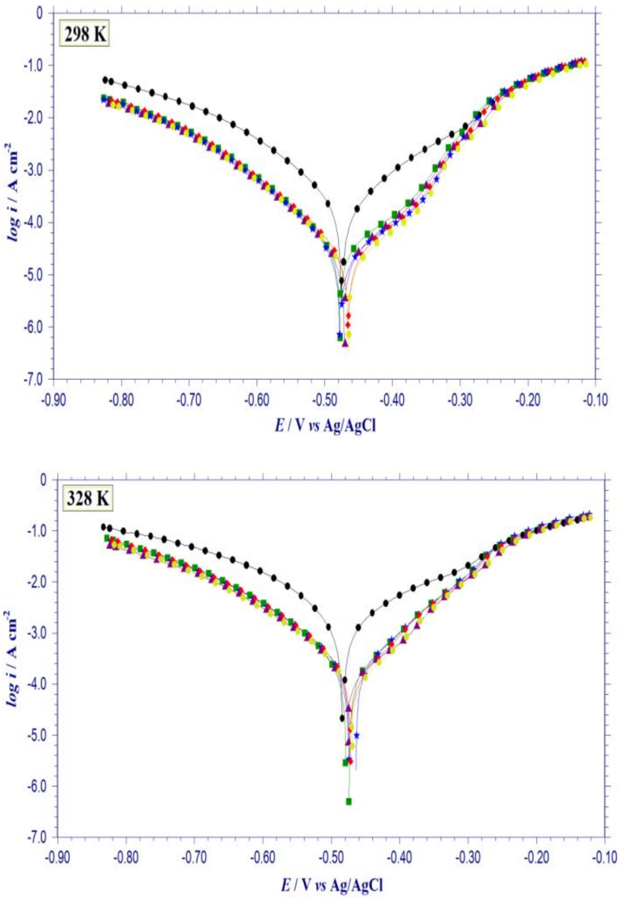

Figure 3. Potentiodynamic polarization curves obtained at 298 K and 328 K temperatures in 1.0 M HCl solutions with and without Thionine.

This reveals that the anodic dissolution of the mild steel and the cathodic reduction of the hydrogen ions are inhibited. For the same temperature in all solutions, the corrosion current density values decreased as the inhibitor concentration increased, and accordingly the inhibition efficiency values rose. The i_{corr} values boosted as temperature increased in both inhibited and uninhibited solutions. In other words, as the ionic conductivity enhances when the temperature is increased from 298 to 328 K, the current density values have boosted in both uninhibited and inhibited media. While the cathodic Tafel constant (-βc) values ranged from 108 mV dec^{-1} to 157 mV dec^{-1} in uninhibited solutions, they ranged from 91 mV dec^{-1} to 116 mV dec^{-1} in inhibited solutions. The fact that the calculated cathodic Tafel constants do not alter significantly except for a few

Table 1. Potentiodynamic polarization parameters of mild steel in 1.0 M HCl solution containing various concentrations of Thionine at four different temperatures

Thionine Concentration (M)	Temperature (K)	E_{corr} (V/ Ag/AgCl)	$-\beta_c$ (mV dec^{-1})	i_{corr} (μA cm^{-2})	η (%)
Blank	298	-0.475	108	265	-
	308	-0.487	109	440	-
	318	-0.488	128	1296	-
	328	-0.484	157	2536	-
1.0 x 10^{-5}	298	-0.477	91	34	87.2
	308	-0.470	100	70	84.1
	318	-0.478	107	175	86.5
	328	-0.479	110	296	88.3
5.0 x 10^{-5}	298	-0.478	93	32	87.9
	308	-0.463	102	61	86.1
	318	-0.467	106	150	88.4
	328	-0.474	114	286	88.7
1.0 x 10^{-4}	298	-0.466	94	28	89.4
	308	-0.463	98	51	88.4
	318	-0.465	110	130	90.0
	328	-0.472	110	260	89.7
5.0 x 10^{-4}	298	-0.470	93	24	90.9
	308	-0.474	99	49	88.9
	318	-0.460	106	109	91.6
	328	-0.475	114	241	90.5
1.0 x 10^{-3}	298	-0.464	92	21	92.1
	308	-0.465	96	47	89.3
	318	-0.466	106	106	91.8
	328	-0.469	116	216	91.5

values in media with and without the Thionine indicates that the hydrogen formation mechanism is neither affected by the addition of inhibitor nor by the temperature.

As seen from Figure 3, the increase in the concentration of the Thionine in the acidic medium reduced both the anodic and cathodic current density and did not change the corrosion potential much. Therefore, it can be said that the Thionine molecule acts as a mixed-type inhibitor in the 1.0 M HCl medium.[23,24] The addition of the Thionine to the medium decreased the current value to approximately -0.25 V in the anodic part. After this potential, it was no matter how much the potential was increased in all the concentrations of the Thionine, and therefore it did not change that of the solution obtained without the inhibitor. This can be explained by desorption of the Thionine molecules adsorbed to the electrode surface.[25]

Furthermore, the cathodic polarization curves are parallel (Figure 3), indicating that no change has occurred with the addition of the Thionine molecule in the hydrogen formation mechanism and that the reduction of the hydrogen ions is carried out by means of a charge transfer mechanism at all temperatures.[26]

As can be seen from Table 1, slight changes in the inhibitor efficiency values with the rise of the temperature drawn attention to the stronger adsorption (chemisorption) of the Thionine molecule on the mild steel surface. This result can be interpreted as the fact that adsorption of the Thionine molecules and the corrosion products formed together give the inhibition of the mild steel surface together.

3.2. Evaluation of adsorption isotherm and inhibition mechanism

Considering that the molecular adsorption at the mild steel/solution interface is mainly depended on a mechanism in the form of corrosion inhibition, the relationship between the metal surface and the inhibitor has been identified by different adsorption isotherms for the Thionine. It has been determined that obey to which type isotherm of the adsorption. Five different isotherms such as Langmuir, Flory-Huggins, Temkin, Frumkin and Freundlich were tested for the adsorption of the Thionine by using surface coverage fraction (θ) values obtained from the potentiodynamic polarization measurements.

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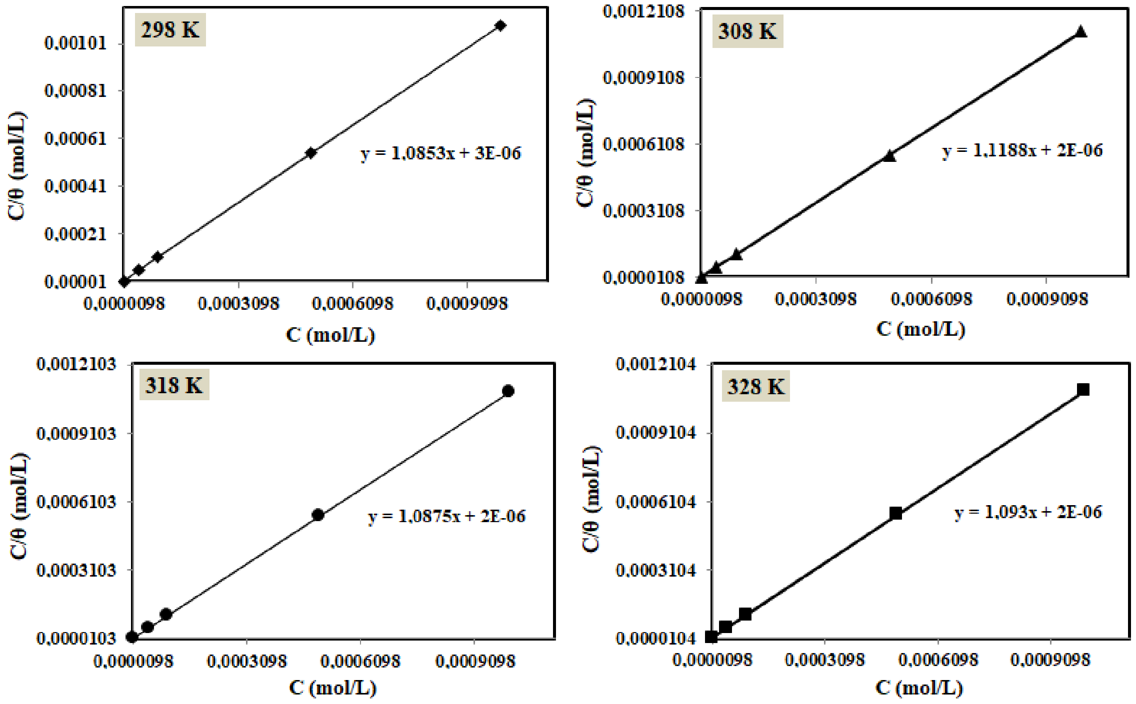

Figure 4. Langmuir adsorption isotherm curves obtained at different temperatures of Thionine inhibitor in 1.0 M HCl solution.

Among these, the best regression constant (R^2) value was obtained by the Langmuir adsorption isotherm presented in Equations (2)[27] and (3).[28]

$$\frac{C}{\theta}=\frac{1}{K}+C \tag{2}$$

Where C is the Thionine concentration and K is the adsorption equilibrium constant of the adsorption process.

$$K_{ads}=\frac{1}{55.5}\exp\left(-\frac{\Delta G^{o}{}_{ads}}{RT}\right) \tag{3}$$

Where 55.5 is the molar concentration of water, R is the universal gase constant, and T is absolute temperature (in Kelvin). The plots of the Langmuir adsorption isotherms in the 298 K-328 K ranges for the five different concentrations of the Thionine are given in Figure 4, and the thermodynamic parameters such as (K_{ads}) and ($\Delta G^{\circ}{}_{ads}$) calculated from these isotherms are submitted in Table 2.

The values of adsorption free energy not higher than -20 kJ mol^{-1} are generally noticed in case of physical adsorption mechanism, where the interacting forces are completely electrostatic (weak) interactions. $\Delta G^{\circ}{}_{ads}$ values, more negative than -40 kJ mol^{-1}, are characteristic for chemical adsorption mechanism.

Table 2. Thermodynamic parameters of Thionine calculated from Langmuir adsorption isotherms

Temperature (K)	K	$\Delta G^{\circ}{}_{ads}$ (kJ mol^{-1})
298	333333.3	-41.46
308	500000.0	-42.46
318	500000.0	-42.46
328	500000.0	-42.46

This mechanism is constituted of chemical bonds between unpaired π-orbitals in the nitrogen, sulphur atoms, and π-electrons in the aromatic rings and unoccupied d-orbitals of the Fe metal.[29,30] Negative $\Delta G^{\circ}{}_{ads}$ values at all temperatures clarify that adsorption is spontaneous. Since all $\Delta G^{\circ}{}_{ads}$ values calculated according to Eq. (3) are more negative than -40 kJ mol^{-1} (see Table 2), it can be said that the adsorption of the Thionine is both spontaneous and chemical adsorption.[31,32]

As a result, it can be concluded that the calculated K_{ads} values are too large and $\Delta G^{\circ}{}_{ads}$ values get negative values than -40 kJ mol^{-1}, and that they show inhibitor influence with the interactions that perform the charge transfer to make coordinated bonding from the Thionine molecule to the mild steel surface. This is also a clear indication that the layer formed on the mild steel surface is stable.

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3.3. Evaluation of activation energy with Arrhenius equation

In order to examine the preventative effect of the Thionine on the corrosion of mild steel with uninhibited and inhibited solutions at each temperature, the Arrhenius equation in Eq. (4) was utilized.

$$\ln(i_{corr}) = \ln A - \frac{E_a}{RT} \tag{4}$$

Where, A is the pre-exponential factor, E_a is activation energy, i_{corr} is corrosion rate, and R is the gas constant. E_a values were calculated from slope of the plot of ln (i_{corr}) against 1/T (see Figure 5) and the obtained values are shown in Table 3. The E_a^* value was found as 63.71 kJ mol^{-1} in the uninhibited medium and it was lower in the Thionine containing medium than in the uninhibited medium (Table 3).

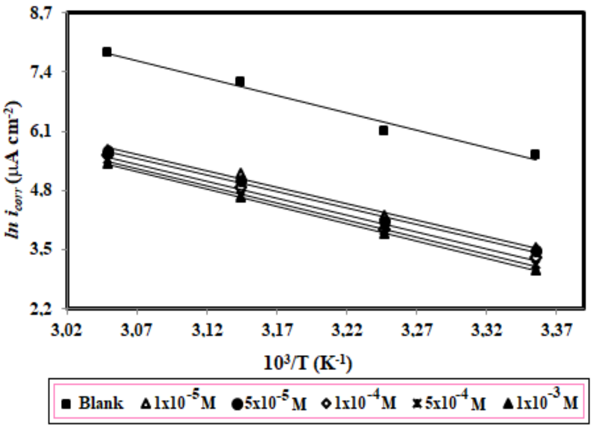

Figure 5. Arrhenius plots obtained in uninhibited and inhibited media.

Accordingly, the activation energy values obtained due to the dissolution of the metal in the solution containing the Thionine is lower than the uninhibited solution, it can be interpreted that the inhibitor molecules have protective effect on the surface with the corrosion products as a result of the dissolution of the metal and as chemically adsorbed to the metal surface with increasing temperature and forming a protective film on the surface.

According to literature findings, low or unchanged E_a^* values in inhibited solutions compared to the acidic medium indicate the chemical adsorption, otherwise physical adsorption.[33]

3.4. Evaluation of surface characteristics of mild steel electrodes by FESEM and AFM analyses

Surface characteristics of mild steel electrodes have been identified by using FESEM and AFM analyses for 120 h. Figure 6 reveals both the FESEM and AFM images of uninhibited mild steel surfaces. Both images clearly spill that the surfaces in blank solution are vigorously disrupted.

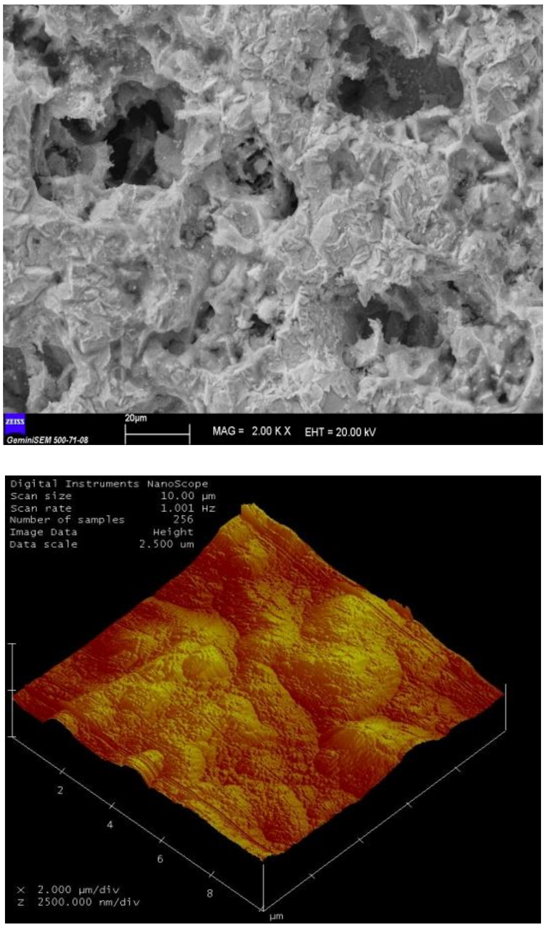

Figure 6. FESEM and AFM images of mild steel electrode immersed in 1.0 M HCl solution for 120 h.

The most important feature that makes FESEM superior to SEM is that it has very high resolution. In both images of the blank solution, large dark spots are monitored in pit appearance. In this case, the electrode immersed in the blank solution is clearly oxidized and the surface is deteriorated. The AFM image of the mild steel in Figure 6 was highly affected by the corrosive solution and turned into a rough surface with large cavities. The average roughness (R_a) value of the electrode surface in the blank solution was measured as about 198 nm.

Referring to Figure 7, when an optimum concentration (1.0 x 10^{-3} M) of the Thionine was added to the medium, the cavities in the blank solution began to decrease and close.

As clearly seen from Figure 7, the surface has a smoother and straighter appearance.

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Table 3. E_a^* values calculated in uninhibited and inhibited solutions

Thionine Concentration (M)	**Blank**	**1.0×10^{-5}**	**5.0×10^{-5}**	**1.0×10^{-4}**	**5.0×10^{-4}**	**1.0×10^{-3}**
E_a^* (kJ mol^{-1})	63.71	60.26	60.67	61.84	62.65	63.44

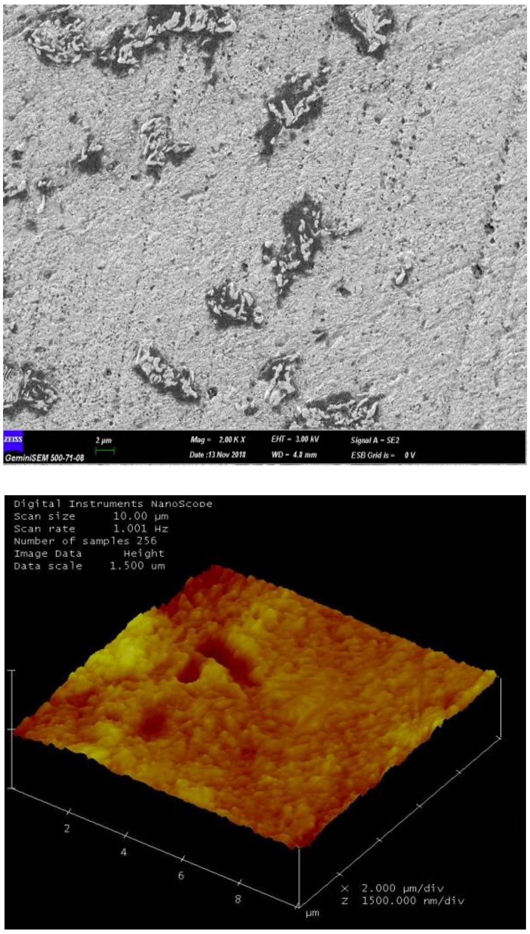

Figure 7. FESEM and AFM images of mild steel electrode immersed in 1.0 M HCl solution containing 1.0 x 10^{-3} M for 120 h.

This may be interpreted to show the protective effect by covering the mild steel surface just like a blanket due to the structure of the Thionine molecules. It is shown that a good preventative film layer on metal surface and also verifies the high inhibiton performance. The average surface roughness value of the mild steel with 1.0 x 10^{-3} M the Thionine added the medium was determined to be approximately 39 nm (Figure 7). When the Thionine was added to the acidic medium, the R_a value was very small. This is another proof that the surface is smoother in the inhibited medium.

4. CONCLUSIONS

In the present study, in order to determine the effect of temperature on the corrosion behavior of the mild steel in the hydrochloric acid medium of the Thionine, the following results are summarized by electrochemical measurements:

- Thionine, which does not contain azo group in its structure and has a metachromatic effect, has been designed to be used as a commercial inhibitor at different temperatures against the corrosion of mild steel in the hydrochloric acid solution and as a result showed a high inhibitory performance.

- Electrochemical behavior of mild steel by potentiodynamic polarization (Tafel extrapolation); semi-logarithmic current-potential plots were investigated in four different temperatures in uninhibited and inhibited media. The Thionine molecule has behaved as a mixed-type inhibitor in this medium, since the increase in Thionine concentration in the acidic medium decreases both anodic and cathodic current density.

- It was determined by the surface coverage fraction values obtained from the potentiodynamic polarization measurements that the Thionine molecule was adsorbed on the mild steel surface according to the Langmuir isotherm.

- It is evidence that the Thionine molecules are chemically adsorbed onto the mild steel surface, as the activation energy value determined in the uninhibited medium is greater than the solutions containing the Thionine molecule.

- The ΔG°_{ads} values calculated at all temperatures were more negative than -40 kJ mol^{-1}, which confirmed that the Thionine molecule was adsorbed spontaneously and effectively to the mild steel surface.

- FESEM and AFM analyses verify that mild steel still has a smooth surface after immersed for 120 h in 1.0 M HCl including Thionine in comparison with blank

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solution. The lower R_a value in the inhibitor-containing medium than in the uninhibited one may be put forward as a proof that the Thionine dye is very well protected by the mild steel surface.

- In the light of these experimental results, Thionine is suitable for use as an inhibitor in mild steel in the hydrochloric acid solution.

Conflict of interest

Author declares that there is no a conflict of interest with any person, institute, company, etc.

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