



Comparative Study of Different Organic Molecules as an Anti-Corrosion for Mild Steel in Kerosene

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KEY WORDS

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ABSTRACT

The investigation on the efficiency of three organic derivatives was done as inhibitors for carbon steel using electrochemical methods at four temperatures (303, 313, 323, and 333 K) and 100 ppm. The results showed that these prepared compounds gave good efficiencies at experimental conditions by adsorption process and they act as mixed-type inhibitor, the data of corrosion were measured and debated. Using SEM, the inhibited surface of specimens was characterized. In addition, for display the interaction between these compounds and the metallic surface, the Fourier transform infrared spectra was used. In addition, the activity of antibacterial of the inhibitors against some types of bacteria was tested.

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1. Introduction

Corrosion is an economic problem for most industrialized countries. It affects all sectors of production, transportation and processing of many commercial equipment and products [1]. In oil production and chemical industry, this is amplified by highly corrosive materials and environmental conditions that are often handled [2]. One of the most practical ways to protect against the dissolution of metals by corrosion is the use of appropriate inhibitors [3]. The Heterocyclic derivatives are compounds have different numbers of a heteroatom in their cyclic structures like nitrogen, oxygen and Sulphur...etc. Among these compounds are triazole, thiadiazol and oxadiazole derivatives [4,5]. These derivatives have great importance in many application fields and they showed different biological activities such as antiviral, anticonvulsant, antibacterial, antifungal, anticancer activities, anti-inflammatory [6-8]. Many researchers highlighted using green and eco-friendly inhibitors to protect steel in different applications [9-16]. The present work aims at a comparative study of three derivatives as corrosion inhibitors with concentration of

100 ppm at four temperatures (303, 313, 323, and 333 K) for carbon steel in kerosene environment in addition to test the antibacterial activity of these inhibitors.

2. Experimental Part

I. Chemicals and materials

Mild steel and kerosene, which used in this study, were supplied from Al-Dura Refinery. The chemical composition of the samples was analyzed by an optical emission spectrometer and the results were as follows: %C (0.1310), %Si (0.3670), %Mn (0.7220), %Cr (0.0132), %Ni (0.0233), %Al (0.0363), %Cu (0.0391), and %Fe (residual). The thickness of the samples were reduced from 6-8 mm to 3-3.2 mm by grinding machine and were cut to square specimens (2×2 cm) using cutting tool (Wire Cut) in the University of Technology / Training. The samples were prepared by grinding and polishing using silicon carbide paper (400, 600, 800, 1000, and 1200 grit) with alumina suspension ($1\mu\text{m}$) to achieve a smooth surface. They were degreased by acetone and washed by water then dried, after that, put in plastic containers to be ready for electrochemical experiments. The solution was prepared by NACE 1D196 standard procedure [17, 18], which consists of several salts: 1.0304g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 2.2386g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and 0.0532g NaCl (Baker, AR grade) with purity 98%, 97%, and 99%, respectively in 0.5 liters of distilled water and 0.125 liters of kerosene to achieve the ratio 8:2. Nitrogen gas with high purity was used for 30 minutes to re-aerated the solution and then purged with CO_2 gas for 15 minutes (controlled pressure is 0.70 Kg.cm^{-2}). Three heterocyclic derivatives were prepared and characterized according to the References [19-21]. These derivatives include 3,5-di(4-hydroxyphenyl)-4-amino-1,2,4-triazol (HAT), 4-[3-(4-methylphenyl)-1,2,4-oxadiazol-5-yl]-phenol (MOP), and 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenol (TTP). 100 ppm of each compound was dissolved in ethanol, and then added to corrosive environment. Chemical structure of these derivatives is shown in Figure 1.

II. Polarization experiments

Potentiostat / galvanostat (WINKINK M Lab 200) was utilized for polarization test in this study with system of three electrode: pure platinum (auxiliary), saturated calomel (reference electrode) and mild steel (working electrode). The emulsion solution of kerosene and salts was prepared by a speedy mixing process using a mechanical stirrer. The specimens were immersed in corrosive solution (with or without inhibitor) and all experiments (303-333 K) were performed. Tafel curves were registered at scan rate of 1 mA.s^{-1} and current was changed automatically from -15 to $+15 \text{ mA}$ to record corrosion of potential, corrosion current and Tafel slopes (β_c and β_a).

III. Surface inspections

Steel specimens were tested before and after corrosion (absence and presence of inhibitors) by SEM at magnification of 1.00kx using TESCAN VEGA3, the topography of surface is measuring using energetic of electron beams because the shorter wavelength of electrons allows image magnifications higher than conventional light microscopy where react electrons with atoms to make signals that contain information about the samples surface topography. FT-IR analyses are useful to discuss the activity of inhibitors and characterization the chemical for organic compounds was selected in powder and film. Fourier transform infrared of the films formed on the steel surface was recorded by using ATR technique by FT-IR-8400 Shimadzu.

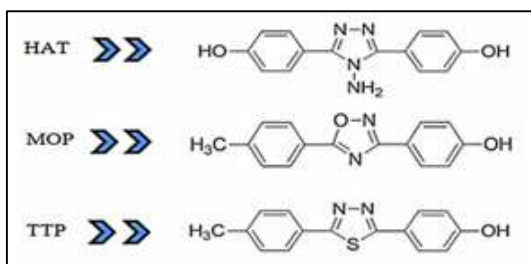


Figure 1: Chemical structure of the prepared compounds

IV. Biological activity

In this work, antibacterial efficiency was studied by agar diffusion method [22] for explain the activity of microbial of the inhibitors on some gram (+Ve) and gram (-Ve) bacteria as *Pseudomonas aeruginosa* and *Acinetobacter bommanil* (-Ve), *Staphylococcus aureus* and *Streptococcus spp* (+Ve), which contribute to rising the corrosion rate of steel in kerosene medium [23]. 50 μL of each inhibitor (100 ppm) in dimethyl sulfoxide (DMSO) was used.

3. Results and Discussion

I. Potentiodynamic measurements

polarization curves of steel specimens in overall solution (kerosene and brine) at the selected temperatures (303, 313, 323, and 333 K) was shown in Figure 2, which was used to generate Fe^{2+} at anodic site and evolution H^+ at cathodic site. While Tafel polarization curves in the presence 100 ppm of three derivatives (HAT, MOP, and TTP) at the selected temperatures was illustrated in Figure 3. The polarization results of steel specimens in kerosene solution with and without of the three compounds was elucidated in Table 1, where the values of E_{corr} are shifted either more positive or more negative that indicated these compounds behaved as a mixed-type inhibitor, i.e., these compounds inhibit or delay the reactions occurring at the cathode (reduction of hydrogen) and prevent further oxidation (dissolution of the iron) at anode. Also, this behavior is confirmed through the decreasing in the Tafel slopes of the cathodic and anodic regions (β_c and β_a , respectively). From Table 1, it was noted that the values of i_{corr} and C_R values have decreased and it was calculated from the

Eq. 1:

$$C_R (\text{mpy}) = 0.13 \times i_{\text{corr}} \times \left(\frac{e}{\rho}\right) \quad (1)$$

Where C_R : rate of corrosion, e : steel equivalent weight and ρ : steel density. The coverage areas by the inhibitor can occur through the formation of the Fe^{2+} -inhibitor complex. The values of IE% were studied according to Eq. 2:

$$\text{IE}\% = \left[1 - \frac{i_{\text{corr}}(\text{inhibited})}{i_{\text{corr}}(\text{uninhibited})} \right] \times 100 \quad (2)$$

Where IE%: the inhibition efficiency, $i_{\text{corr}}(\text{inhibited})$ and $i_{\text{corr}}(\text{uninhibited})$: the corrosion current density with and without inhibitor, respectively. The compounds are inhibiting process of corrosion by adsorption themselves on steel surface. These adsorbed inhibitors (Inh_{ads}) replace the reaction that involves removing the number of water molecules “n” from metallic surface, as in the following equation:



The values of IE% show the three compounds are good inhibitors, and the best is MOP followed by HAT and then TTP at four different temperatures. These inhibitor molecules work through adsorption mechanism by the functional groups in the chemical structure, such as $-\text{OH}$ and $-\text{NH}_2$ groups in their chemical structures in addition to N, O and S heteroatoms within the heterocyclic rings that were attracted to the charged metal surface. In addition, there is another interaction occurs by π bonds in aromatic rings and the surface of steel [24, 25].

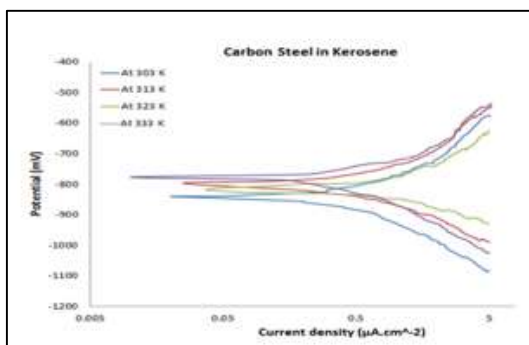


Figure 2: Tafel plot of steel in kerosene at four temperatures

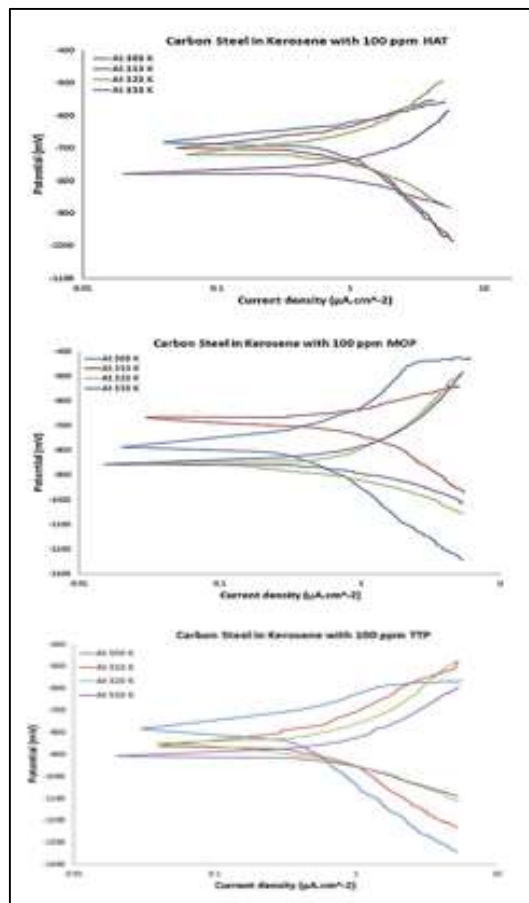


Figure 3: Tafel plot of steel in kerosene in the presence of 100 ppm of three inhibitors at four temperatures

Table 1: Corrosion data for polarization of inhibition in kerosene medium in the absence and presence 100 ppm of three inhibitors at four temperatures

Inhibitor	Temp. K	$-E_{\text{corr}}$ mV	i_{corr} $\mu\text{A.cm}^{-2}$	$-\beta_c$	$+\beta_a$	C_R	$C_R\%$	IE%
Blank	303	840	504.66	243.6	237.5	235.51	-	-
	313	797	628.90	215.2	233.9	293.49	-	-
	323	818	878.06	161.6	226.9	409.76	-	-
	333	777	1070.0	148.4	223.7	499.33	-	-
HAT	303	682	125.76	59.4	52.5	58.69	24.92	75.08
	313	699	134.69	66.4	50.8	62.86	21.42	78.58
	323	720	140.77	56.1	66.4	65.69	16.03	83.97
	333	779	145.19	59.4	77.5	67.76	13.57	86.43
MOP	303	790	113.78	163.4	199.3	53.10	22.55	77.45
	313	697	121.58	101.8	120.1	56.74	19.33	80.67
	323	849	127.36	54.5	72.2	59.43	14.50	85.50
	333	856	141.88	37.3	44.4	66.21	13.26	86.74
TTP	303	806	127.82	212.1	142.1	59.65	25.33	74.67
	313	862	135.58	121.7	207.5	63.27	21.56	78.44
	323	837	137.58	94.3	109.7	64.20	15.67	84.33
	333	874	151.74	75.0	79.9	70.81	14.18	85.82

II. SEM analyses

The morphology images in Figure 4 shows that the surface of the polished metal was smooth, while in Figure 5, the corroded samples appear significant surface damage in both the anode and cathode

regions. The surface of inhibited samples was covered by the inhibitor as clusters form as shown in Figure 6.

III. FTIR

Figure 7 shows the FTIR of the prepared compounds, from the chemical formula of these compounds, it can be seen the most important band to C=C stretching in benzene ring at approximately 1600 and 1475 cm^{-1} , the peak at 1608 cm^{-1} attributed to C=N, stretching bands of C-H aromatic at 3050 cm^{-1} , and at 3111 cm^{-1} represent to the broad peak of O-H. HAT spectrum indicates the presence of the N-H stretching in primary amine occurs as two bands, symmetrical and asymmetrical, at 3320 and 3200 cm^{-1} , while the spectrum of MOP shows stretching bands of C-H aliphatic at $2960\text{--}2850\text{ cm}^{-1}$ of methyl group, and the spectrum of TTP observed, the peak at 1155 cm^{-1} is attributed to stretching of C-S. Figure 8, indicates the FTIR spectrum of film formed through adsorption of the three compounds on surface of steel indicating the decreases in intensity of amino and hydroxyl groups in HAT, hydroxyl groups in MOP and TTP. In addition to the decreasing in the intensity of C=C bonds of benzene rings because of the formation of links through these rings [19-21].

IV. Antibacterial test

The examination of microbial activity was demonstrated the ability of the inhibitor compounds to inhibit bacterial growth in kerosene tanks. Aromatic and aliphatic hydrocarbons can be degrading by gram-positive bacteria such as *Staphylococcus aureus*, *Streptococcus spp.* and gram-negative bacteria like *Pseudomonas acuginosa* and *Acinetobacter bommanil* [26, 27]. The disk diffusion approach was utilized to show the zone of inhibition activity in 100 ppm of each compound. The results are listed in Table 2, showed that the concentration of HAT, MOP and TTP compounds have different activity against bacteria and good inhibitor for some types of bacteria. The inhibition zone of the tested compounds was expressed by -, +, ++ and +++.

V. Inhibition mechanism

This adsorption is achieved through functionally groups that have an electronic density as pairs of free electron or π electrons that interact by nucleophile attacks and facilitate the adsorption process on the surface of the metal. In the present compounds, it can be seen hydroxyl and amine groups in addition to electron pairs on O, N, and S atoms.

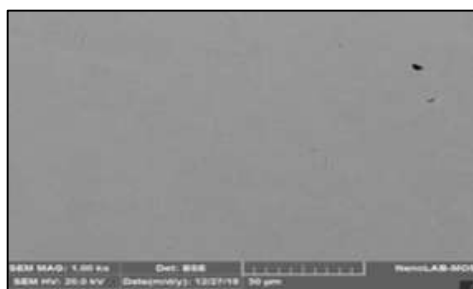


Figure 4: SEM images for polished surface

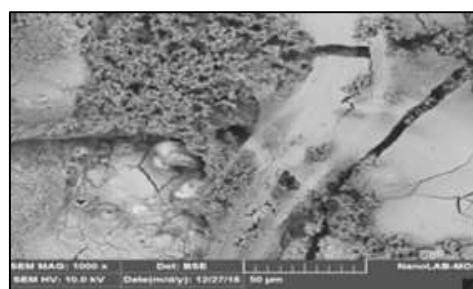


Figure 5: SEM images after corrosion in kerosene medium

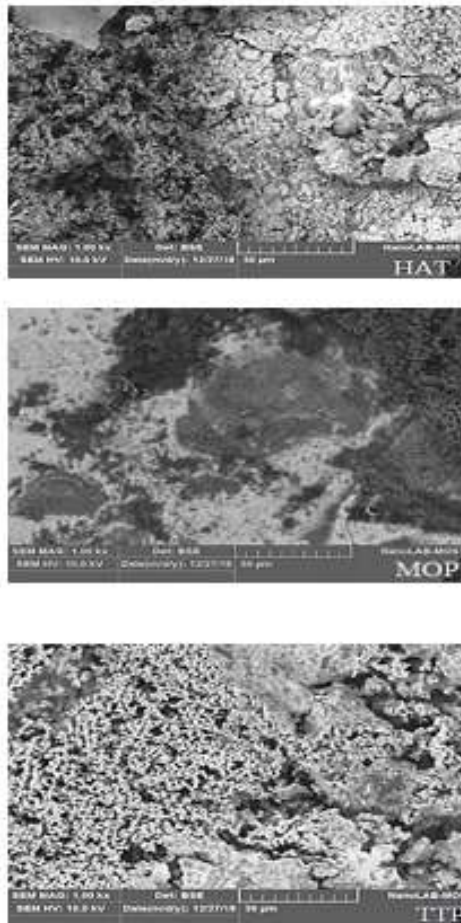


Figure 6: SEM images after inhibition with three inhibitors in kerosene medium

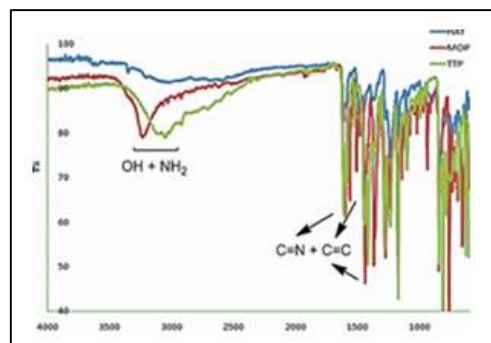


Figure 7: FTIR spectra of the prepared compounds

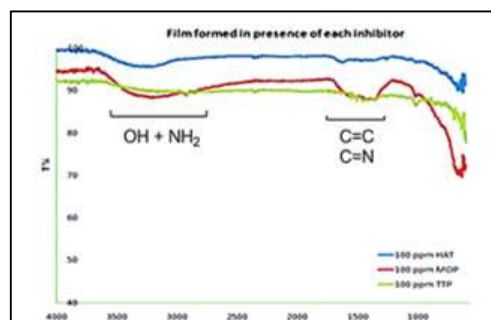


Figure 8: FTIR spectra of film formed by adsorption of the compounds on carbon steel

Table 2: Data of antibacterial test for 100 ppm of inhibitors

Bacteria	HAT	MOP	TTP
<i>Staphylococcus aureus</i>	—	++	+++
<i>Streptococcus spp</i>	—	+++	+++
<i>Pseudomonas aeruginosa</i>	—	+++	+++
<i>Acinetobacter baumannii</i>	—	+	—

4. Conclusions

1. The heterocyclic derivatives, represented by 3,5-di(4-hydroxyphenyl)-4-amino-1,2,4-triazol (HAT), 4-[3-(4-methylphenyl)-1,2,4-oxadiazol-5-yl]-phenol (MOP), and 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenol (TTP), confirmed their role as an inhibitor to protect steel in a kerosene-brine environment at 303-333 K and 100 ppm.
2. These inhibitors acted as a mixed-type according to the values of corrosion potentials, and they gave good inhibition through the calculated values of inhibition efficiency.
3. The SEM and FTIR confirmed the inhibition action of prepared inhibitors.
4. These compounds have activity against some types of bacteria.

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