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Oxathiadiazole Derivative as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid

Ammar M. Al-Bayati[1],Khalida F. Al‑Azawi[1]
Applied Chemistry Division, Applied Science Department, University of Technology, Baghdad, Iraq

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Abstract:Iraq as an oil country, many researchers are trying to find cheap, easy to manufacture corrosion inhibitors that derived from organic compounds. In the present study, a new Shiff base derived from oxathiadiazole namely 5-(4-((4-nitrobenzylidene) amino) phenyl) -1, 3, 4-oxadiazole-2-thiol (NPOT) is utilized as an efficient and an inexpensive corrosion inhibitor for mild steel in hydrochloric acid solution. The study is carried out in 1.0 M HCl environment utilizing potentiodynamic polarization techniques and scanning electron microscopy. The maximum inhibition efficiency was found to be 99% at all tested concentrations. SEM analysis confirming the inhibitive behavior of the NPOT versus the mild steel corrosion in corrosive environment. Quantum chemical calculations (DFT) utilized to estimate significant electronic parameters of the NPOT molecule so as to realize correlation between the NPOT chemical structure and inhibition properties.

Keywords:*Schiff base, Corrosion inhibitor, DFT, HOMO, LUMO.*

I. Introduction

Mild steel “MS” is quite applied in considerable manufacturing applications such as chemicals, pickling, acid cleaning, oil, gas, and storage and pipeline transportation”. MS Sevier from corrosion due to corrosive solutions and lead to the degradation of the alloy, resulting in considerable economic losses for several industries. The degradation of MS is an effect of contact of MS with the acidic solutions which were quite used in manufactures for diverse applications [1–10].

Carbon nitrogen double bond which some compounds have known as Schiff base and were prepared from the reaction of aliphatic and/or aromatic amines (primary) with the compounds having carbonyl groups in their structures. Schiff bases consider as important kinds of medical and pharmaceutical molecules due to biological utilization such as antimicrobial [11], and anti-cancer [12-14] and they also investigated as ligands that react with metals to produce metal complexes and the reaction done via carbon nitrogen double bond. The Schiff base molecules, which are employed as inhibitors, can block the metals from oxidation reaction through a certain mechanism [18]. Perusals of several studies in University of Technology demonstrate the use of new organic compounds as corrosion inhibitors [19-29]. The primary goal of the present investigation is to synthesis and study the inhibitive effect of new Shiff base derived from oxathiadiazole namely 5-(4-((4-nitrobenzylidene) amino) phenyl) -1, 3, 4-oxadiazole-2-thiol (NPOT) on the corrosion of mild steel in a 1.0 M HCl media. The evaluation of the corrosion potency was

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examined using potentiodynamic polarization. The surface morphology of the mild steel was investigated through scanning electron microscopy (SEM). The chemical structure of the synthesized inhibitor was shown in Fig. 1.

Experiments

Mild steel coupons and chemical compounds

Mild steel "MS" coupons have been tested for corrosion inhibition with composition of "Fe 98.31, C 17%, Si 0.24%, P 0.017%, S 0.038%, Mn%0.60, Cr 0.02%, Ni 0.01%, Mo0.07%, Cu 0.13% and Al 0.03%". The effective surface zone wars (1.0 cm^2). The coupons were cleaned regarding to ASTM G1-03 technique [29].
Chemical molecules which were utilized in the current investigation were buy from Chemicals company namely Sigma Aldrich.

Corrosion Studies

Coupons have been tested in 1.0 M HCl in the absence and presence of synthetic inhibitor with five concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M). Potentiostat WINKIK MLab 200 was used to test corrosion at scan rate of 5 mV.sec^{-1}, by changing the applied potential $\pm$200 mV around open circuit potential. Form this test can be measure corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes ($-b_c$& $+b_a$) and corrosion rate in weight loss (W.L). Corrosion rate (C_R), inhibition efficiency (IE %) and polarization resistance (R_p) wascalculated according to the following equations:

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

Where: $\boldsymbol{e}$ and $\boldsymbol{\rho}$ is equivalent weight and density of metallic substrate.

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

Where: $i_{inhibited}$ and $i_{uninhibited}$ are corrosion current density in the presence and absence of inhibitor respectively.

$$R_p = \frac{(b_c \times b_a)}{2.3 \times i_{corr}\,(b_c + b_a)} \quad \dots\dots(3)$$

DFT Calculations

The structure with optimized conditions were performed utilizing Gaussian/09/Revision/A.02. B3LYP function was utilized for optimum structure. The EHOMO and ELUMO were also estimated [25,26]. The mechanism of Inhibition related quantum parameters which were referred as in equations. (4) – (10) [24-27]:

Results and discussion

ΔE Energy gap = ELUMO−EHOMO ………… (4)
X"“"Electron affinity"”" = −HOMO ………….. (5)
I"“"Ionization potential"”" = −LUMO ………….. (6)
η "“"Global hardness"”" =1/2(EHOMO−ELUMO) …….. (7)
S "“"Chemical softness"”" =1/ η ………………………….(8)
χ "“"Electronegativity"”" = 1/2(EHOMO−ELUMO) ……………(9)
ω "“"electrophilicity index"”"= u^2/2 η ……………………….(10)

Polarization Behavior

Inhibitors which have used in industrial process were the economic method for good protect of coupon surface. Organic molecules are the dominant that are used in the oil industrial process because of forming of a film on the coupon metallic surface. In general, the inhibitors are containing hetro atoms, such as azoles.Corrosion test was achieved to investigate the role of synthetic compounds as inhibitor in 1 M HCl solution.

Five concentrations of synthetic inhibitor (0.1, 0.2, 0.3, 0.4 and 0.5 M) were tested to inhibit MS in tested solution at three temperatures (303, 313 and 323 K), the polarization behavior is shown in Fig. (2). this figure illustrates the cathodic and anodic regions where the dissolution of iron can occur at anode as follow:

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$$Fe \rightarrow Fe^{2+} + 2e \quad \ldots\ldots (11)$$

While the reduction of hydrogen ions takes place at cathode according to the following equation:

$$2H^{+} + 2e \rightarrow H_2\uparrow \quad \ldots\ldots (12)$$

The presence of inhibitor led to shift corrosion potential toward negative values, this means that 5-(4-((4-nitrobenzylidene) amino) phenyl)-1,3,4-oxadiazole-2-thiol (NPOT) act as cathodic inhibitor. The decreasing in corrosion current density value confirms that the (NPOT) works as inhibitor due to heterocyclic compound with atoms have electronic density such as nitrogen, oxygen and sulfur in addition to the benzene and triazole rings. –SH and $–NO_2$ groups may be attracted to metallic surface by adsorption process as follow:

$$\text{Org. molecules}_{(aq)} + nH_2O_{(ads)} \rightarrow \text{Org. molecules}_{(ads)} + nH_2O_{(solu)} \quad \ldots\ldots (13)$$

The inhibitors were adsorbed on the surface through replacing H_2O molecules with inhibitor molecules to form a protective layer. Ione pairs and Pi bonds in the structures of inhibitor molecules facilitate transfer of the electron from the inhibitor to the empty d-orbital of Fe atoms.

The inhibition could be due to **(i)** Adsorption of the molecules or its ions on anodic and/or cathodicsites**(ii)** increase in cathodic and/or anodic over voltage, and **(iii)** the formation of a protective barrier film. The role of (NPOT) molecules as inhibitor is shown through the increasing in Tafel slopes values and polarization resistance as shown in Tables (1) to (6). Also, the good values of IE% gave clear evidence for this inhibition by (NPOT).

Table 1: Measured corrosion parameters for five concentrations of inhibitor in 1M HCl solution at 303 K.

Con. (M)	$-E_{corr}$ (mV)	i_{corr} ($\mu A/cm^2$)	$-b_c$ (mV/dec)	$+b_a$	W.L ($g.cm^2.d^{-1}$)
Blank	432.9	398.71	64.60	39.40	35.024
0.1	485.3	0.051	164.3	206.7	0.304
0.2	505.9	0.042	124.7	166.8	0.282
0.3	466.3	0.034	117.6	210.9	0.30
0.4	493.9	0.024	68.20	114.2	0.238
0.5	475.0	0.014	90.30	75.60	0.269

Table 2: Calculated corrosion parameters for five concentrations of inhibitor in 1M HCl solution at 303 K.

Con. (M)	R_P ($\Omega.cm^2$)	C_R (mpy)	IE%
Blank	26.652	184.004	-
0.1	779,363	23×10^{-3}	99.987
0.2	737,701	19×10^{-3}	99.989
0.3	980,485	15×10^{-3}	99.991
0.4	772,539	11×10^{-3}	99.993
0.5	1,279,000	6.4×10^{-3}	99.996

Table 3: Measured corrosion parameters for five concentrations of inhibitor in 1M HCl solution at 313 K.

Con. (M)	$-E_{corr}$ (mV)	i_{corr} (μA/cm^2)	$-b_c$ (mV/dec)	$+b_a$	W.L (g.cm^2.d^{-1})
Blank	427	568.03	102.9	94.2	18.915
0.1	475	0.0385	136.1	232.2	0.248
0.2	497	0.0347	125.3	140.1	0.235
0.3	489	0.0311	119.0	125.1	0.226
0.4	501	0.0305	108.5	134.4	0.235
0.5	494	0.0182	65.7	60.5	0.146

Table 4: Calculated corrosion parameters for five concentrations of inhibitor in 1M HCl solution at 313 K.

Con. (M)	R_P (Ω.cm^2)	C_R (mpy)	IE%
Blank	37.593	262.145	-
0.1	980,485	19×10^{-3}	99.993
0.2	844,725	15×10^{-3}	99.994
0.3	854,241	14×10^{-3}	99.994
0.4	868,933	13×10^{-3}	99.994
0.5	855,504	8.3×10^{-3}	99.996

Table 5: Measured corrosion parameters for five concentrations of inhibitor in 1M HCl solution at 323 K.

Con. (M)	$-E_{corr}$ (mV)	i_{corr} (μA/cm^2)	$-b_c$ (mV/dec)	$+b_a$	W.L (g.cm^2.d^{-1})
Blank	419	712.07	118.9	92.9	12.118
0.1	495	0.0394	148.2	135.1	0.287
0.2	504	0.0383	136.3	153.0	0.283
0.3	510	0.0352	125.7	134.1	0.250
0.4	500	0.0317	116.4	125.3	0.272
0.5	504	0.0295	105.0	118.8	0.247

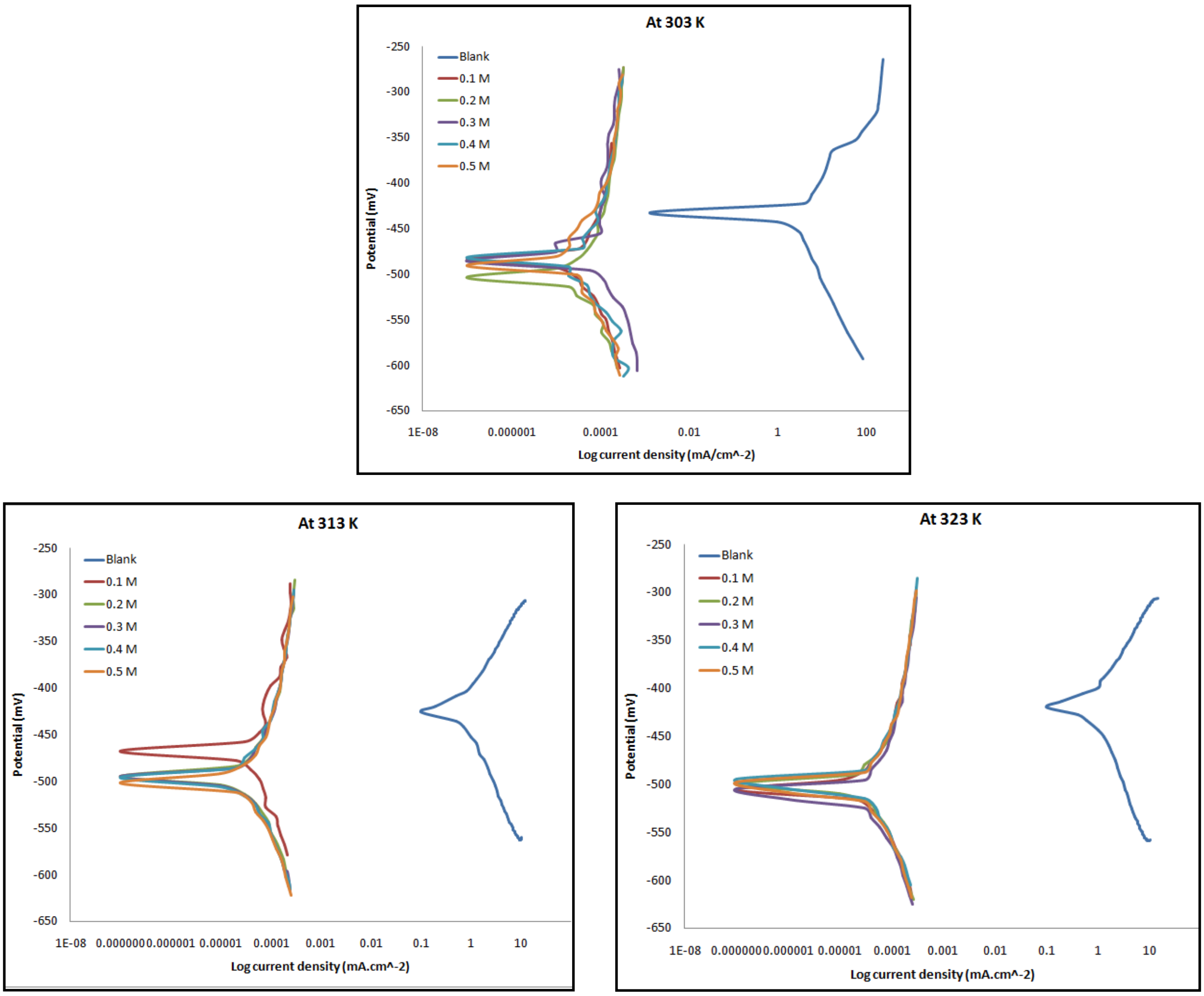

Fig. (2): Tafel plots for inhibition by (NPOT) at 303K.

Table 6: Calculated corrosion parameters for five concentrations of inhibitor in 1M HCl solution at 323 K.

Con. (M)	**R_P ($\Omega.cm^2$)**	**C_R (mpy)**	**IE%**
Blank	31.802	328.620	-
0.1	786,861	17×10^{-3}	99.994
0.2	823,685	17×10^{-3}	99.994
0.3	804,938	16×10^{-3}	99.995
0.4	845,223	14×10^{-3}	99.995
0.5	834,552	13×10^{-3}	99.995

Morphology characterization

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The scanning electron microscopy (SEM) pictures of tested surface of mild steel in the absence and presence of NPOT as tested corrosion inhibitor are demonstrate in Figs. 3 and 4. The mild steel morphology in acidic media In absence of NPOT as tested corrosion inhibitor shows an quite rough obvious striations and isolated groove because of serious damage from corrosion (Figure 3).Furthermore, the mild steel surface in the presence of optimum concentration of NPOT demonstrate a relatively smoother surface (Figure 4). In corrosive media, the NPOT molecules were adsorbed on the mild steel surface and form a protective layer on mild steel surface.

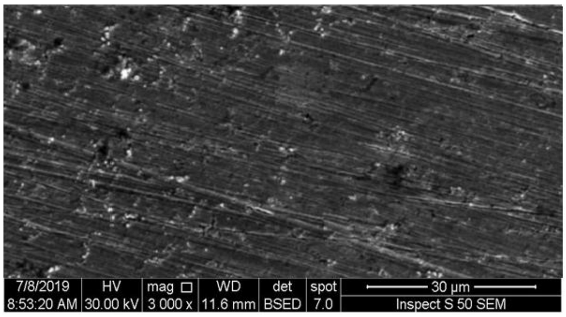


Figure 3. SEM image of mild steel in 1.0 M HCl.

This layer isolate the mild steel from the acidic solution through a film between mild steel surface/ acidic environment interface and hence impedance the effect of corrosive solution.

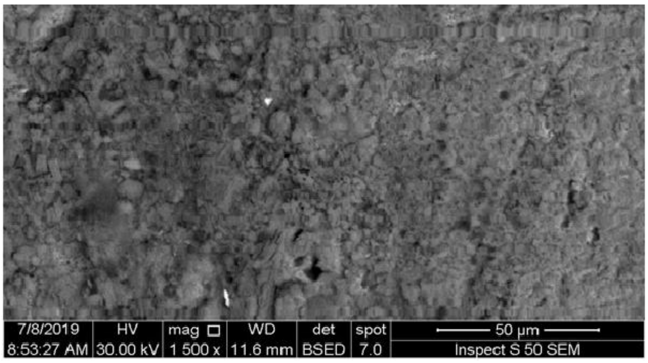


Figure 4. SEM image of mild steel the presence of inhibitor.

Theoretical Calculations

Applying DFM method to investigate the role of (NPOT) as inhibitor, confirm the a good performance of this compound by limit the electrical density centers on molecules that attracted to positively charged metallic surface as shown in Figures 5 and 6.

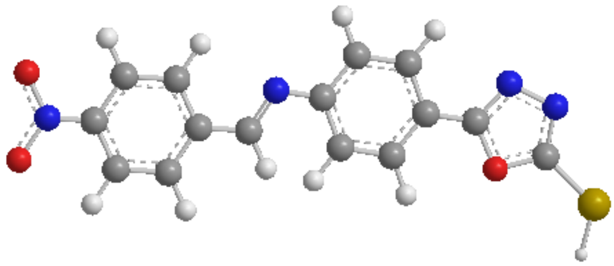
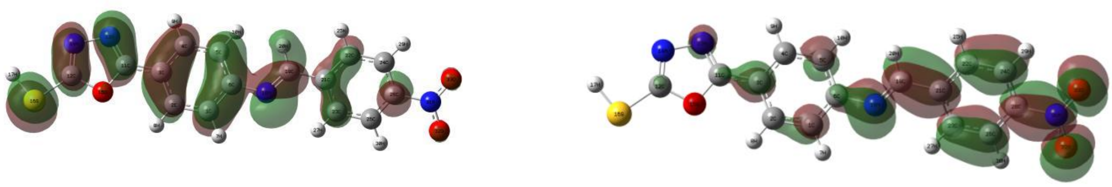


Fig. (5): 3D image of (NPOT) molecule.



HOMO LUMO

Fig. (6): HOMO and LUMO images of (NPOT) molecule.

Table 5 demonstrate the measured factors for the tested compound NPOT. The HOMO and LUMO frontier of NPOT molecule was demonstrated in Figure 7. As display in Figure 7, the distributions

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of HOMO was generally distributed was around the whole NPOT molecule and for LUMO frontier the electronic distribution around the whole NPOT molecule except the oxathiadiazole ring. The population densities of NPOT molecule have uniform density as in Figure 7.

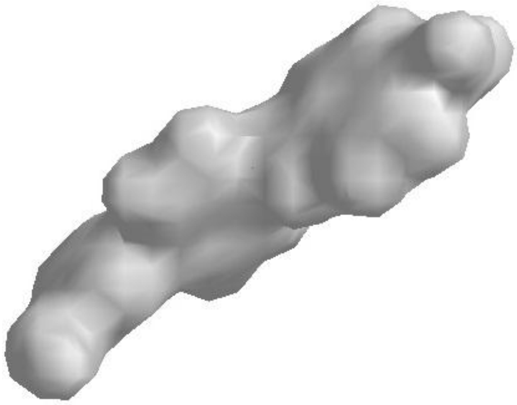

Figure 7. The population densities of NPOT molecule

Table 5. The Molecular factors of NPOT measured with B3LYP/6-31G

Compound	E_{HOMO}	E_{LUMO}	E_{HOMO}- E_{LUMO}	Dipole Moment
NPOT	-9.384	-3.789	5.595	4.24

The Mulliken charges of the NPOT molecule was estimated as displayed in Table 6 and Figure 9. It obvious that the nitrogen and oxygen atoms have the highest atomic charged and may forms adsorption active centers.

Table 6. The atomic charges of NPOT molecule

Atom	**Charge**	**Atom**	**Charge**	**Atom**	**Charge**	**Atom**	**Charge**
O(1)	-0.10545	C(7)	-0.048978	N(13)	0.894548	C(19)	-0.00.235658
C(2)	-0.334666	C(8)	-0.0371225	C(14)	0.0846505	C(20)	-0.0.608196
N(3)	-0.39746	C(9)	-0. 145008	C(15)	0.0558203	N(21)	1.32145
N(4)	-0.36384	C(10)	0.246489	C(16)	-0.0609694	O(22)	-0.764275
C(5)	0.369142	C(11)	-0.48857	C(17)	-0.00377853	O(23)	-0.764197
S(6)	0.10257	C(12)	-0.0370648	C(18)	0.143742	H(24)	0.0359926

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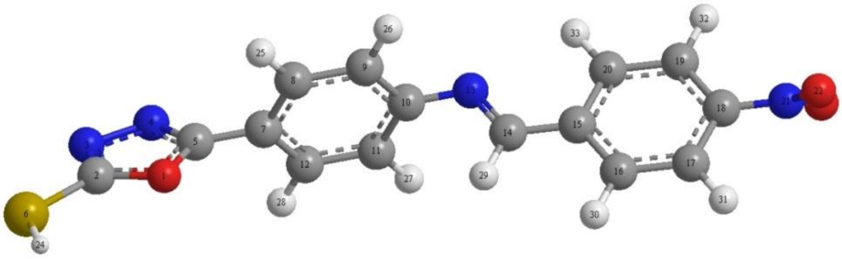

Figure 8. The molecular structure of NPOT molecule.

Conclusion

The inhibition impacts of the tested corrosion inhibitor namely 5-(4-((4-nitrobenzylidene) amino) phenyl)-1,3,4-oxadiazole-2-thiol on coupon surface in corrosive environment was tested utilizing polarizationand SEM methods. DFT was used as complemented technique to compare with the methodological results. The polarizationresults show that 5-(4-((4-nitrobenzylidene) amino) phenyl)-1,3,4-oxadiazole-2-thiol impedance the corrosive environment and the IE was raised with increasing of concentration. IE was 99 % that showed the good protection vsHCl. 5-(4-((4-nitrobenzylidene) amino) phenyl)-1,3,4-oxadiazole-2-thiol impedance the corrosion by adsorbing on the mild steel surface. The SEM pictures indicate that the synthesized inhibitor adsorbed on mild steel surface.

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