Development of new corrosion inhibitor tested on mild steel supported by electrochemical study

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ABSTRACT

Mild steel is a metal which is commonly used in industrials and manufacturing of equipment for most industries round the world. It is cheaper cost compared with the other metals and its durable, hard and easy-to-wear physical properties make it a major choice in the manufacture of equipment parts. The main problem through the uses of mild steel in industry is its resistance against corrosion, especially in acidic solutions. This case led to raise the cost of maintenance of equipment that used mild steel and as a result increased costs for the company. Organic corrosive inhibitors that also act as green chemicals, 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol have been synthesized. This inhibitor is tested as corrosion inhibitor on a mild steel sample MS in 1 M hydrochloric acid solution (HCl) using electrochemical measurements test includes PD (Potentiodynamic), EIS (Electrochemical impedance spectroscopy), OCP (Open circuit potential) and EFM (electrochemical frequency modulation). The obtained results indicate that 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol acts as a good corrosion inhibitor for mild steel sample in HCl solution with efficiency above 90%. Changes in the impedance parameters postulated adsorption on the mild steel specimens' surfaces of, which it going to the formation of protective coating layer. It also shows that 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thia diazol corrosion inhibitors are effective in helping to reduce and slow down the corrosion process that occurs on mild steel surface in hydrochloric acid solution. Increase of corrosion inhibitor concentration provides a protective layer of mild steel. However, this protective layer becomes weak when the temperature of the solution increases.

Introduction

Mild steel is the steel that is used widely in the manufacturing and construction industries. Iron steel is an iron alloy that has a low quantity of carbon in the range of 0.5–0.26% [1]. The main problem is the use of mild steel industry is when dissolution in acidic media solution. Nature of very weak resistance to corrosion makes mild steel is easily to corrode. Among the areas that use mild steel are cleaning industrial, oil field, petrochemical processing, heat exchangers, tanks and other. The metallic structure, chemical composition and its matter often go under damaged due to the aggressive corrosion behaviour of acidic environment and with present of hydrochloric acid which it has high aggressive rate to corrosion process which lead to issues serious consequences to industrial unity processing on cost and product aspect [2].

Corrosion may be subdivided into two kinds of dry and/or wet corrosion. Dry one occurs when direct clash of atmospheric gases such as oxygen gas with metals. This clash led to the formation of the metal oxide layer called 'Theory of Wagner' [3]. For wet corrosion, it occurs when the liquid medium involved. In this process, one part will act as the anode and undergo a process of oxidation, while the other one acts as a cathode and undergo a process of reduction. In wet corrosion, the liquid medium involved acting as an electrolyte which serves as an electron transfer medium using ion [4].

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Industrial equipment exposed to corrode through using materials to clean them such as hydrochloric acid and sulphuric acid which are using in wide rang to clean and remove rust on metal surface after end of processes and in, this case protection form corrosion should apply to protect metal from corrode [5]. The incorporation effective of inhibitor has been among the present and give hopeful techniques to reduce the rate and impacts of corrosion process in past few years [6]. Mechanism and the rate of the corrosion process are depending on various factors (type of material, acidic or basic conditions). The mild steel surface corrosion in corrosive environment proceeds regarding to the overall reaction: $M + 2H^+ \rightarrow M^{2+} + H_2$. This reaction consist of ion transferring the anode and/or cathode side. Electrochemical reaction in mild steel involving process of oxidation/reduction reactions [7]. The anode has oxidation reaction: $M \rightarrow M^{2+} + 2e^-$ while the cathode has reduction process: $2H^+ + 2e^- \rightarrow H_2$. Bubbles of hydrogen gas will be released as product of corrosion.

In general, the corrosion inhibitors can be divided to, organic inhibitors and inorganic inhibitors, this division done according to chemical constituents of inhibitors [8]. In literature found that some selected inorganic inhibitors like phosphate and dichromate's in addition to arsenates and these inorganic inhibitors were usually avoided due to cost, toxicity and degradation behaviors. Moreover, it is too critical to maintain the pH of a solution and the concentration of inorganic inhibitors [7]. Therefore, using nontoxic organic corrosion inhibitors was the good decision to get significant strategy for corrosion prevention process on mild steel and includes instead of inorganic ones [9].

From the literature reports we found and indicated that most organic molecules having double bonds, heteroatoms, which can donate single pair electrons to the metal surface and can prevent the corrosion form initiation [10]. In particular, heterocyclic molecules having nitrogen atoms performance demonstrates potential of inhibition toward corrosion process on surface of metals in corrosive environment [11]. The efficiency of inhibition having the sequence oxygen < nitrogen < sulfur < phosphorous [12], and these atoms if found in organic molecules having, especially nitrogen atom will lead to reduce corrosion attack on steel, studied in some detail has been done [13]. The organic inhibitors effectiveness depends on the rate of adsorption on the surface of the metal and covering abilities on metal surfaces. The adsorption on the surface of metal depend on the structures of the organic inhibitors molecules and the charge of the metal [14]. Adsorbed inhibitors on the surface of metal in aqueous solutions replace water molecules. Electrostatic interactions of organic inhibitor compounds and alloys are clear in corrosion process during this inhibition action [15].

Adsorption of inhibitors on alloy surface depends on, inhibitor group physicochemical properties, such as density of the electron at the donor atom, orbital character and electronic structure of the molecule [16]. Thiadiazole ring systems have been reported and so far a diversity of anti-cancer properties has been investigated for huge number of similar compounds. 1,3,4-thiadiazoles were synthesized starting from the precursors, utilized for the prepared of several derived and large varieties of impacts such as anti-

inflammatory, antituberculosis, anticonvulsant, and antibacterial were proved [17]. The resonance structure of the 2-amino-1,3,4-thiadiazole ring systems assumes biological impacts. The studied compound 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thia diazol as inhibitor has hetro-aromatic ring, aromatic benzene ring, azomethane group and heteroatoms, N, O, and S that have higher electron density and were act as protected layer on the surface of alloy by forming a coordination bonds between the inhibitor and the surface of iron. The inhibition performance of this inhibitor versus the corrosion of alloy in acidic solution could be demonstrate regarding to adsorption sites number, charge density and the performance to form a coordination bonds. The selection of our inhibitor was regarding to molecular structure.

The inhibitor 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3, 4-thiadiazol is synthesized, and its chemical structure was cleared and confirmed by using spectroscopic techniques. The corrosion inhibitor effectiveness of 4-hydroxybenzylideneaminomethyl-5-e thyl-1,3,4-thiadiazol on the corrosion process on mild steel sample in 1.0 M HCl was investigated by using electrochemical measurements.

Materials and methods

Chemistry

The studied inhibitor prepared by condensation of 2-amino-5-ethyl-1,3,4-thiadiazol (0.004 mol) with 4-hydroxybenzaldehyde (0.004 mol) in methanol (25 mL) and the mixture was refluxed for six hours with stirring. The progress of reaction was monitored by TLC. The reaction mixture was concentrating, and solid was recrystallized from ethanol, yield 58%. The purity of inhibitor molecules was approved through Thin Layer Chromatography as in Fig. 1. Thin Layer Chromatography sheets have been coated by silica gel on aluminum 60F–254. IR: 3396.4 cm^{-1} (OH), 3077.8 cm^{-1} (aromatic group) and (C=N) 1611.2 cm^{-1}. ^{1}H NMR (DMSO-d_6); δ: 1.54 (t, 3H for CH$_3$), 3.01 (m, 2H for CH$_2$), 5.83 (s, 1H for OH), 6.87–7.17 (m, 4H, Aromatic) and 8.29 (s, 1H for —N=CH—).

Electrochemical measurements

Mild steel tested as metal sample immersed in acidic solution contain 1 M hydrochloric acid (HCL) with different concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitor. Electrochemical measurements used in this study were carried out on Gamrry Instrument and Gamrry software where they designed with EuroCell (Three electrode cell) kit used for electrochemical corrosion tests. EuroCell designed to hold cylindrical samples of metal, it is consist of working electrode, counter electrode and reference electrode. Gamrry water bath connected to the three electrode cell to control the temperature during running the test. Gamrry instrument designed to perform potential of corrosion process, electrochemical impedance spectroscopy (EIS), potentio-dynamic polarization (PD) and electrochemical frequency modulation (EFM). PD curve was varied from −0.2 to 0.2
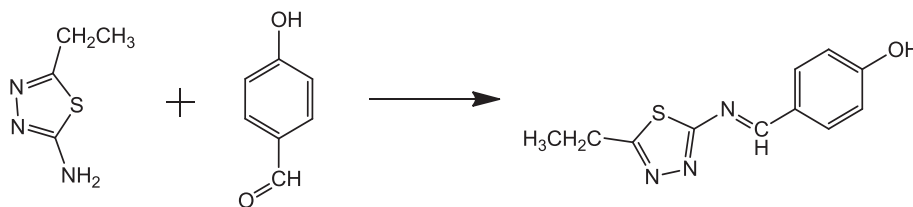

Fig. 1. The chemical formation of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol.

V_{SCE} through scanning rate range of 0,5 mV/s. Electrochemical impedance spectroscopy carried out by using AC signal with 5 mV multitude of peak-peak at corrosion potential with range of frequency $100 * 10^3$ to 0.1 Hz. By using Gamrry Echem analyst, all data of EFM impedance were fitted to appropriate equivalent circuit (EC). The data of electrochemical measurements started and began to be gathered after 30 min from immersing the working electrode in the acidic solution that's time is to allow steady state potential to stabilize.

Electrochemical polarization methods are classified as a method to control the potential (potentio-static, potentio-dynamic) and to control current (*I*), (Galvano static) approaches. Studies and works were done on potentio-static and potentio-dynamic methods and were used for measurement and corrosion rate control. For Potentiostat method is automatically adjusts the applied polarizing potential between the reference electrode (RE) and the working electrode (WE) at any prescribed value to measure the density of the current on the counter electrode (CE). The curve that associated with a potentio-dynamic method is polarization curve allows detailed study of the important parameters that impact the formation and growth of passive films (E_{corr}) and pit propagation (E_{pit}).

Results and discussion

Synthesis

To synthesize 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as a corrosion inhibitor, the reaction sequence outlined in Fig. 2 was followed, starting from commercially available 5-ethyl-1,3,4-thiadiazol-2-amine. The synthesis was carried out by refluxing 2-amino-5-ethyl-1,3,4-thiadiazol in methanol with 4-hydroxybenzaldehyde. The molecular weight of the synthesized corrosion inhibitor is 233.06, which is calculated based on the molecular formula ($C_{11}H_{11}N_3OS$) and supported via mass spectrometry. 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thia diazol can be dissolved in acetone, dichloromethane, dimethylformamide, dimethylsulfoxide, ethanol or methanol solutions. The FT-IR spectrum of this compound shows absorption bands at 3396.4 cm^{-1} for hydroxyl group. The band at 3077.8 cm^{-1} for aromatic ring, In addition the band at 1611.2 cm^{-1} was for azomethane group. H-NMR spectrum exhibits a triplet at 1.54 ppm and m at 3.01 ppm for due to the methyl and methylene protons respectively.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS)

These tests involve mild steel corrosion process (sample) in a solution of acidic media in the presence the compound of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitors at different concentrations. Acid solution used is 1 M hydrochloric acid. The electrochemical measurement is a method used to measure the corrosion rate prevailing on mild steel sample in 1 M hydrochloric acid with and without corrosion inhibitor.
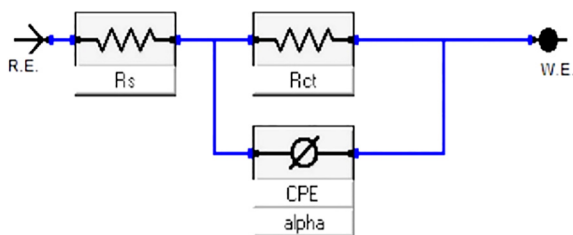

Fig. 2. Constant Phase Element (CPE).

Among the experiments will carried out are: electrochemical impedance spectroscopy (EIS) This analysis will be conducted to test the effectiveness of corrosion inhibitors to protect the surface of mild steel in acidic solutions. It will be done at 30 °C with different concentrations of corrosion inhibitor that is 0.05 M, 0.1 M, 0.2 M 0.4 M, 0.5 M after that all data is obtained, a comparison will be made with the blank sample (no corrosion inhibitors used in the solution). After the decision spectroscopy electrochemical impedance (EIS) is measured, constant phase element CPE is used for matching circuit. It consists of a solution resistance R_s, charge transfer resistance R_{ct} and constant phase element CPE as shown in Fig. 2.

CPE resistance value will be calculated using the formula below:

$$Z_{CPE} = A_o^{-1}(j\omega)^{-n}$$

where *A* is a constant factor and *n* is proportional to the phase shift [18]. Inhibitor efficiency is calculated as follow:

$$IE\ (\%) = \frac{R_{ct} - R_{ct}^o}{R_{ct}} \times 100$$

where R_{ct} and R_{ct}^o are the charge transfer resistance without and with corrosion inhibitor. Table 1 and Fig. 3 show the effective of increasing the concentration through fix temperature respectively.

Using Gamry Echem Analyst software, EIS experimental data can be analysed that data matching CPE for mild steel/sample, calculating solution resistance R_s and constant phase element CPE, calculate the charge transfer resistance R_{ct} and charge double layer [19]. These data will proves that the corrosion inhibitor molecules have to absorb the mild steel sample surface thus form a protective layer on the mild steel. Large charge transfer resistance corresponding to a corrosive system slowly [20]. With the increase in the value R_{ct}, the efficiency and capacity of inhibition (IE) will increased up to 90.86% at a concentration of 0.5 mm. The large transfer charge resistance corresponds to a slowly corrosive system [21]. With the increase in R_{ct} value, the efficiency and inhibition capacity (IE) also increased up to 90.86% at a concentration of 0.5 Mm.

Next in Table 2 and Fig. 4 show the experiment using the same concentration of corrosion inhibitors ie 0.5 mM but at different temperatures at temperatures of 30, 40, 50 and 60 °C. Based on Fig. 4 it can be seen that the semi-circular graph at 60 °C is the smallest and at 30 °C is the largest. This shows that the diameter of the semi-circle is narrowing with temperature rise. In other words, the higher the temperature increase, the smaller the semi-circle diameter. This result shows that the rate of corrosion inhibition is decreasing with increasing temperature. The increase in the temperature of the solution will lead to accelerate the corrosion process rate which is caused by the change of operating mechanism of corrosion [22].

Potential dynamic polarization

Measurements was done to obtain the potential curve of a mild steel in a 1 M hydrochloric acid solution at a different concentration of corrosion inhibitors at 30 °C, Fig. 5. The parameters obtained from the extrapolation of the Tafel line are the gradients of the anonical βa and cathodic βc Tafels, the density of corrosion current (i_{corr}), the potential of corrosion (E_{corr}) and the rate of corrosion. The data for this parameter is shown in Table 3. Inhibition efficiency (IE) can be calculated using the formula:

$$IE\ (\%) \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100$$

where i_{corr}^o and i_{corr} are the density values of corrosion current without and with corrosion inhibitors.

Table 1
CPE matching data for mild steel sample in 1.0 M HCl with the concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at 30 °C.

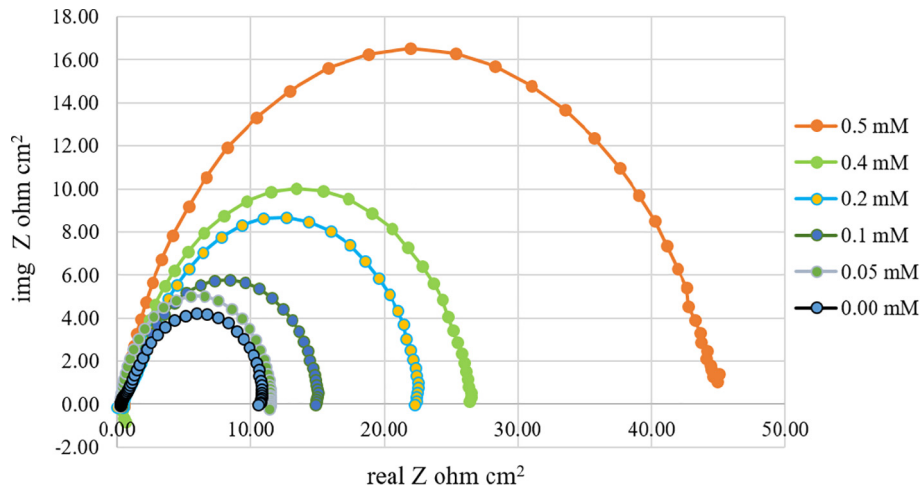| Concentration (mM)	R_s (ohm cm^2)	R_{ct} (ohmcm^2)	CPE$_{dl}$		C_{dl} (μFcm^{-2})	IE (%)
			Y_o (μS s$^\alpha$ cm^{-2})	α		
Blank	0.2499	0.0778	924.6	0.9174	338.7	0
0.05	0.3587	0.7607	5050	0.7096	375.1	89.77
0.10	0.3597	0.7694	3812	0.7258	820.9	89.89
0.20	0.3672	0.7808	2065	0.7793	954.7	90.04
0.40	0.3935	0.7796	1690	0.8006	365.9	90.02
0.50	0.5488	0.8509	435.4	0.8584	266.2	90.86

Fig. 3. Nyquist plots for mild steel in different concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol in 30 °C.

Table 2
CPE matching data for mild steel in 1.0 M HCl with 0.5 mM concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at different temperatures.

| Temp. (°C)	Concentration (mM)	R_s (ohm cm^2)	R_{ct} (ohm cm^2)	CPE$_{dl}$		C_{dl} (μFcm^{-2})	IE (%)
				Y_o (μSs$^\alpha$cm^2)	A		
30	Blank	0.2540	0.0779	924.6	0.9174	338.7	0.00
	0.5	0.5509	0.8480	435.4	0.8584	266.2	90.86
40	Blank	0.2481	0.2205	4526	0.9278	502.0	0.00
	0.5	0.2299	0.3519	500.2	0.8381	398.5	72.96
50	Blank	0.2315	0.1511	1634.01	0.7321	835.9	0.00
	0.5	0.2127	0.3380	507.5	0.8392	266.1	56.67
60	Blank	0.1840	0.1103	2172.87	0.8470	920.8	0.00
	0.5	0.1699	0.2501	451.4	0.8619	554.5	52.21
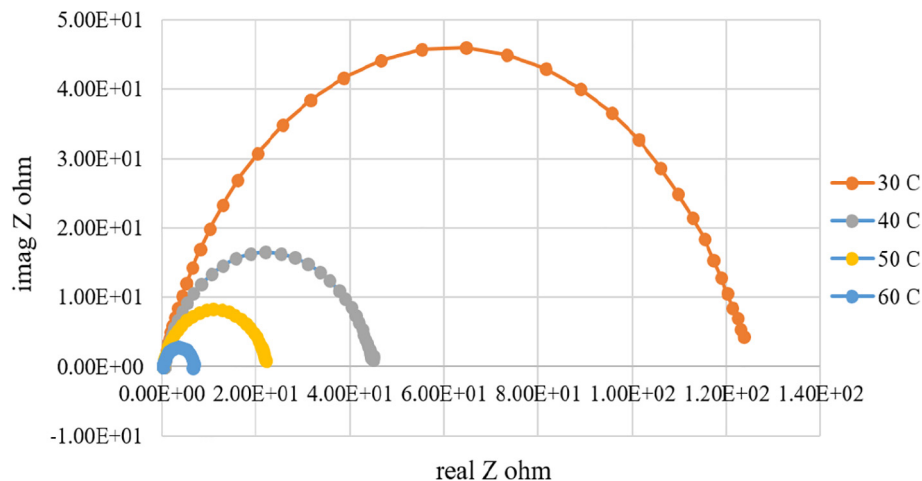
Fig. 4. Plot Nyquist for mild steel at a concentration of 0.5 mM of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitor at different temperatures.
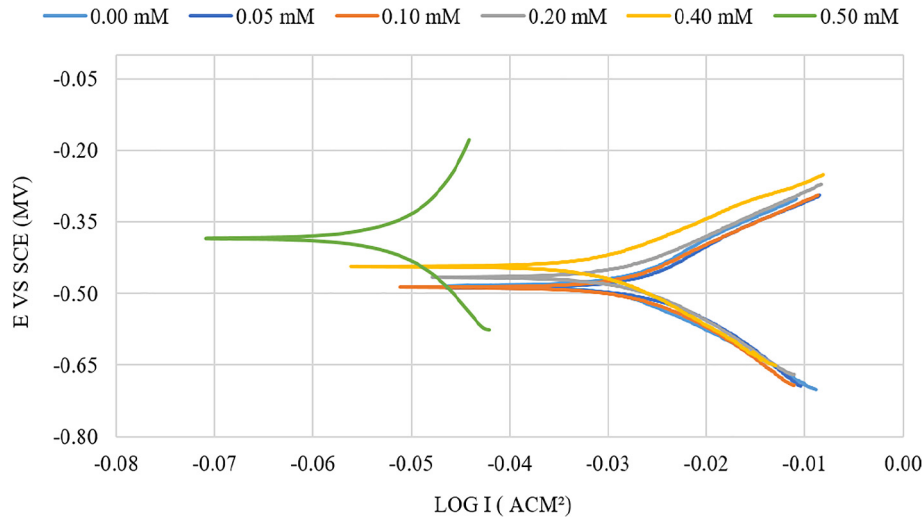
Fig. 5. The potentio-dynamic polarization curve for mild steel in 1.0 M HCl with different concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol.

Table 3
The polarization parameters for mild steel in 1.0 M HCl with different concentrations of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol.

Concentration (mM)	Potential Dynamic Polarization Parameters					
	β_a (V dec^{-1})	β_c (V dec^{-1})	I_{corr} (μAcm^{-2})	$-E_{corr}$ (mV vs SCE)	Corrosion rate (mpy)	IE (%)
Blank	0.1360	0.1298	659.00	489.00	7.6010	0.00
0.05	0.1291	0.1286	601.00	478.00	7.0040	10.53
0.10	0.1139	0.1209	408.00	468.00	4.8360	40.01
0.20	0.1021	0.1179	339.00	456.00	4.0150	48.60
0.40	0.0887	0.1140	180.00	449.00	2.0380	74.39
0.50	0.6012	0.4029	44.590	390.00	0.0529	93.21

Based on Fig. 5, E_{corr} value change to more negative can be detected with increased corrosion inhibitory concentrations. This suggests that a layer of protection on a mild steel sample was produced due to the absorption of corrosion inhibitor molecules on the surface of the metal sample [23]. Along with this, it also proves that the reduced density of anodic and cathodic current causes the absorption of molecules over the surface of the mild steel sample more easily and rapidly [24].

Based on Table 3 and Fig. 5 above, it is seen that the decreasing current density (I_{corr}) value decreases as the concentration of corrosion inhibitors increases and thus increases the efficiency (IE) of corrosion inhibitors as well. In addition, the anonical (βa) and cathodic tafels (βc) gradients change with increasing concentration of corrosion inhibitors. This shows that the concentration of corrosion inhibitors concentration affects the anodic and cathodic action and reaction [25].

The inhibition efficiencies increased with increasing of inhibitor concentration and this could have explained on the basis of

amount of adsorption with surfactant coverage molecules, increases with increasing concentrations. The inhibition performance increased parallel regarding to concentration inhibitor increased, that suggests the retardation of surface of mild steel corrosion in inhibited solution compared to uninhibited environment.

Next part of this experiment is using the same concentration of corrosion inhibitors ie 0.5 Mm but at different temperatures at temperatures of 30, 40, 50 and 60 °C. Based on Table 4 and Fig. 6, E_{corr} to more negative values can be detected from 376 to 464 mV with a value change of 285 mV. From literature found that if $E_{corr's}$ value exceeds 85 mV, it can be categorized as anodic or cathodic corrosion inhibitor [26]. This proves that the protective layer produced by the corrosion inhibitor molecule is weakening when the temperature of the solution increases. High temperatures result in corrosion inhibiting of corrosion inhibitor molecules on the surface of mild steel samples [27]. The Gamry Analyst software provides data as shown in Table 4 below. Corrosion resistance (i_{corr}) and corrosion rate are higher when the temperature of the solution

Table 4
Parameters of polarization for mild steel in 1.0 M HCl with 0.5 mM concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at different temperatures.

| Temp. (°C)	Concitra. (mM)	Potential Dynamic Parameter (PD)					
		β_a (Vdec^{-1})	β_c (Vdec^{-1})	I_{corr} (μAcm^{-2})	$-E_{corr}$ (mV vsSCE)	Corrosion rate(mpy)	IE (%)
30	Blank	0.1360	0.1298	667.00	487.00	7.6010	0.00
	0.5	0.5994	0.3990	45.020	376.00	0.4987	93.21
40	Blank	0.7021	0.6695	550.00	660.00	76.7000	0.00
	0.5	0.0711	0.1063	134.00	540.00	13.7200	76.05
50	Blank	0.9692	0.7201	819.00	669.00	114.7980	0.00
	0.5	0.1301	0.1300	420.00	479.00	419.1000	50.21
60	Blank	4.0200	2.0296	1559.00	680.00	630.4000	0.00
	0.5	0.1389	0.1430	0998.00	464.00	1015.9000	35.93
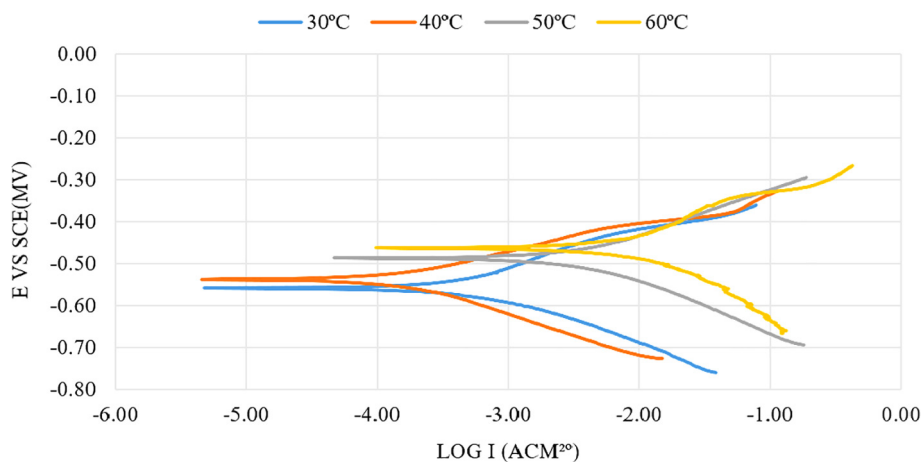
Fig. 6. The potentio-dynamic polarization curve for mild steel in 1.0 M HCl with 0.5 mM concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at different temperatures.

increases while the inhibition efficiency (IE) is decreasing as the corrosion inhibitor molecules on the surface of the mild steel sample are weakening and allowing the corrosion process to occur more quickly.

Electrochemical frequency modulation (EFM)

EFM is a corrosion-measuring technique that can directly provide corrosive values without the need to know the Tafel constant [28]. Like EIS, it is a small AC signal technique. Unlike EIS, however, two sine waves at different frequencies are used and applied to cells at the same time. This is due to the non-linear potential of the current, so the system reacts in a non-linear way to potential excitation [29]. Flow response not only contains frequency input, but also, the frequency component which is the increase, difference, and multiple input frequency gain [30]. The use of the Gamry Echem Analyst software for EFM has provided electrochemical parameters such as current density (Icorr), Tafel gradients (β1 and β2) and causality factors (CF-2 and CF-3).

Tables 5 and 6 shows EFM electrochemical parameters for mild steel sample in 1.0 M HCl at temperature of 30 °C with different corrosion-inhibitory concentrations and with same concentration 0.5 nM in different temperature. The reduced corrosion rate from 389.8 mpy to 30.79 mpy indicates the effectiveness of corrosion inhibitors used. Referring to the standard data provided by Venzlaff et al. [31] for factor causality values of factor 2 and 3, it can be concluded that the data below is accurate where the range of difference is only 0.1–0.3.

In addition, the efficiency of corrosion inhibitors (IE) is increasing by decreasing the density of the corrosion current (I_{corr}). The efficiency of the inhibitor is calculated by using the following formula:

$$IE \ (\%) \ \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$

where i^o_{corr} and i_{corr} are the density values of corrosion current without and with corrosion inhibitors.

Corrosion is a process that occur in nature and needs to be addressed and monitored primarily through industries that use mild steel as the main material of equipment which it always exposed to chemicals. This is because the corrosion process has a great impact on the metal surface. Prevention measures need to be taken before the corrosion problem is increasingly critical. By using corrosion inhibitors we can slow down the corrosion process

Table 5
EFM electrochemical parameters for mild steel in 1.0 M HCl at temperature of 30 °C with different concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol.

Cons. (mM)	I_{corr} (mAcm^{-2})	β_1 (mVdec^{-1})	β_2 (mVdec^{-1})	Corrosion rate (mpy)	IE$_{EFM}$ (%)	CF-2	CF-3
Blank	3.699	82.07	94.05	389.8	0.00	1.101	3.26
0.05	2.796	101.84	154.8	290.3	24.96	2.028	2.250
0.10	1.680	87.90	125.0	167.1	55.95	1.983	2.851
0.20	1.601	88.64	133.0	162.2	58.88	1.940	3.410
0.40	0.894	91.01	122.0	88.76	77.08	2.068	5.101
0.50	0.0106	104.2	110.9	30.97	99.68	1.657	3.702

Table 6
EFM electrochemical parameters for mild steel in 1.0 M HCl at different temperatures with 0.5 mM concentrations of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol.

| Temp. (°C)	Con. (mM)	I_{corr} (mAcm^{-2})	β_1 (mVdec^{-1})	β_2 (mVdec^{-1})	Corr. rate (mpy)	IE$_{EFM}$ (%)	CF-2	CF-3
30	Blank	3.6990	82.07	94.05	389.8	0.00	1.201	3.19
	0.5	0.0106	103.93	110.9	30.92	99.68	1.598	3.702
40	Blank	6.8100	90.03	112.0	693.00	0.00	1.988	3.004
	0.05	1.706	85.97	108.1	170.40	76.05	2.011	4.594
50	Blank	19.24	94.08	110.0	1950.00	0.00	2.060	5.807
	0.5	3.612	86.75	124.1	360.10	61.50	1.950	3.298
60	Blank	57.04	118.96	145.9	5806.0	0.00	1.803	2.920
	0.5	10.79	143.9	193.0	1110.0	60.97	1.909	3.095
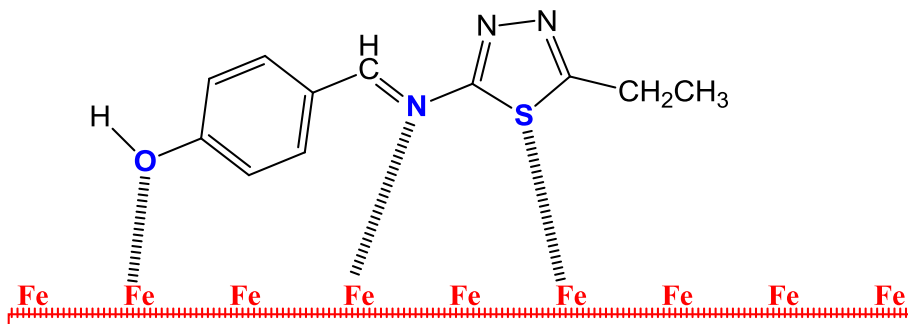
Fig. 7. Suggested mechanism of the inhibitor on mild steel.

or can be prevent it from occur. Experiments that carried out in this paper are electrochemical measurements to test the effectiveness of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitors on mild steel in 1.0 M solution of hydrochloric acid (HCl). Among running the experiments the electrochemical impedance spectroscopy (EIS), Potentio-dynamic Polarization, Open Circuit Potential (OCP) and electrochemical frequency permits (EFM) were carried out to prove efficiency of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitor.

Conclusions

The results of electrochemical impedance spectroscopy (EIS), Potentio-dynamic Polarization and electrochemical frequency modulation (EFM) show that the corrosion-resistant of 4-hydroxy benzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol was able to reduce and slow down the corrosion process on mild steel caused by hydrochloric acid solution (HCl). For experiments using different concentrations at the same temperature, the results showed that the highest inhibitory efficiency was at 0.5 mM concentration with 90.86% for EIS, 93.21% for potentio-dynamic polarization and 99.65% for EFM. While for experiments using the same concentration at different temperatures, giving the opposite result where the highest inhibitor efficiency is at the lowest temperature at 30 °C where 90.86% for EIS, 93.21% for potentio-dynamic polarization and 99.65% for EFM. Based on the data received from the Gamry Analyst software, it is obvious that the increased concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol provides a protective layer that helps to prevent or slow down the corrosion process of mild steel while the increase in temperature of the solution causes a weakness in the corrosion prevention layer of corrosion inhibitor protection further more allowing and accelerating the process of corrosion on the mild steel.

The mechanism of inhibition

The inhibition performance of this inhibitor versus the corrosion of alloy in acidic solution could be demonstrate regarding to adsorption sites number, charge density and the performance to form a coordination bonds. The selection of our inhibitor was regarding to molecular structure. The molecular structure was in Fig. 7. The inhibition effectiveness of this 4-hydroxybenzylidenea minomethyl-5-ethyl-1,3,4-thiadiazol have consist fundamentally on nature and structure of the adsorb layers on the surface of alloy. Our inhibitor has hetro-aromatic ring, aromatic benzene ring, azomethane group and heteroatoms, N, O, and S that have higher electron density and were act as protected layer on the surface of alloy by forming a coordination bonds between the inhibitor and the surface of iron as in Fig. 7.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.rinp.2018.02.015.

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