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Study of the influence of new quinoxaline derivatives on corrosion inhibition of mild steel in hydrochloric acidic medium

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Abstract

The effect of a new corrosion inhibitors, namely 3,7-dimethylquinoxalin-2 (1H)-one (DMQ=O) and 3,7-dimethylquinoxalin-2 (1H)-thione (DMQ=S), on corrosion of mild steel in 1 M HCl was investigated by weight loss measurement and various electrochemical techniques. Results obtained reveal that all the compounds perform excellently as corrosion inhibitors for mild steel in acidic media. Potentiodynamic polarization studies have shown that all these compounds slow down both the anodic and cathodic processes and then act mixed-type inhibitors. Double layer capacitance and charge transfer resistance values were derived from Nyquist plots. Changes in impedance parameters are indicative of adsorption of these compounds on the metal surface. The inhibition efficiency mainly depends on the nature of the investigated compounds. The adsorption of these compounds on mild steel surface is found to obey Langmuir adsorption isotherm.

Key words: Quinoxaline derivatives, corrosion inhibition, adsorption, mild steel, hydrochloric acidic medium

1. Introduction

Hydrochloric acid is widely used in industries, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. It is also used for removal of oxide from metallic parts before applying coating. The use of acid solution during industrial applications leads to the corrosive attack on metal. Therefore, inhibitors are commonly used to minimize metal dissolution and acid consumption.

Various types of organic compounds are widely used as corrosion inhibitors for protection materials against corrosion deterioration [1]. A perusal of the literature on acid corrosion inhibitors reveals that most organic substance employed as corrosion inhibitors act by adsorption on the metal surface. Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surface [2–10]. The adsorption mainly depends on the presence of π-electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface mild steel [11–15]. The compounds containing both nitrogen and sulphur can provide excellent inhibition compared to those containing only nitrogen or sulphur [16]. In recent years, N- and S-containing triazole derivatives have attracted more attention for their excellent corrosion inhibition performance [17–24]. In contrast to most commercial acid corrosion inhibitors which are highly toxic, many N- and S-containing triazole derivatives are environmentally friendly corrosion inhibitors [18,19].

In view of the excellent performance of N- and S containing organic compounds, were newly synthesized in our organic laboratory partner, with the objective to evaluate the influence of these compounds on corrosion inhibition of mild steel in 1M HCl. The mode of adsorption mechanism is also discussed.

2. Experimental details

2.1. Material preparation

The structural formulas of the inhibitors examined in this study are shown in Fig. 1. Corrosion tests were performed on a mild steel of following percentage composition 0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and remainder iron. The surface of specimens was carried out by grinding with emery paper of different grit sizes, rinsing with distilled water, degreasing in ethanol, and drying before use. The aggressive solution of 1 M HCl was prepared by dilution of Analytical Grade 37% HCl with distilled water.

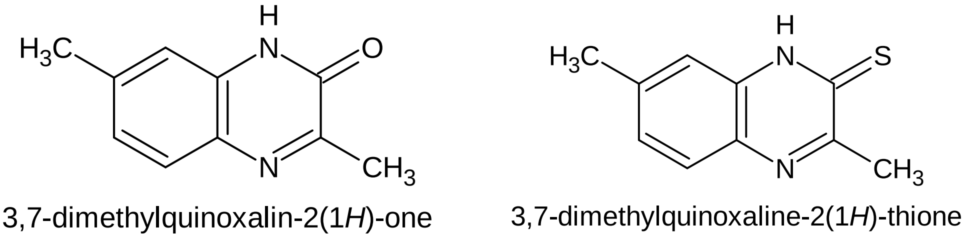

Figure 1 : The chemical formulas of the studied organic compounds.

2.2. Weight loss measurements

Weight loss measurements were carried out as described in the literature [25]. Rectangular ordinary steel specimens of size (4 cm ×1 cm × 0.05 cm) were used as samples for corrosion tests. After having been polished with emery paper (400–1200 grade) successively and weighted, the samples were immersed for one day in 100 ml of uninhibited and inhibited solutions at 20°C in the air. At the end of experiments, the specimens were cleaned according to ASTM G-81 and reweighed to 10^{-4}g for determining corrosion rate [25].

The inhibition efficiency (IE%) is defined as follows:

$$IE\ (\%) = \frac{\omega_0 - \omega}{\omega_0} \times 100 \qquad (1)$$

The values of surface coverage (θ) have been obtained from weight loss measurement for various concentrations of compound. Here, θ can be given as [17]:

$$\theta = \frac{\omega_0 - \omega}{\omega_0 - \omega_m} \qquad (2)$$

Where ω_0 and ω are the values of corrosion weight loss after immersion in solution without and with inhibitor, respectively, and ω_m is the corrosion weight loss giving a maximum inhibition obtained in our case at 10^{-4} M and 10^{-2} M for DMQ=O and DMQ=S, respectively.

2.3. Electrochemical measurements

For electrochemical measurements, a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference was used. Mild steel cylindrical rod of the same composition as working electrode were pressure fitted into a polytetrafluoroethylene holder (PTFE) exposing only 1 cm^2 surface to the solution. The test solution was thermostatically controlled at 20°C in air atmosphere without bubbling. All potentials were measured against SCE.

The polarization curves were recorded by changing the electrode potential automatically with a Potentiostat/Galvanostat type PGZ 100, at a scan rate of 1 mV/s. Before each experiment, the working electrode was immersed in the test cell for 30 min until reaching steady state.

The data in Tafel region have been processed for evaluation corrosion kinetic parameters by plotting the polarization curves. The linear Tafel segments of the anodic curves were extrapolated to corrosion potential for obtaining the corrosion current values. The inhibition efficiency was evaluated using the relationship:

$$IE\ \% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad (3)$$

Where i^0_{corr} and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (VoltaLab PGZ 100), with a small amplitude ac. Signal (10 mV rms), over a frequency domain from 100 KHz to 10 mHz at 20°C and an air atmosphere. To determine the impedance parameters of the mild steel specimens in acidic solution, the measured impedance data were analyzed using Bouckamp program based upon the electric equivalent circuit [27]. The inhibition efficiency of the inhibitor has been found from the relationship:

$$IE = \frac{R_t - R_t^0}{R_t} \times 100 \qquad (4)$$

Where R_t^0 and R_t are the resistance transfer charge values in the absence and the presence of inhibitor, respectively.

3. Results and discussion

3.1. Corrosion weight loss tests

Table 1 summarized values of the inhibition efficiency obtained from weight loss measurements and surface coverage of mild steel at different inhibitors concentrations in 1 M HCl at 20°C after 24 hours of immersion. Two tests of corrosion weight loss were realized and apparent precision resulting from used material and reproducibility was esteemed to 86%.

The inhibition efficiency increases with the increase of inhibitor concentration and reaches a maximum at 10^{-4} M for DMQ=O and at 10^{-2} M for DMQ=S. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of inhibitors with the increase of their concentration.

Table 1 : Inhibition efficiency of mild steel in 1M HCl obtained from weight loss measurements at 20°C for various concentrations of inhibitors

Compounds	Conc. M	Corrosion weight loss ($mg.cm^{-2}.h^{-1}$)	θ	IE%
Blank solution	00	0.2510	--	--
DMQ=O	10^{-6}	0.0750	0.8622	70
	10^{-5}	0.0677	0.8979	73
	10^{-4}	0.0469	1	81
	10^{-3}	0.1172	0.6556	67
	10^{-2}	0.1266	0.6096	50
DMQ=S	10^{-3}	0.0505	0.929	80
	5×10^{-3}	0.0448	0.959	82
	10^{-2}	0.0354	1	86
	5×10^{-2}	0.0445	0.955	82

3.2. Polarization curves

Figures 2 and 3 show polarization curves for mild steel in 1M HCl with and without various concentration of DMQ=O and DMQ=S. It is clear that the addition of inhibitors hindered the acid attack on the steel electrode and a comparison of curves in both cases, showed that, with respect to the blank, increasing the concentration of the inhibitors gave rise to a consistent decrease in anodic and cathodic current densities indicating that inhibitors acts as mixed type inhibitor [28].

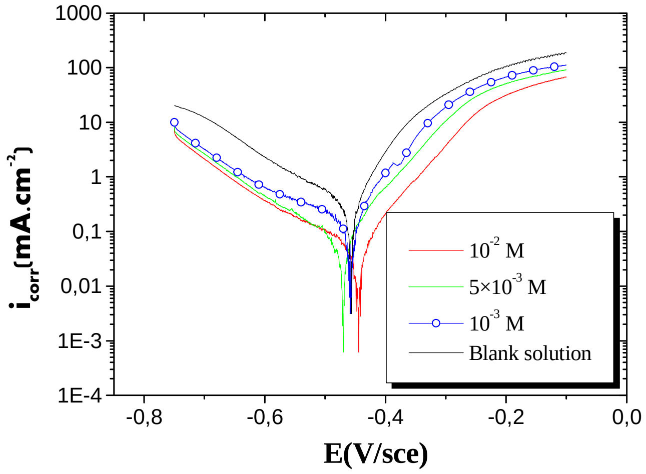

Figure 2: Polarization curves of mild steel recorded in 1M HCl at different concentrations of DMQ=S

Table 2 : Inhibition efficiency and electrochemical parameters for the mild steel corrosion in 1M HCl at 20°C, for various concentrations of DMQ=O and DMQ=S

Compounds	Conc. (M)	E_{corr} (mV/sce)	i_{corr} (μA/cm^2)	b_a (mV/deÿÿ	b_c (mV/dec)	IE °/°
Blank solution	ÿÿ	-456	290	64.5	-146.4	-
DMQ=O	10^{-6}	-453.1	82	66.6	-133.1	72
	10^{-5}	-451.2	76	66.5	-123.5	74
	10^{-4}	-455.5	54	63.3	-142.4	81
	10^{-3}	-452.5	98	66.3	-134.2	66
	10^{-2}	-450.8	154	87.9	-143.6	47
DMQ=S	10^{-3}	-470.9	100	77	-162.3	65
	5×10^{-3}	-460.2	71.3	70.9	-256.9	75
	10^{-2}	-446.1	57.2	77.3	-200.6	80

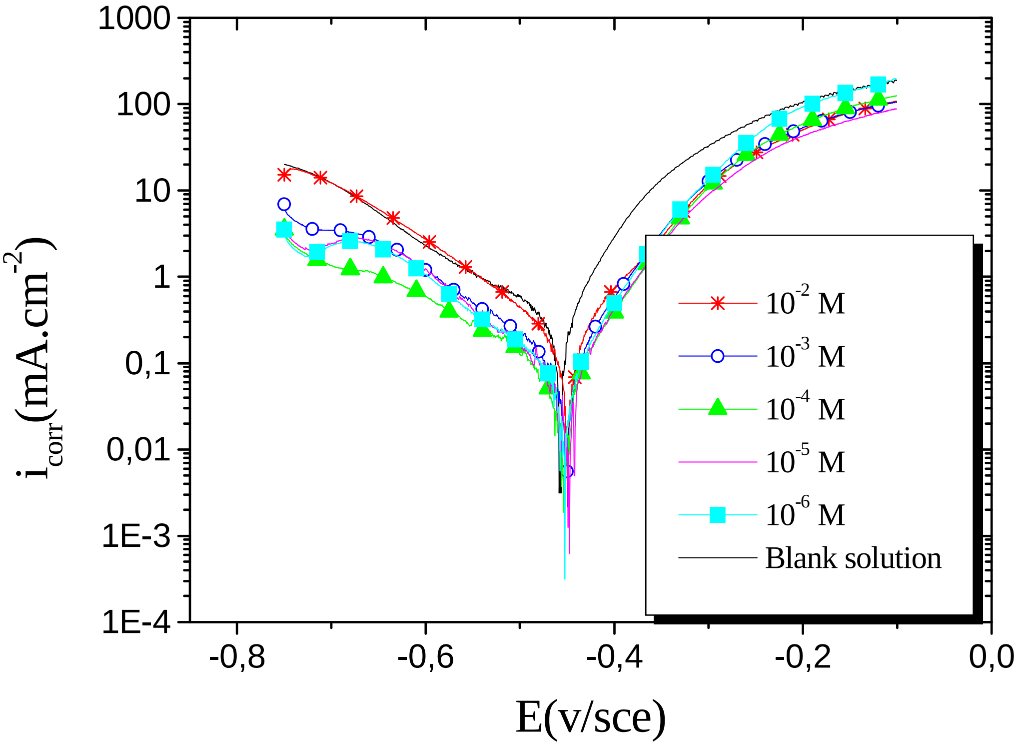

Figure 3 : Polarization curves of mild steel recoded in 1M HCl at different concentrations of DMQ=O

3.3. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of mild steel in 1 M HCl solution in the presence of the studied organic compounds was also investigated by the EIS method at 20°C after 30 min of immersion. Typical Nyquist diagrams obtained in the presence of these compounds at different content in 1 M HCl are shown in Fig. 4 and 5. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [30, 31].

It is apparent from these plots that the impedance response of mild steel in uninhibited HCl solution has significantly changed after the addition of inhibitors. The kinetic parameters derived from the Nyquist plots and percentage inhibition efficiency are given in Table 3. The greatest effect was observed at 10^{-2} M of DMQ=S where R_t is 893 Ω.cm^2, and at 10^{-4} M of DMQ=O which produced R_t value of 503 Ω.cm^2 in 1M HCl. For all compounds, when the concentration increased the C_{dl} values decreased. These results can be imputed to a decrease result in local dielectric constant and/or an increase in the thickness of the electrical double layer suggests that the inhibitors molecules function by adsorption at the metal–solution interface [32]. The inhibition efficiency of DMQ=S is found to be greater than of DMQ=O. This may be due to the availability of more sites on metallic surface in inhibitor DMQ=S solution because of the easer adsorption of the sulphur ions on the steel surface [33]. EIS impedance study also confirms the inhibiting character of inhibitors obtained with polarization curves and weight loss measurements in 1M HCl medium.

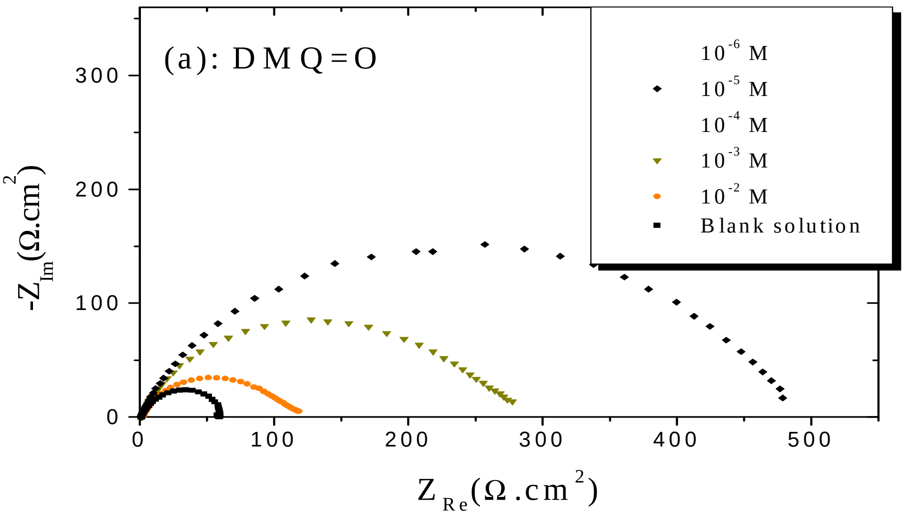

Figure 4: Nyquist diagrams for mild steel in 1M HCl at different concentrations of DMQ=O.

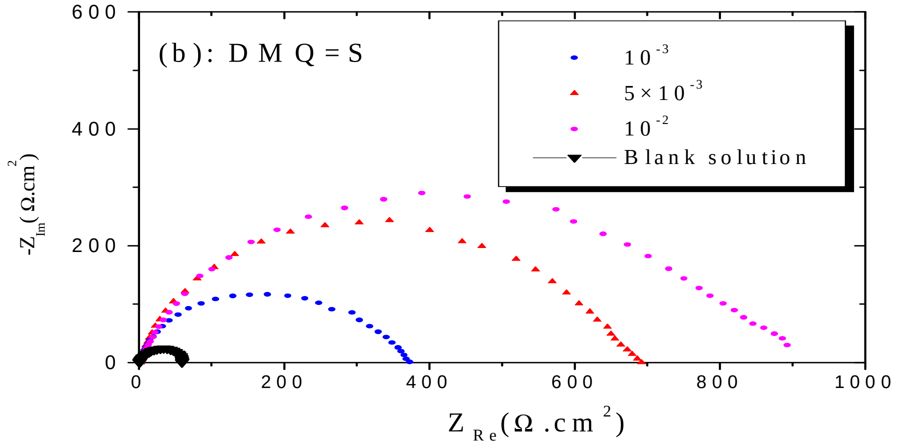

Figure 5: Nyquist diagrams for mild steel in 1M HCl at different concentrations of DMQ=S.

Table 3: Impedance data and inhibition efficiency for mild steel in 1M HCl at different concentration of inhibitors.

Compounds	Conc. (M)	E_{corr} (mV/sce)	R_t ($\Omega.cm^2$)	C_{dl} ($\mu F.cm^{-2}$)	IE °/°
Blank solution	00	-490	60	912	------
DMQ=O	10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2}	-491 -490 -474 -468 -468	469 478 503 277 118	334 333 330 353 511	87.20 87.44 88.07 78.33 49.15
DMQ=S	10^{-3} 5×10^{-3} 10^{-2}	-510 -483 -492	400 700 893	320 230 100	85.01 91.42 93.27

3.4. Effect of temperature

The effect of temperature on inhibition efficiency was determined in 1M HCl containing 10^{-2} M of DMQ=S and 10^{-4} M of DMQ=O at range temperatures 20-60°C using potentiondynammic polarization curves. The results are given are given in table 4. Corrosion current density for steel increased more rapidly with temperature in the absence of inhibitor. These result confirmed that these compounds act as efficient inhibitors in the studied rang of temperature. The corrosion reaction can be regarded as an Arrhenius-type process, the rate of which is:

$$i_{corr} = K\ exp\ (-\ E_a/RT) \qquad (5)$$

where I_{corr} is the corrosion current density, E_a is the apparent activation corrosion energy, T is the absolute temperature, K is the Arrhenius pre-exponential constant and R is the universal gas constant.
This equation can be used to calculate the E_a values of the corrosion reaction without and with 10^{-2} M of DMQ=S and 10^{-4} M of DMQ=O. Plotting the logarithm of the corrosion current density against 1/T., the activation energy can be calculated from the slope. Arrhenius plots for the corrosion current density of mild steel are given in figure 6. The calculated values of the apparent activation corrosion energy in the absence and the presence of DMQ=O and DMQ=S are 50.54 $KJ.mol^{-1}$, 10.17 $KJ.mol^{-1}$ and 8.08 KJ mol^{-1}, respectively. The reduction in the activation energy in the presence of inhibitors may be attributed to the chemisorptions of inhibitors on steel surface [34, 35].

Table 4: Electrochemical parameters of mild steel in 1 M HCl with and without 10^{-2} M of DMQ=S and 10^{-4} M of DMQ=O at various temperatures.

	Temperature (°C)	E_{corr} (mV/sce)	i_{corr} ($\mu A/cm^2$)	IE %
Blank solution	20	-459	290	--
	30	-440	392	--
	40	-441.9	492	--
	50	-448.2	1628	--
	60	-441.5	3293	--
DMQ=O	20	-455.5	54	80
	30	-431.5	75	74
	40	-444.1	75	74
	50	-431.7	84	70
	60	-431.5	95	67
DMQ=S	20	-446.1	57	80
	30	-446.4	69	76
	40	-397.6	75	74
	50	-398.3	85	70
	60	-402.6	84	70

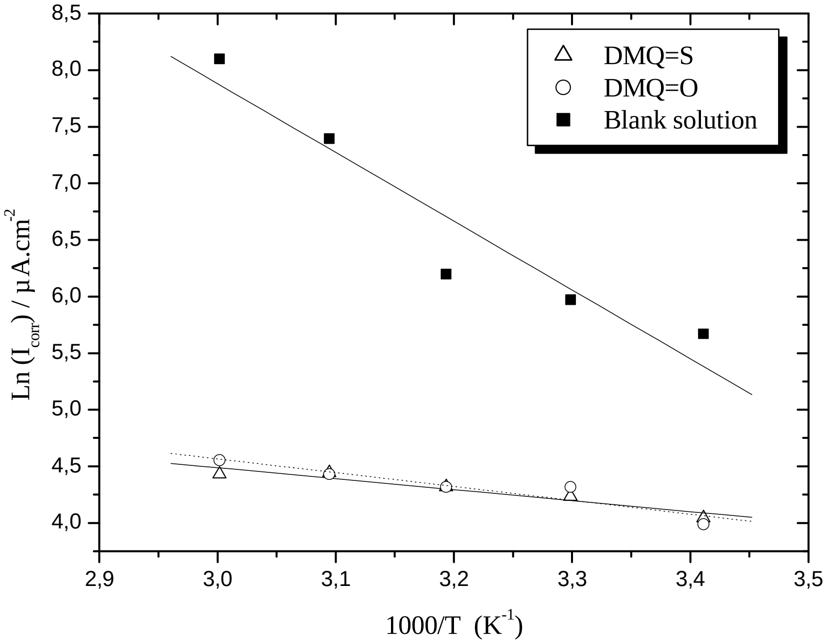

Figure 6: Relation between corrosion rate and reciprocal of temperature with and without inhibitors

3.5. Immersion time

Figure 7 and 8 show the impedance spectra obtained after different immersion times in aerated 1 M HCl with and without 10^{-2} M of DMQ=S and 10^{-4} M of DMQ=O, separately .

The evolution of the characteristic parameters associated with the capacitive loop with time is summarized in Table 5. The diameter of the capacitive loop increases in size with increasing immersion time, reaching a maximum after 2 h, and then starts to decrease. These results indicate that the adsorption model, arrangement and orientation of inhibitor on the surface of the carbon steel, changes with time. Considering that adsorption is essentially controlled by electrostatic attraction, as the immersion time increases, more chlorides will be adsorbed on the surface helping to the formation of the inhibitor layers [36].

However as soon as all the active sites become saturated with inhibitor, the development of the inhibitor layer is gradually slows down. Furthermore, with time it seems the inhibiting effect decreases probably because some defects exist on the film leading to the access of aggressive anions to the mild steel/inhibitor interface. The formation of these weaker sites can be explained with basis in literature [37], where the decrease of the inhibition efficiency was attributed to the formation of film by the initially deposited inhibitor molecules, reducing the effective area covered by the inhibitor.

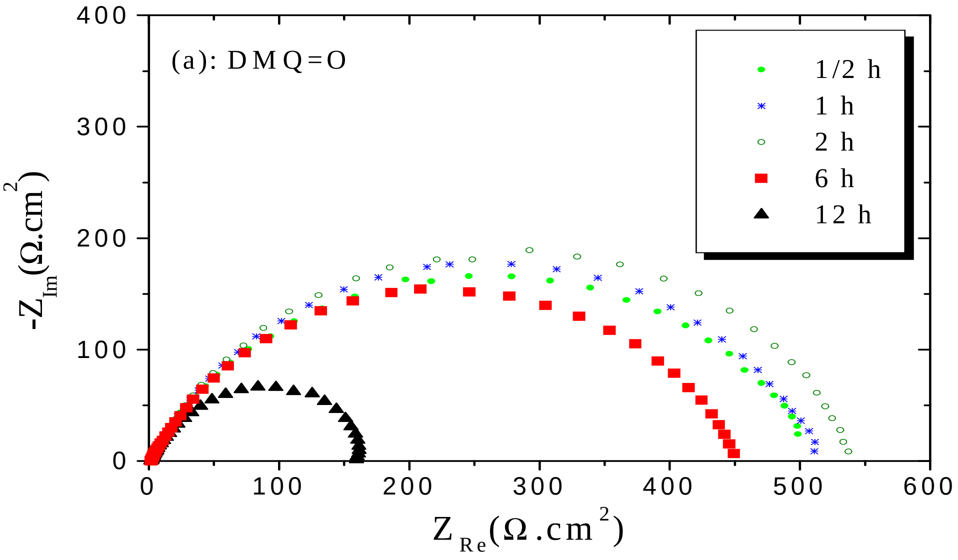

Figure 7 : Nyquist diagrams for mild steel in 1M HCl at different time immersion of 10^{-4} M for DMQ=O

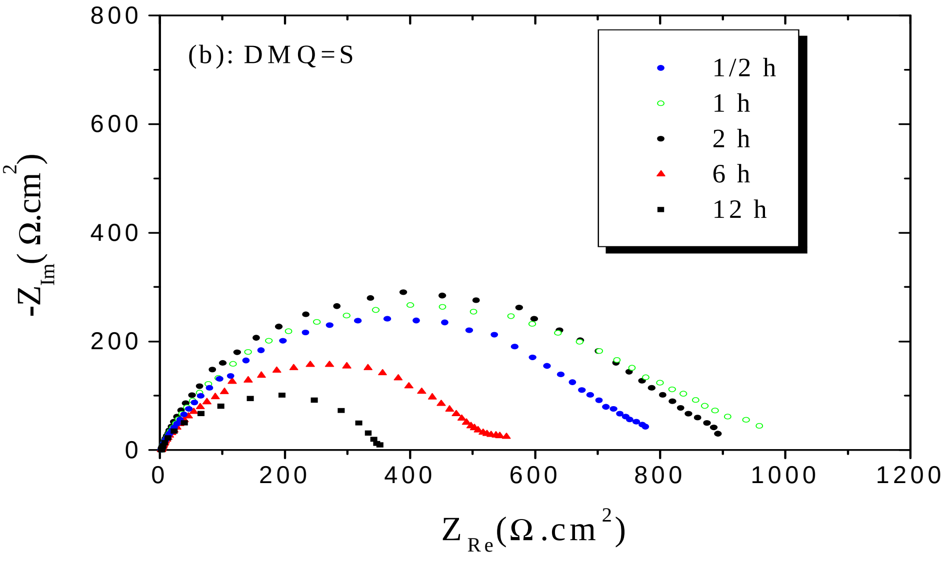

Figure 8 : Nyquist diagrams for mild steel in 1M HCl at different time immersion of 10^{-2} M for DMQ=S

Table 5: EIS parameters for mild steel in 1 M HCl with 10^{-2} M of DMQ=S and 10^{-4} M of DMQ=O after different immersion times

Compounds	Immersion time (h)	E (mV/sce)	R_t ($\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)
DMQ=O	1/2	-474	503	330
	1	-484	537	310
	2	-486	513	313
	4	-490	452	404
	6	-488	416	447
	12	-496	155	600
DMQ=S	1/2	-492	893	100
	1	-455	958	98
	2	-510	967	101
	4	-518	776	160
	6	-548	551	178
	12	-560	352	200

3.5. Adsorption isotherm

The values of surface coverage, θ, corresponding to different concentrations of DMQ=O and DMQ=S have been used to explain the best isotherm to determine the adsorption process. The adsorption of an organic adsorbatate at a metal-solution interface can be represented as substutional adsorption process between the organic molecules in the aqueous solution Org (sol) and the water molecules on the metallic surface H_2O (ads) [38]:

$$\text{ORG (sol)} + \text{Y } H_2O \text{ (ads)} \rightleftharpoons \text{ORG (ads)} + \text{X}H_2O \text{ (sol)}$$

Where ORG (sol) and ORG (ads) are the organic molecules in the aqueous solution and adsorbed on the metallic surface, respectively, H_2O (ads) is the water molecules on metallic surface, Y is the size ratio representing the number of water molecules replaced by one molecule of organic adsobate

The values of surface coverage θ have been obtained from weight loss measurement for various concentrations of inhibitors. Attempts were made to fit θ values to various isotherms including frumkin, Longmuir and Timken. By far the best fit was obtained with the Longmuir isotherm. This Longmuir model has been used for other inhibitor systems [39,36].

A correlation between θ and inhibitor concentration (C) in the electrolyte can be represented by the Langmuir adsorption isotherm [40]:

$$\theta = \frac{KC}{1+KC} \tag{6}$$

Rearranging this equation

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{7}$$

where K is the constant of adsorption. The relation between C/ θ and C at 20°C for both compounds is shown in Figure 9 and 10. The plot of C/ θ versus inhibitor concentration (C) showed a linear correlation of slope close to unit. The strong correlation (r = 0.99967 with DMQ=O and r = 0, 99975 with DMQ=O and DMQ=S for the Langmuir adsorption isotherm plot confirmed the validity of this approach. The constant K may be determined from the intercept in Figure 9 and 10.

The adsorption constant K is in relation with the free energy of adsorption [41]:

$$K = \frac{1}{55.55} \exp(-\frac{\Delta G_{ads}}{RT}) \tag{8}$$

where R is the universal gas constant, value 55.55 is the water concentration in the solution (mol/l).

The value of the adsorption free energy ΔG_{ads} is calculated from the adsorption isotherm, it is about -31.27 kJ.mol^{-1} and -44.51 kJ.mol^{-1} with DMQ=S and DMQ=O, respectively, at 20°C. Generally, the values of ΔG_{ads} below -20 kJ. mol^{-1} are consistent with electrostatic interaction, while those above -40 kJ.mol^{-1} involve chemisorption [42]. The value of ΔG_{ads} for DMQ=O and DMQ=S point to the spontaneity of the adsorption process under investigated experimental conditions and it also point out the adsorption of this compound occur predominantly by chemisorption. The largest negative value of $\Delta G°_{ads}$ in the case of 1M HCl with DMQ=S indicates that the inhibitor is strongly adsorbed on the steel surface [43].

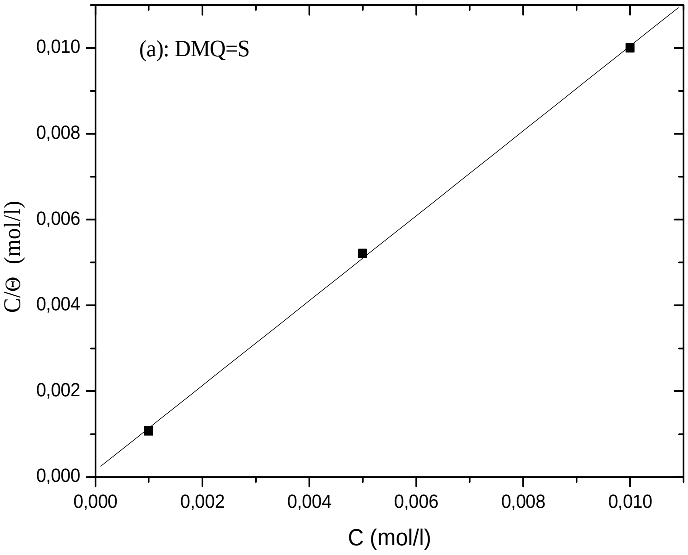

Figure 9: Langmuir isotherm adsorption of DMQ=S in 1M HCl from weight loss measurements at 20 °C

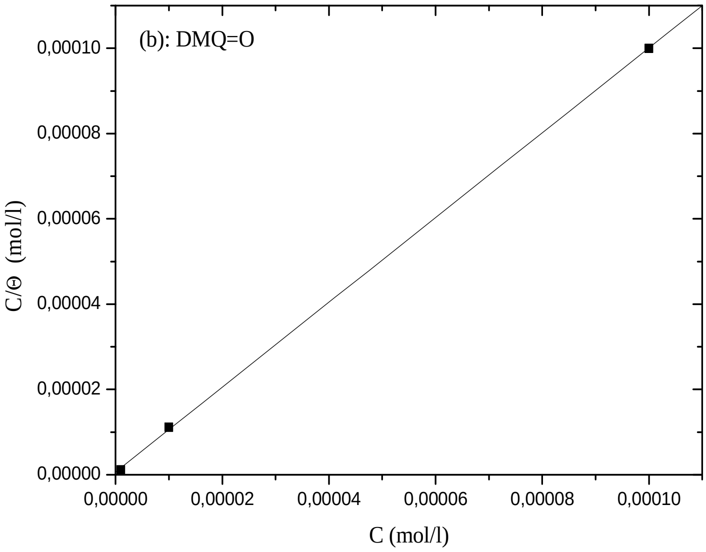

Figure 10: Langmuir isotherm adsorption of DMQ=O in 1M HCl from weight loss measurements at 20 °C

4. Conclusion

DMQ=O and DMQ=S inhibits the corrosion of mild steel in 1 M HCl medium and the better performance is seen in the case of DMQ=S.

The adsorbed inhibitors molecules are assumed to retard corrosion by reducing the number of available surface sites for corrosion and also by slowing the rate of the corrosion reactions.

DMQ=O and DMQ=S are found to effect both the cathodic and anodic process; that is, the inhibitors are of mixed type. The concentration dependence of the inhibition efficiency calculated from weight loss measurements and electrochemical studies has the same tendency.

The inhibition efficiency of inhibitors is temperature dependent and its addition leads to a decease in activation corrosion energy.

Adsorption of DMQ=S and DMQ=O on mild steel surface in 1 M HCl flow the Langmuir isotherm , indicating that the main inhibition process occurs via adsorption . The negative values of ΔG_{ads} obtained from this study indicate that inhibitors are strongly adsorbed on the steel surface.

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