New synthesized 1,4-benzodiazine derivatives as corrosion inhibitors for mild steel in sulphuric acid

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ABSTRACT

A new corrosion inhibitors namely 3,7-dimethylquinoxalin-2(1H)-one (CH3-Q=O) and 3,7- dimethylquinoxaline-2(1H)-thione (CH3-Q=S) were undertaken and their inhibitive performance towards mild steel corrosion of in 0.5 M sulphuric acid at 20°C has been investigated. The study of corrosion inhibition was conducted by weight loss, polarization curves and electrochemical impedance spectroscopy (EIS) measurements. These studies have shown that CH3-Q=O and CH3-Q=S were with distinguishable inhibition efficiencies in sulphuric acid. Polarization measurements reveal that the CH3-Q=O was cathodic type inhibitor whereas CH3-Q=S was a mixed-type inhibitor. Data obtained from EIS were analyzed to model the corrosion inhibition process through equivalent circuit. Comparable results were obtained by the different chemical and electrochemical methods used. Activation energies of the corrosion process in absence and presence of inhibitors were obtained by measuring the temperature dependence of the corrosion current density. The adsorption of inhibitors on metallic surface in corrosive medium was found to obey Langmuir's adsorption isotherm.

Keywords: Quinoxaline derivatives, Acidic media, Corrosion and inhibition, Mild steel, EIS.
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INTRODUCTION

Corrosion problems have received a considerable amount of attention because of their economic and safety consequences. The use of inhibitors is one of the most practical methods for protection against corrosion. Due to its prominent properties, hydrochloric and sulfuric acids are widely used in industry, for example, acid pickling, industrial acid cleaning, acid descalling and oil well cleaning. In previous works, the influence of organic compounds containing nitrogen on the corrosion of mild steel in acidic media has been studied [1-6]. So, most of the excellent acid inhibitors are organic compounds containing nitrogen [7-12], sulfur [11-19], oxygen [10, 16, 20-24], phosphorus [25] and both nitrogen and oxygen or sulfur [26,27].

Other studies confirm that the adsorption of corrosion inhibitors depends mainly on certain physicochemical proprieties of the molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons [28,29] and also on the electronic structure of the molecules [30]. The CH3-Q=O and CH3-Q=S, is an example of a new class of corrosion inhibitors whose inhibiting effect has already been shown recently in 1 M HCl [26].

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The aim of the present work is to investigate its efficiency for corrosion in 0.5 M H_2SO_4. Several chemical and electrochemical techniques have been used. The mode of adsorption and the corrosion inhibition mechanism on steel in acidic solution are also discussed.

MATERIALS AND METHODS

The molecular formulas of the studied inhibitors CH3-Q=O and CH3-Q=S 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. Steel rods were mounted in Teflon (surface area 1 cm^2). 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 corrosion solution of 0.5 M H_2SO_4 were prepared by dilution of analytical grade 95-97% H_2SO_4 with doubly distilled water.

Weight loss measurements carried out using the mild steel (4cm×1cm×0.05cm). The time of immersion was 6 hours and the solution volume was 50 mL. The cleaned samples weighed before and after immersion in acidic solution. The weight loss was expressed in g cm^{-2} h^{-1}.

The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the mild steel rod as working electrode (WE), platinum mesh as counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode.

The electrode potential was allowed to stabilize during 30 min before starting the measurements. All experiments were conducted at 20°C. Measurements were performed with a Potentiostat/Galvanostat PGZ 100, along with a computer for collecting the data. Volta Master 4.0 Software was used for plotting, graphing and fitting data.

Tafel curves were obtained by changing the electrode potential automatically from circa (-300 mV_{SCE} to $+300$ mV_{SCE}) versus open circuit potential with scan rate of 1 mV s^{-1}. The data in Tafel region have been processed for evaluation corrosion kinetic parameters by plotting the polarization curves. The linear Tafel segments, in a large domain of potential, were extrapolated to the corresponding corrosion potentials to obtain the corrosion current values. The inhibition efficiency was evaluated using the following relationship:

$$IE_{I-E}\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \qquad (1)$$

i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitors, respectively.

EIS measurements were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 10 mV peak-to-peak using ac signals at open circuit potential. The inhibition efficiency of the inhibitors has been determined from the relationship:

$$IE_{imp}\% = \frac{R_t - R_t^0}{R_t} \times 100 \qquad (2)$$

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

RESULTS AND DISCUSSION

3.1. Corrosion weight loss tests
The corrosion parameters such as inhibition efficiency (IE%) and corrosion rate at different concentrations of CH3-Q=O and CH3-Q=S in 0.5 M H_2SO_4 at 20°C are presented in Table 1. From the determined weight loss values, the inhibition efficiencies, $IE_W\%$, were calculated using the following equation [31]:

$$IE_W(\%) = \frac{\omega_0 - \omega}{\omega_0} \times 100 \qquad (3)$$

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ω_0 and ω are the weight loss in the absence and the presence of inhibitor, respectively.

The values of surface coverage (θ) have been obtained from weight loss measurements for various concentrations of inhibitors, Here, θ can be given as [32]:

$$\theta = \frac{\omega_0 - \omega}{\omega_0 - \omega_{max}} \qquad\qquad (4)$$

ω_{max} is the corrosion weight loss giving a maximum inhibition.

We note that CH3-Q=O and CH3-Q=S inhibited the corrosion of mild steel in acidic media. As corrosion rate decreased, inhibition efficiency increased with increasing concentration and reach a maximum at 10^{-4} M and 10^{-2} M CH3-Q=O and CH3-Q=S, respectively. The presence of CH3-Q=S gave high inhibiting efficiencies and CH3-Q=O somewhat lower efficiency in 0.5 M H_2SO_4. This is probably due to the presence of sulphur atom in the case of CH3-Q=S. According to Every and Riggs [33], the organic compounds containing the nitrogen and sulphur have better inhibition efficiency, in acidic media, compared to the organic compounds containing nitrogen or sulphur. Beside, inhibitors containing oxygen are more recognized to be efficient in hydrochloric acid than in sulphuric one. Indeed, CH3-Q=O has exhibited an inhibiting efficiency of 81 % in 1 M HCl [26] whereas in 0.5 M H_2SO_4, it attains almost 40%.

3.2. Polarization curves
Figures 2 and 3 show polarization curves for mild steel in 0.5 M H_2SO_4 with and without various concentrations of CH3-Q=O and CH3-Q=S. It is clear that the addition of inhibitors hindered the acid attack on the mild steel electrode and a comparison of curves in both cases, showed that, with respect to the blank solution, increasing the concentration of CH3-Q=S gave rise to a consistent decrease in anodic and cathodic current densities indicating that inhibitors acts as a mixed type inhibitor [34]. Whereas we note for CH3-Q=O that only the cathodic branch is affected by CH3-Q=O addition and that the corrosion potential E_{corr} shifts cathodically in 0.5 M H_2SO_4 indicating that CH3-Q=O acts as cathodic type inhibitor.

Table 2 shows the electrochemical kinetics parameters, as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a, b_c) and corrosion current density (i_{corr}), obtained by extrapolation of the Tafel lines. The fact that cathodic process slow down can be due to the covering of the surface with monolayer of the tested molecules due to the adsorbed inhibitors on the mild steel surface then reducing the electrolyte infiltration to the interface. This idea is investigated in separate section by plotting of suitable adsorption isotherm. From Table 2, it can also be seen that i_{corr} values decreased substantially with increasing inhibitors concentration and reached a minimum at 10^{-3} M whereas $IE_{I-E}\%$ increases with inhibitors concentration.

3.3. EIS Measurements
Nyquist representation of mild steel in uninhibited and inhibited acidic solution containing various concentrations of CH3-Q=O and CH3-Q=S are presented in Figs. 4 and 5. It is obvious from these plots that the impedance response of mild steel has significantly changed after addition of both inhibitors; the shapes of the impedance diagrams for inhibited electrodes are not substantially different from those of uninhibited electrodes except in terms of size. Accordingly, the presence of the undertaken inhibitors increases the impedance but does not change other aspects of the behavior.

To determine the impedance parameters of the mild steel specimens in sulphuric solution, the measured impedance data were analyzed using Bouckamp program [35] based upon the electric equivalent circuit given in Fig. 6. The equivalent circuit consists of Constant Phase Element (CPE) in parallel with charge transfer resistance R_{ct} which are in series with solution resistance R_s. Values of these components and inhibition efficiencies are derived from EIS measurements and presented in Table 3. It is clear from Table 3 that the impedance of the inhibited system increased and the CPE values decreased with increasing CH3-Q=O and CH3-Q=S concentrations. Decrease in the CPE, which can result from a decreases 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 [36]. The inhibition efficiencies of CH3-Q=S is found to be greater than of CH3-Q=O. This may be due to the availability of more sites on the metal surface in inhibitor CH3-Q=S solution because of the lesser adsorption of the sulphur ions on the steel surface [37]. EIS study also confirms the inhibiting character of inhibitors obtained with polarization curves and weight loss measurements.

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3.4. Effect of temperature

Figures 7-9, show the Tafel plots of mild steel in 0.5 M H_2SO_4 in absence and presence of 10^{-4} M of CH3-Q=O and 10^{-2} M of CH3-Q=S in temperature range 20-60°C. Effect of temperature has been studied in order to recognize the activation energy of the corrosion process and the thermodynamics of inhibitors adsorption on mild steel surface. Data in Table 4 show that by increasing the temperature the corrosion rate increases in absence and presence of both inhibitors. Also, the corrosion rate increases rapidly in absence of inhibitors. On addition of CH3-Q=O at 10^{-4} M and CH3-Q=S at 10^{-2} M, the corrosion rate rapidly decrease i.e. CH3-Q=O and CH3-Q=S are efficient inhibitors in the temperature range 20-60 °C and the values of inhibition efficiency is almost constant in the temperature range 30-60 °C (Table 4).

The activation parameters are calculated from Arrhenius-type plot according to equation [38]:

$$i_{corr} = K \exp(\frac{-E_a}{RT}) \tag{5}$$

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 preexpotential constant and R is the universal gas constant.

The activation energy is derived from the slope Arrhenius plots for the corrosion current density of mild steel are given in Fig. 10. The calculated values of the apparent activation corrosion energy in the absence and the presence of CH3-Q=O and CH3-Q=S are 50 kJ mol^{-1}, 41.96 kJ mol^{-1} and 44.23 kJ mol^{-1}, respectively. The reduction in the activation energy in the presence of inhibitors may be attributed to the chemisorption of inhibitors on metallic surface [39,40]. With increasing the temperature, some chemical changes occur in the inhibitor molecules, leading to an increase in the electron densities at the adsorption centers of the molecule, causing an improvement in inhibitor efficiency [41].

3.5. Adsorption isotherm

In order to gain more information about the mode of adsorption of CH3-Q=O and CH3-Q=S on mild steel surface at 20°C, the experimental data have been tested with several adsorption isotherms. the adsorption of an organic adsorbate at the 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) [42]:

$$\text{ORG (sol)} + Y\ H_2O\ \text{(ads)} \quad \rightleftharpoons \quad \text{ORG (ads)} + XH_2O\ \text{(sol)} \tag{6}$$

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 adsorbate.

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, Langmuir and Temken. By far the best fit was obtained with the Langmuir isotherm. This Langmuir model has been used for other inhibitors systems [43]. A correlation between θ and inhibitor concentration (C_{inh}) in the electrolyte can be represented by the Langmuir adsorption isotherm [44]:

$$\theta = \frac{KC_{inh}}{1 + KC_{inh}} \tag{7}$$

Rearranging this equation

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \tag{8}$$

This equation predicts a linear plot between values of C_{inh}/θ and C_{inh} (Fig. 11), K_{ads} is a constant.

The strong correlation exemplified in Figure 11 (r= 0,9998 with CH3-Q=O and r=0,9997 with CH3-Q=S) for the Langmuir adsorption isotherm plot for inhibitors at 20 °C confirms the validity of this approach.

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The values of the adsorption free energy can be calculated from the Langmuir–type adsorption isotherm [45] using the following equation:

$$K_{ads} = \frac{1}{55.55} \exp(\frac{-\Delta G_{ads}}{RT})$$ (9)

The values of the free energy of adsorption in 0.5 M H_2SO_4 with 10^{-4} M of CH3-Q=O and 10^{-2} M CH3-Q=S were about -30.59 kJ.mol^{-1} and -29.57 kJ.mol^{-1}, respectively. The largest negative value of $\Delta G°_{ads}$ in the case of these inhibitors indicates that the inhibitors are spontaneously adsorbed on the steel surface [46].

Adsorption of CH3-Q=O and CH3-Q=S onto the mild steel surface can be achieved by two modes of adsorption, through the free lone pairs on nitrogen atoms as well as π-electrons of the phenyl rings and protonated species of CH3-Q=O and CH3-Q=S as they are present in acidic media, nitrogen atoms accept protons from the acid solution and form cations which electrostatically attracted to the pre-adsorbed SO_4^{2-} anions on the mild steel surfaces.

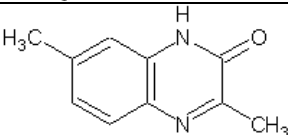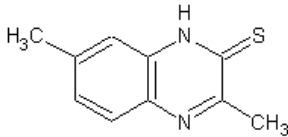**Table 1. Molecular structures, names and abbreviations of the studied quinoxaline derivatives**

Quinoxalinee Formula	Name	Abbreviation
	3,7-dimethylquinoxalin-2(1H)-one	CH3-Q=O
	3,7-dimethylquinoxalin-2(1H)-thione	CH3-Q=S

Table 2. Inhibition efficiency, coverage surface and corrosion rate data obtained from weight loss measurements for mild steel in 0.5M H_2SO_4 for various concentrations of inhibitors

Inhibitor	Concentration C / mol L^{-1}	Corrosion weight loss ω_{corr} / mg cm^{-2} h^{-1}	Coverage ratio θ	IE$_W$% %
Blank	00	0.0486	-	-
CH3-Q=O	10^{-5}	0 ,0370	0 ,591	24
	10^{-4}	0.0313	1	40
	10^{-3}	0.0290	0.883	36
	10^{-2}	0.0354	0,673	27
CH3-Q=S	10^{-3}	0.0250	0.588	49
	5×10^{-3}	0.0101	0.960	79
	10^{-2}	0.0085	1	82

Table 3. Electrochemical kinetic parameters of mild steel in 0.5M H2SO4 without and with various concentrations of inhibitors
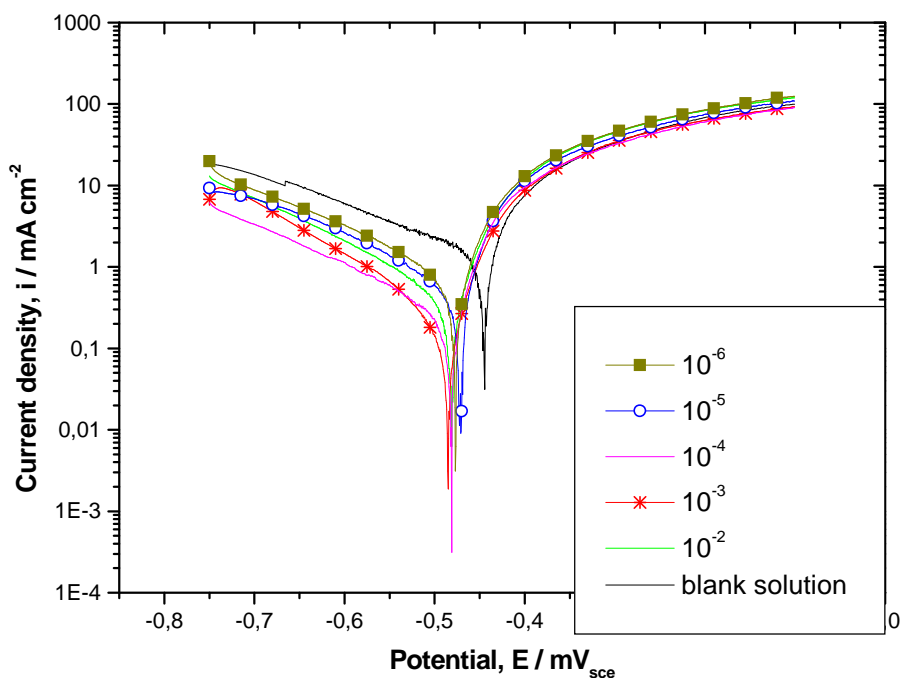
Inhibitor	Concentration mol L^{-1}	E$_{corr}$ mV$_{sce}$	| β$_c$ | mV dec^{-1}	b$_a$ mV dec^{-1}	i$_{corr}$ μA cm^{-2}	IE$_{I-E}$ %
Blank	00	-444	148	65	367	-
CH3-Q=O	10^{-6}	-482	161	62	334	08
	10^{-5}	-478	156	51	257	30
	10^{-4}	-487	78	38	152	59
	10^{-3}	-483	98	40	206	44
	10^{-2}	-471	151	42	242	34
CH3-Q=S	10^{-3}	-508	80	50	165	55
	5×10^{-3}	-503	264	43	61	83
	10^{-2}	-405	141	56	34	91

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Table 4. Impedance data for mild steel in 0.5 M H₂SO₄ containing different concentrations of the studied inhibitors

Inhibitor	Concentration mol L^{-1}	R_{ct} Ω cm^2	C_{dl} μF cm^{-2}	IE_{imp} %
Blank	00	60	856	—
CH3-Q=O	10^{-5}	86	199	30
	10^{-4}	162	97	63
	10^{-3}	107	107	44
	10^{-2}	99	163	39
CH3-Q=S	10^{-3}	136	773	56
	5×10^{-3}	473	443	87
	10^{-2}	653	41	91

Table 5. Electrochemical characteristics of mild steel in 0.5 M H₂SO₄ with and without 10^{-2} M of CH3-Q=S and 10^{-4} M of CH3-Q=O of the studied inhibitors at different temperatures derived from current-voltage *I-E* characteristics

Inhibitor	Temperature °C	E_{corr} mV$_{sce}$	i_{corr} μA cm^{-2}	IE_{I-E} %
Blank	20	-444	367	-
	30	-436	1062	-
	40	-434	2065	-
	50	-430	3108	-
	60	-478	4071	-
CH3-Q=O	20	- 483	206	44
	30	-470	491	54
	40	-469	880	57
	50	-478	1311	58
	60	-479	1614	60
CH3-Q=S	20	-404	34	91
	30	-406	85	92
	40	-387	154	92
	50	-364	231	92
	60	-406	303	92

Fig. 1: Polarization curves of mild steel in 0.5 M H₂SO₄ containing different concentrations of CH3-Q=O
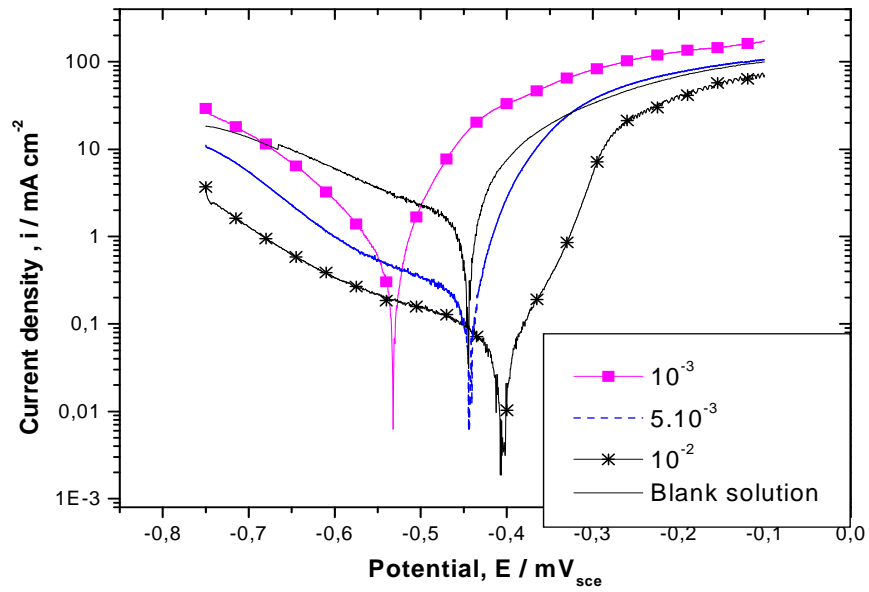
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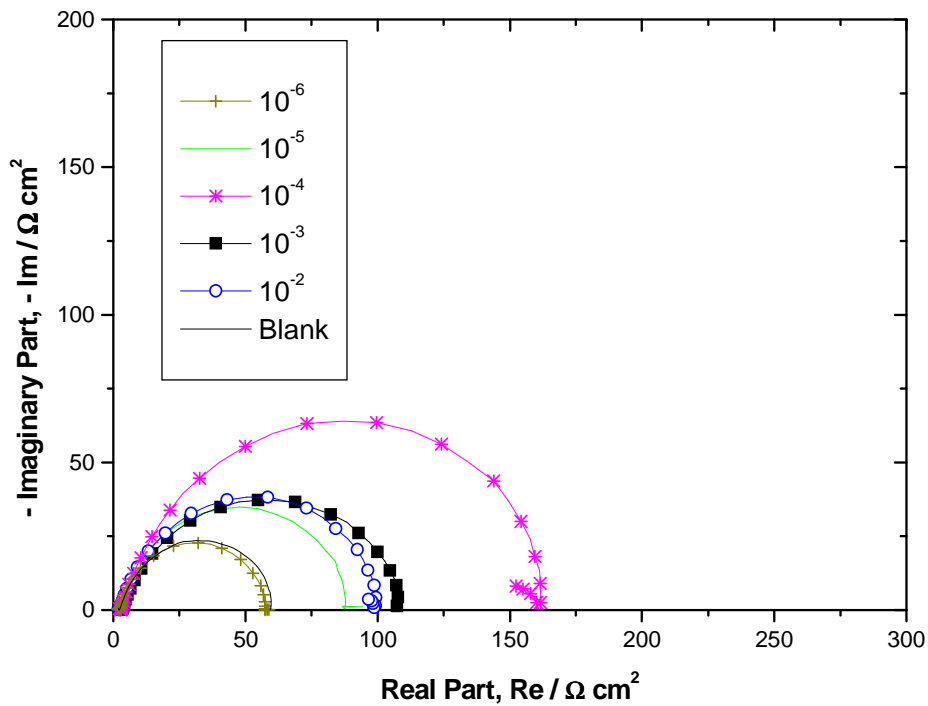**Fig. 2: Polarization curves of mild steel in 0.5 M H$_2$SO$_4$ containing different concentrations of CH3-Q=S**

Fig. 3: Nyquist diagrams for mild steel in 0.5M H$_2$SO$_4$ containing different concentrations of CH3-Q=O
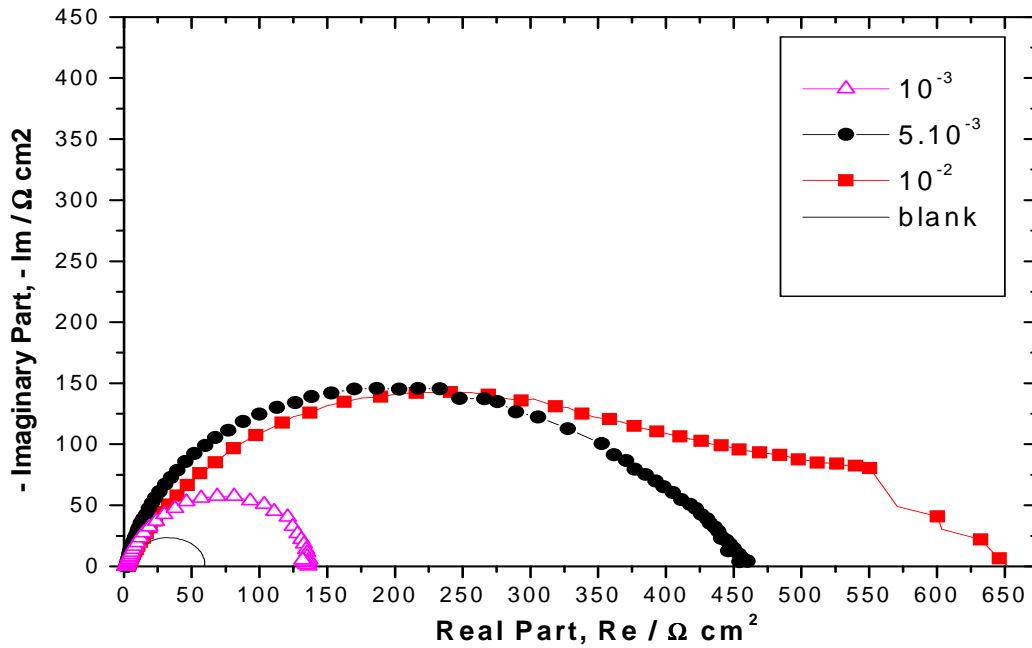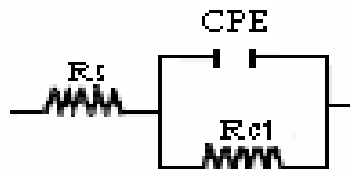
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Fig. 4: Nyquist diagrams for mild steel in 0.5 M H$_2$SO$_4$ containing different concentrations of CH3-Q=S

Fig. 5: Equivalent circuit model for studied inhibitor, R$_s$ solution resistance, R$_{ct}$ charge transfer resistance and CPE constant phase element
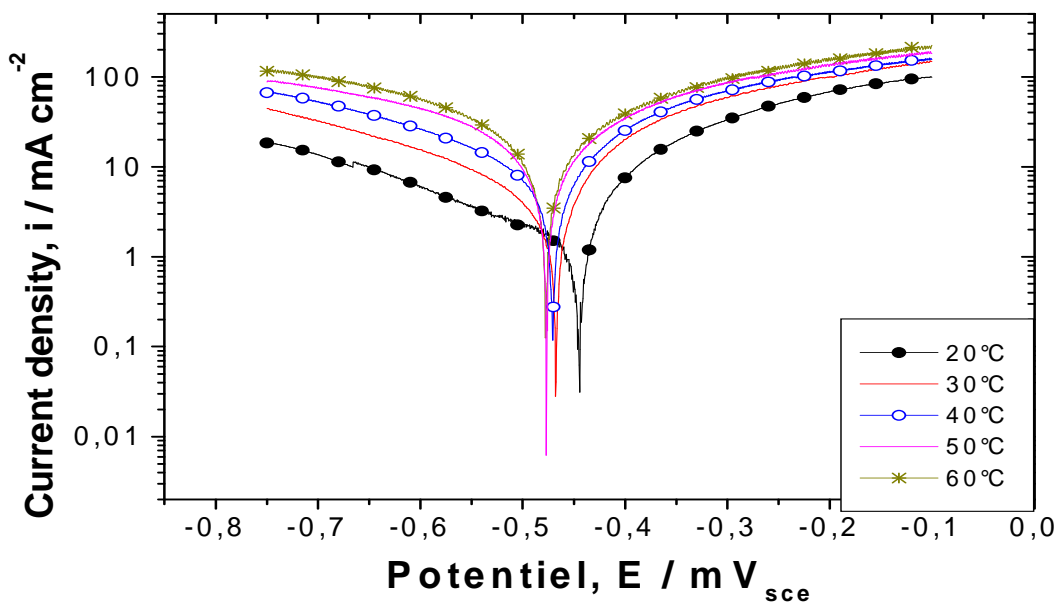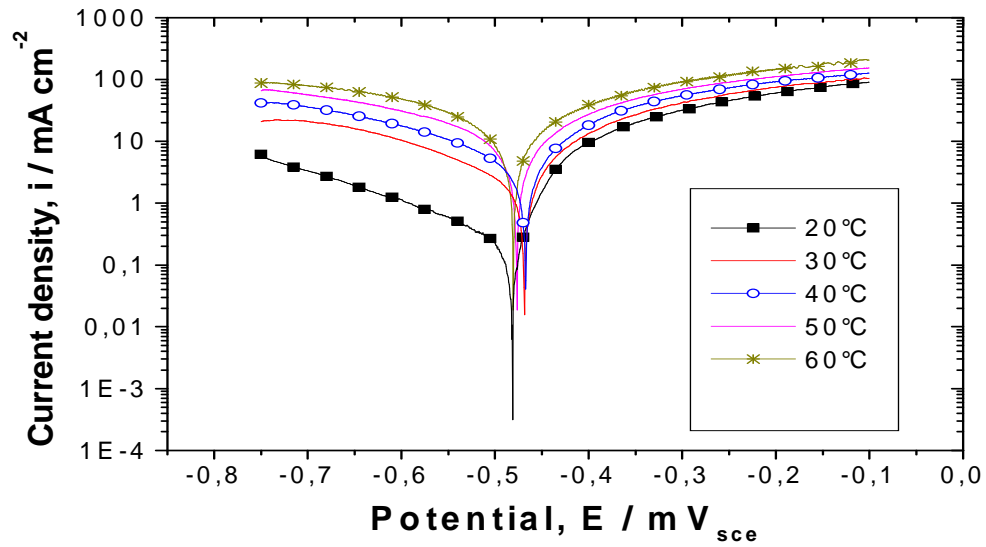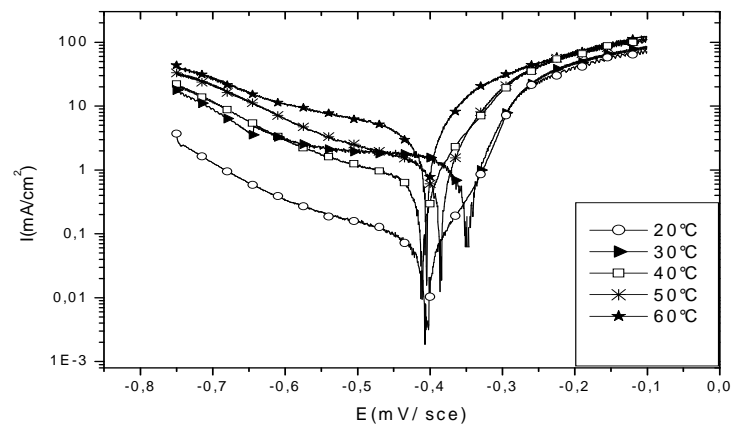
Fig. 6: Effect of temperature on the cathodic and anodic responses for mild steel in 0.5M H$_2$SO$_4$

Fig. 7: Effect of temperature on the cathodic and anodic responses for mild steel in 0.5 M H$_2$SO$_4$ for 10^{-4} M of CH3-Q=O

Fig. 8: Effect of temperature on the cathodic and anodic responses for mild steel in 0.5M H$_2$SO$_4$ for 10^{-2} M of CH3-Q=S
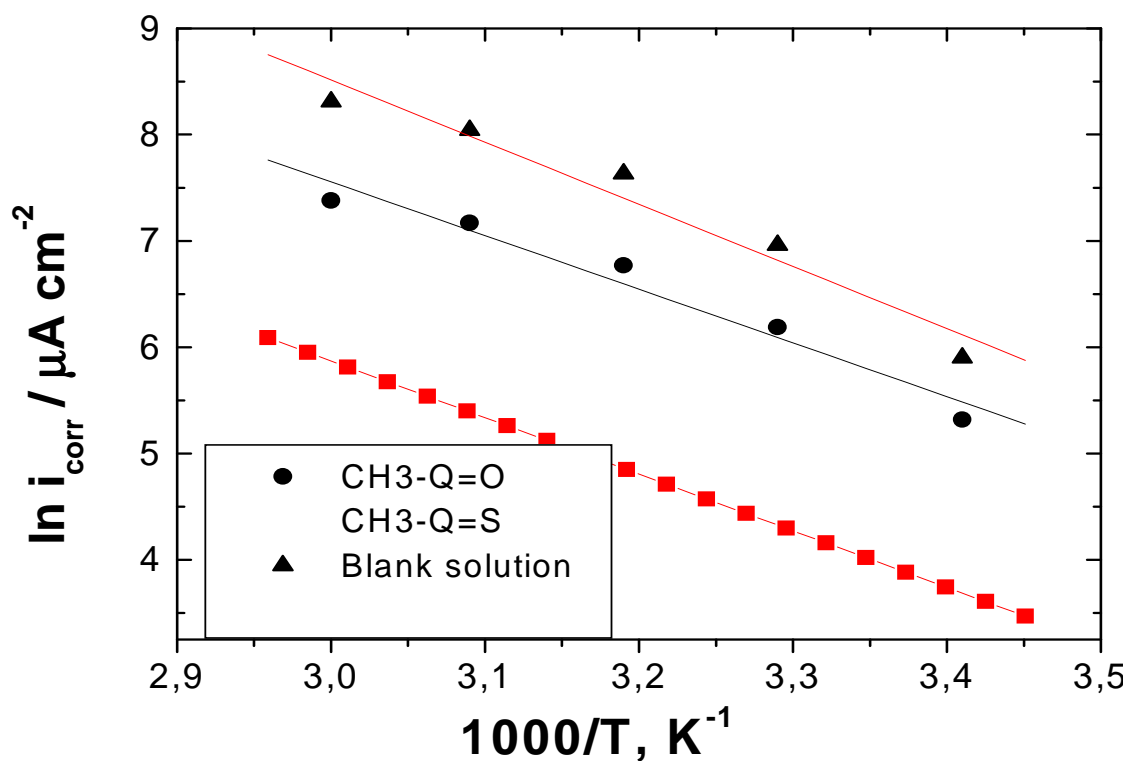
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Fig. 9: Arrhenuis plots calculated from corrosion current density for mild steel in 0.5 M H₂SO₄ with and without 10⁻² M of CH3-Q=S and 10⁻⁴ M of CH3-Q=O of the studied inhibitors at different temperatures derived from current-voltage *I-E* characteristics
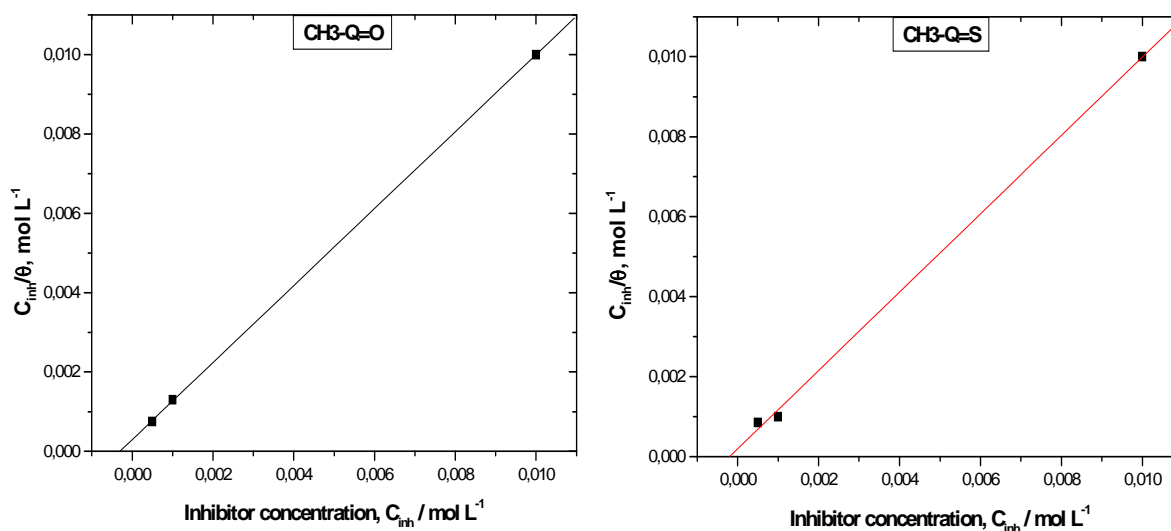

Fig. 10: Langmuir isotherm adsorption (C$_{inh}$/ Ө vs. C$_{inh}$) of CH3-Q=S and CH3-Q=O in 0.5 M H₂SO₄ from weight loss measurements at 20° C

CONCLUSION

In this study, it was shown that CH3-Q=S and CH3-Q=O inhibits the corrosion of mild steel in acidic solution and the better performance is seen in the case of CH3-Q=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.

Polarization data showed that CH3-Q=O is a cathodic inhibitor and CH3-Q=S is found to effect both the cathodic and anodic process; that is, the inhibitor is of mixed type. The concentration dependence of the inhibition efficiency

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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.

The adsorption of CH3-Q=S and CH3-Q=O on mild steel surface in 0.5 M H_2SO_4 flows the Langmuir isotherm, indicating that the main inhibition process occurs via adsorption.

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