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# Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio} propanohydrazide as an effective inhibitor of mild steel corrosion in HCl solution

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#### Abstract

Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio} propanohydrazide (QMQTPH) was synthesized, characterized and tested as a corrosion inhibitor for mild steel in 1 M and 2 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Polarization resistances calculated from the EIS measurements were in good agreement with those obtained from direct current (DC) polarization measurements. The mild steel samples were also analyzed by scanning electron microscopy (SEM). The results showed that QMQTPH is an excellent inhibitor for mild steel in acid medium. The inhibition was assumed to occur via adsorption of the inhibitor molecule on the metal surface. It acts as an anodic inhibitor. In the 30° to 60 °C temperature range, the QMQTPH adsorption follows Langmuir isotherm model. The protection efficiency increased with increasing inhibitor concentration in the range  $10^{-5} - 10^{-3}$  M, but slightly decreased with increasing temperature.

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#### 1. Introduction

Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms. It has been reported that many heterocyclic compounds containing heteroatoms like N, O, S, have been proved to be effective inhibitor for the corrosion of steel in acid media [1–8]. The influence of such organic compounds, on the corrosion of mild steel in acidic solution has been investigated by several authors [8–10]. The inhibition property of these compounds is attributed to their molecular structure. The planarity and the lone electron pairs in the heteroatoms, are important features that determine the adsorption of these molecules on the metallic surface. They can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate.

The aim of this work is to investigate the role played by newly synthesized quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propanohydrazide (QMQTPH) on the corrosion behaviour of mild steel in 1 M and 2 M HCl. The molecular design of the new compound is based on the fact that quinoline (a nitrogen – heterocycle) containing trifluoromethyl group, thio and hydrazide groups would contribute more effectively towards inhibition of corrosion of mild steel in acid medium.

In view of this, QMQTPH (2) was synthesized in the laboratory and characterized using NMR, IR, Mass & Elemental analysis techniques. The inhibitive action of it on the corrosion behaviour of mild steel in 1 M and 2 M HCl solution at five levels of concentrations and at four different temperatures was measured. Corrosion

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inhibition was investigated using potentiodynamic and AC impedance spectroscopic methods and their results were compared. Mild steel samples were analyzed by scanning electron microscopy for further confirmation.

#### 2. Experimental method

# 2.1. Inhibitor

Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propane hydrazide (QMQTPH, **2**) was synthesized in the laboratory using well-established methods and characterized by spectral and elemental analysis methods. The IR spectra (in KBr pellets) were recorded on a Perkin–Elmer spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Jeol JMS-D 300 spectrometer operating at 70Ev. Mass spectra were recorded on a Jeol SX-102 (FAB). Elemental analysis carried out in Thermo Electron Corporation Flash EA 1112 series CHN analyzer.

# 2.2. Synthesis

In the laboratory Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propanohydrazide (QMQTPH, 2) was synthesized from 3-{[8-(trifluoromethyl) quinolin-4yl]thio}propanohydrazide (1) following the procedure described below:

A mixture of 3.15 g (0.01 mol) of 3-{[8-(trifluoromethyl) quinolin-4-yl]thio} propane hydrazide (1), 1.73 g of 5-quinoline carboxaldehyde (0.011 mol), 0.2 ml of glacial acetic acid and 25 ml of dry methanol was refluxed for 8 h. The crystalline product thus obtained was filtered, washed, dried and recrystallised in ethanol to afford the crystals of **2**, yield 92% and m.p. 217–218 °C. The required intermediates were prepared following reported procedures [11]. Their purity was monitored by TLC, and its structure was established by spectral and elemental analyses. The synthesis sequence is given in Scheme 1.

#### 2.3. Material and Medium

For Corrosion measurement mild steel rods of chemical composition C 0.18 %, Mn 0.6%, S 0.05%, P 0.04%, Si 0.1% and the remainder iron were used. The samples were pol-

ished with different emery papers up to 4/0 grades, cleaned with acetone, washed with doubly distilled water and finally dried. For the electrochemical measurement the arrangement used was a conventional three-electrode Pyrex glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The working steel specimen is covered in Teflon so that its cross sectional area  $0.785 \text{ cm}^2$  was in contact with the solution. Experiments were carried out at constant temperature  $\pm 0.5$  °C using a calibrated thermostat. Analar grade hydrochloric acid (Merck) and doubly distilled water were used to prepare 1 M and 2 M acid solutions for all experiments.

# 2.4. Tafel polarization Studies

Tafel polarization studies were carried out by using an electrochemical work station (Auto Lab 30, Metrohm). Polished mild steel specimens of  $0.785 \text{ cm}^2$  surface area was exposed to 100 ml of acid solution (1&2 M) at 30 °C with out and with various concentrations (10 to 500 ppm or  $2.2 \times 10^{-5}$  to  $1.1 \times 10^{-3}$  M) of inhibitors in the acid solution. The potentiodynamic current - potential curves were recorded by changing the electrode potential automatically from -250 mV to +250 mV vs. OCP with scan rate of  $1 \text{ mV s}^{-1}$  and the corresponding corrosion current *i*, were recorded. From E vs. log *i* plot,  $E_{corr}$  and  $i_{corr}$  were determined. The corrosion rate (C.R.), in mm/ year, is calculated using the relation: C.R. (mm/year)=  $\frac{K \times i_{\text{corr}} \times \text{Equivalent weight}}{\text{density}}$  where K is 3272, a constant that defines density the unit for the corrosion rate,  $i_{corr}$  is current density in A cm<sup>-2</sup> and density is in g cm<sup>-3</sup>.

The surface coverage  $\theta$  is calculated as:

$$\theta = \frac{\left[i_{\text{corr(uninh)}} - i_{\text{corr(inh)}}\right]}{i_{\text{corr(uninh)}}}$$

The percentage protection efficiency (%P) is given by  $\% P = \theta \times 100$ .

The experiments were repeated for 40°, 50° and 60°C. Corrosion rate,  $\theta$  and %P were determined.

# 2.5. Electrochemical impedance spectroscopy (EIS) studies

The corrosion rate for all the above conditions were also obtained from EIS technique. EIS measurements were



Scheme 1.

carried out in a frequency range of 1,00,000 Hz to 0.05 Hz using an amplitude of 10 mV peak to peak using AC signal at the open circuit potential. The corrosion current density  $i_{\rm corr}$  was calculated using the charge transfer resistance,  $R_{\rm ct}$  together with Stern–Geary equation [12].

$$I_{\rm corr} = \frac{[b_{\rm a} \times b_{\rm c}]}{[2.303R_{\rm ct}A(b_{\rm a} + b_{\rm c})]}$$

where A is the electrode surface area and  $b_a$  and  $b_c$  are the Tafel slopes of the anodic and cathodic processes, respectively.  $R_{ct}$  value was obtained from Nyquist plot. The percentage protection efficiency, % P, was calculated from the following equation.

$$\%P = \frac{\left(\frac{1}{R_{\rm et}}\right)_0 - \left(\frac{1}{R_{\rm et}}\right)}{\left(\frac{1}{R_{\rm et}}\right)_0} \times 100$$

where  $(R_{ct})_0$  and  $(R_{ct})$  are the uninhibited and inhibited charge transfer resistances, respectively [4].

# 2.6. Scanning electron microscopy (SEM)

Immersion corrosion analysis of mild steel samples in the acidic solutions with and without the optimal concentration of the inhibitor was performed using SEM. Immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface conditions. SEM Jeol JSM-6380 was used for the experiments.

#### 3. Results and discussion

#### 3.1. Characterization of 2

 $3-\{[8-(trifluoromethyl) quinolin-4-yl]thio\}$  propanohydrazide (1), on treatment with 5-quinoline carboxaldehyde in methanol containing trace of glacial acetic acid as catalyst, yielded Quinolin-5-ylmethylene- $3-\{[8-(trifluorom$  $ethyl)quinolin-4-yl]thio\}$  propanohydrazide (QMQTPH, 2). The characterization data of 2 are given below.

<sup>1</sup>**H** NMR:  $\delta$  2.49 (triplet, -CH<sub>2</sub>-CO),  $\delta$  3.48 (triplet, S-CH<sub>2</sub>-),  $\delta$  9.30 (singlet, -NH),  $\delta$  8.48 (singlet, N=CH-). In

the spectrum, trifluoromethylquinoline protons appeared as 4 doublets and one triplet as follows: a doublet at  $\delta$ 7.40–7.39 (J = 4.8 Hz, C-2 proton), a triplet at  $\delta$  7.53– 7.51 (J = 8 Hz, C-4 proton), a doublet at  $\delta$  8.28– 8.26 (J =8 Hz, C-5 proton), and a doublet at  $\delta$  8.28– 8.26 (J =8 Hz, C-5 proton), and a doublet at  $\delta$  8.73–8.72 (J =4.8 Hz, C-1 proton). The other quinoline ring protons appeared as 4 doublet and 2 triplets as follows: a triplet at  $\delta$  7.34–7.32 (J = 4.4 Hz, C-5 proton), a doublet at  $\delta$ 7.53–7.51 (J = 7.6 Hz, C-6 proton), a triplet at  $\delta$  7.64– 7.60 (J = 8 Hz, C-2 proton), a doublet at  $\delta$  8.81–8.79 (J = 7.5 Hz, C-3 proton), a doublet at  $\delta$  8.90–8.88 (J = 8.8 Hz, C-1 proton).

**IR**: (KBr) v cm<sup>-1</sup>: 3380 (NH str), 2990 (C–H str), 1720 (C=O str), 1170 (C–F str).

**MASS** (M<sup>+</sup>): The molecular ion peak (M<sup>+</sup>) appeared at 454, which corresponds to its molecular formula  $C_{23}H_{17}F_3N_4OS$ , confirming the formation of the compound **2**. The base peak appeared at 455 is due to protonated molecular ion peak (M + H)<sup>+</sup>, the presence of which confirms the structure of **2**.

**Elemental analysis**: Found (calcd): 60.75 (60.78); H, 3.74 (3.78); N, 12.38 (12.33) %; C<sub>23</sub>H<sub>17</sub>F<sub>3</sub>N<sub>4</sub>OS.

# 3.2. Corrosion measurement

The Tafel experimental results obtained for the corrosion of mild steel with and without inhibitors are summarized in the Table 1. The results indicate that the mild steel in the absence of inhibitor corrodes severely in 2 M HCl, while the corrosion rate is slightly less in 1M HCl. Increase in temperature increases the corrosion rate. Presence of inhibitor brings down the corrosion rate considerably; the effect is being more at high concentration of the inhibitor. In acid solutions the anodic process of corrosion is the passage of metal ions from metal surface into the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen gas or reduction of oxygen. The inhibitor may affect either of them or both anodic and cathodic processes.

Table 1

Corrosion rates and % Protection efficiency on mild steel by potentiodynamic polarization test (Tafel technique)

| Medium  | Temp. (°C) | Corrosion rate, mm/year (% Protection efficiency) |             |             |             |             |             |  |  |  |
|---------|------------|---|-------------|-------------|-------------|-------------|-------------|--|--|--|
|         |            | Inhibitor concentration                           |             |             |             |             |             |  |  |  |
|         |            | 0 ppm   | 10 ppm (%)  | 50 ppm (%)  | 100 ppm (%) | 250 ppm (%) | 500 ppm (%) |  |  |  |
| 1 M HCl | 30         | 15.9  | 6.1 (61.5)  | 3.3 (79.4)  | 2.2 (86.2)  | 1.7 (89.3)  | 1.1 (93.1)  |  |  |  |
|         | 40         | 19.2  | 10.2 (47.1) | 5.1 (73.2)  | 3.6 (81.1)  | 2.7 (86.0)  | 1.8 (90.8)  |  |  |  |
|         | 50         | 26.0  | 14.5 (44.0) | 8.1 (68.9)  | 5.7 (78.0)  | 5.0 (80.9)  | 3.4 (86.9)  |  |  |  |
|         | 60         | 34.4  | 20.7 (40.0) | 14.8 (57.0) | 10.0 (70.9) | 8.2 (76.2)  | 5.9 (83.0)  |  |  |  |
| 2 M HCl | 30         | 19.0  | 9.1 (52.2)  | 5.5 (71.3)  | 2.9 (84.7)  | 2.3 (87.8)  | 1.8 (90.8)  |  |  |  |
|         | 40         | 24.4  | 14.0 (42.6) | 8.6 (64.8)  | 5.4 (77.9)  | 4.0 (83.4)  | 3.4 (86.1)  |  |  |  |
|         | 50         | 30.1  | 19.0 (36.9) | 13.8 (54.2) | 11.0 (63.4) | 7.8 (74.2)  | 5.4 (82.0)  |  |  |  |
|         | 60         | 39.2  | 30.0 (23.5) | 25.0 (36.2) | 14.7 (62.5) | 11.8 (70.0) | 9.3 (76.3)  |  |  |  |



Fig. 1. Polarization curves of mild steel in 1 M HCl at 40 °C in presence of different concentration of QMQTPH: (a) 0.0, (b)  $2.2 \times 10^{-5}$ , (c)  $1.1 \times 10^{-4}$ , (d)  $2.2 \times 10^{-4}$ , (e)  $5.5 \times 10^{-4}$ , (f)  $1.1 \times 10^{-3}$  M.

Fig. 1 shows anodic and cathodic potentiodynamic polarization curve for mild steel in 1 M HCl at 40° in absence and presence of QMQTPH in various concentrations. Values associated with electrochemical parameter and % protection efficiency (%P) are given in Table 2. The values of  $i_{\rm corr}$  decreased with increasing inhibitor concentration. The decrease in  $i_{\rm corr}$  with increasing inhibitor concentration was associated with shift of corrosion potential  $E_{\rm corr}$  to more positive potential. With increase in inhibitor concentration anodic current densities decreased, were

as similar change was not observed for cathodic current density. This indicates that QMQTPH suppressed anodic reaction. These observations suggest that OMOTPH behaves mainly as anodic inhibitor [4]. The adsorbed inhibitor may form a surface film, which acts as a physical barrier to restrict diffusion of ions to or from the metal surface and hence retard the corrosion process. The interactions of the adsorbed inhibitors with surface metal atoms may prevent the metal atoms from participating the anodic reaction of corrosion. This simple blocking effect decreases the number of surface metal atoms participating and hence decreases corrosion. It has been observed that the protection efficiency increased with increase in surface coverage,  $\theta$ . The high protection efficiency is due to the bonding of (adsorbed) QMQTPH on to the metals. The strong bonding is mainly attributed to higher electron densities at active functional groups, present in the adsorbate molecules [13].

The experimental results of EIS measurements obtained for the corrosion of mild steel with and with out inhibitors are summarized in Table 3. Fig. 2 shows the complex-plane impedance plots for mild steel in 1 M HCl with out and with various concentrations of QMQTPH at 40 °C. The equivalent circuit models used to fit the experimental results are as previously reported [4,14,15]. The Charge transfer resistance,  $R_{\rm ct}$  was determined by analysis of complex-plane impedance plots and the values of  $R_{\rm ct}$  and % protection efficiency are given in the

Table 2 Electrochemical parameters for mild steel with QMQTPH at 40  $^{\circ}\mathrm{C}$  in 1 M and 2 M HCl

| Concentration in ppm | 1 M HCl                               |                                       |                                |   |      | 2 M HCl                                |                                       |                                       |   |      |
|----------------------|---------------------------------------|---------------------------------------|--------------------------------|---|------|--|---------------------------------------|---------------------------------------|---|------|
|                      | $E_{ m corr}$<br>(mV <sub>SCE</sub> ) | $b_{\rm c}$<br>(mV/dec <sup>1</sup> ) | $b_{\rm a} \ ({\rm mV/dec}^1)$ | $I_{\rm corr}$<br>( $\mu$ A/cm <sup>2</sup> ) | %P   | $E_{\rm corr}$<br>(mV <sub>SCE</sub> ) | $b_{\rm c}$<br>(mV/dec <sup>1</sup> ) | $b_{\rm a}$<br>(mV/dec <sup>1</sup> ) | $I_{\rm corr}$<br>( $\mu$ A/cm <sup>2</sup> ) | %P   |
| 0                    | -460                                  | 111                                   | 073                            | 1617  | _    | -441                                   | 102                                   | 078                                   | 2054  | -    |
| 10                   | -447                                  | 108                                   | 069                            | 855   | 47.1 | -430                                   | 106                                   | 072                                   | 1178  | 42.6 |
| 50                   | -438                                  | 106                                   | 064                            | 433   | 73.2 | -424                                   | 108                                   | 069                                   | 724   | 64.8 |
| 100                  | -431                                  | 108                                   | 061                            | 305   | 81.1 | -420                                   | 107                                   | 062                                   | 455   | 77.9 |
| 250                  | -424                                  | 104                                   | 059                            | 226   | 86.0 | -416                                   | 110                                   | 060                                   | 340   | 83.4 |
| 500                  | -412                                  | 111                                   | 053                            | 148   | 90.8 | -414                                   | 102                                   | 055                                   | 285   | 86.1 |

Table 3

| Corrosion rates and % Protection | n efficiency of | mild steel by | EIS measurements |
|----------------------------------|-----------------|---------------|------------------|
|----------------------------------|-----------------|---------------|------------------|

| Medium  | Temp. (°C) | Corrosion rate, mm/year (% Protection efficiency) |             |             |             |             |             |  |  |  |
|---------|------------|---|-------------|-------------|-------------|-------------|-------------|--|--|--|
|         |            | Inhibitor concentration                           |             |             |             |             |             |  |  |  |
|         |            | 0 ppm   | 10 ppm (%)  | 50 ppm (%)  | 100 ppm (%) | 250 ppm (%) | 500 ppm (%) |  |  |  |
| 1 M HCl | 30         | 17.3  | 6.4 (63.0)  | 3.2 (81.3)  | 2.3 (86.7)  | 1.7 (90.2)  | 1.1 (93.6)  |  |  |  |
|         | 40         | 20.5  | 10.4 (49.0) | 5.2 (74.5)  | 3.7 (81.9)  | 2.6 (87.5)  | 1.8 (91.4)  |  |  |  |
|         | 50         | 27.3  | 15.1 (44.9) | 8.2 (70.0)  | 5.6 (79.5)  | 4.8 (82.4)  | 3.3 (87.9)  |  |  |  |
|         | 60         | 35.9  | 21.0 (41.5) | 14.9 (58.5) | 9.7 (73.0)  | 7.5 (79.1)  | 5.6 (84.4)  |  |  |  |
| 2 M HCl | 30         | 20.3  | 7.1 (54.1)  | 5.5 (72.9)  | 2.8 (86.3)  | 2.3 (88.9)  | 1.7 (91.6)  |  |  |  |
|         | 40         | 25.7  | 15.1 (41.5) | 8.9 (65.5)  | 5.9 (77.1)  | 4.0 (84.4)  | 3.3 (87.1)  |  |  |  |
|         | 50         | 31.2  | 19.3 (38.1) | 13.7 (56.0) | 11.1 (64.4) | 7.9 (74.7)  | 5.3 (83.0)  |  |  |  |
|         | 60         | 40.6  | 30.3 (25.5) | 26.2 (35.6) | 15.4 (62.2) | 11.4 (72.0) | 9.0 (77.8)  |  |  |  |



Fig. 2. Complex-plane impedance of mild steel in 1 M HCl at 40 °C in presence of different concentration of QMQTPH: (a) 0.0, (b)  $2.2 \times 10^{-5}$ , (c)  $1.1 \times 10^{-4}$ , (d)  $2.2 \times 10^{-4}$ , (e)  $5.5 \times 10^{-4}$ , (f)  $1.1 \times 10^{-3}$  M.

Table 4. The value of % protection efficiency obtained from EIS and potentiodynamic polarization measurements are in sequence.

#### 3.3. Application of adsorption isotherm

In order to understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbate on the steel surface must be known. The degree of surface coverage  $(\theta)$  for different concentration of inhibitor has been evaluated from potentiodynamic polarization measurements. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting  $\log[\theta/(1-\theta)]$  against log C, suggesting that the adsorption of the compound on mild steel surface follows Langmuir adsorption isotherm model [13]. The Langmuir adsorption isotherm relationship is represented as,  $\log \left[ \theta / (1 - \theta) \right] = \log \theta$  $K + \log C$ , where  $\theta \rightarrow$  fractional surface coverage,  $K \rightarrow$ adsorption equilibrium constant,  $C \rightarrow molar$  concentration of inhibitor in bulk of the solution. Adsorption isotherm for OMOTPH on the surface of mild steel in 1 M HCl is shown in Fig. 3.

# 3.4. Activation energy $(E_a)$

Activation energy is calculated using the relation:

$$\ln\left[\frac{r_2}{r_1}\right] = \frac{E_a(T_2 - T_1)}{RT_1T_2}$$

1.2 0.8 0.4 0.0 0.0 -0.4 -4.8 -4.4 -4.0 -3.6 -3.2 -2.8 Log C [M]

Fig. 3. Adsorption Isotherm for QMQTPH on the surface of mild steel in 1 M HCl at different temperatures: (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C.

where  $r_1$  and  $r_2$  are the corrosion rates at temperature  $T_1$ and  $T_2$ , respectively. The activation energies obtained are given in Table 5.  $E_a$  increases with increase of inhibitor concentration that indicates strong adsorption of inhibitor molecules at the metal surface. During the corrosion reaction mechanism the charge transfer is blocked with adsorption of QMQTPH molecules to the metal surface, causing the increase of activation energy [5,16–18].

# 3.5. Free energy of adsorption $(\Delta G_{ads})$

 $\Delta G_{\rm ads}$  is calculated using the relation,  $\Delta G_{\rm ads} = -RT \ln \left[\frac{55.5\theta}{C(1-\theta)}\right]$  where C is the concentration of the inhibitor expressed in mole dm<sup>-3</sup>. The negative value of  $\Delta G_{\rm ads}$  ensure the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, the values of  $\Delta G_{\rm ads}$  around  $-20 \text{ kJ mol}^{-1}$  or lower are consistent with physisorption, while those around  $-40 \text{ kJ mol}^{-1}$  or higher involve chemisorptions [1,19]. The value of  $\Delta G_{\rm ads}$  for QMQTPH is given in Table 6 and these values indicate that the inhibitor molecules are chemisorbed. The nitrogen, oxygen and sulphur atoms of the inhibitor molecules make it adsorbed readily on the metal surface forming an insoluble stable films on the metal surface thus decreasing metal dissolution.

| Table 4                   |   |                     |
|---------------------------|---|---------------------|
| AC impedance data of mild | steel with QMQTPH at 40 $^\circ\mathrm{C}$ in | 1.0 M and 2.0 M HCl |

| Concentration in ppm | 1 M HCl                            |  | 2 M HCl    |                                    |   |      |
|----------------------|------------------------------------|--|------------|------------------------------------|---|------|
|                      | $R_{\rm ct} \ \Omega \ {\rm cm}^2$ | $1/R_{\rm ct}\ \Omega^{-1}\ {\rm cm}^{-2}$ | % <b>P</b> | $R_{\rm ct} \ \Omega \ {\rm cm}^2$ | $1/R_{\rm ct} \ \Omega^{-1}  {\rm cm}^{-2}$ | %P   |
| 0                    | 15.1                               | 0.066                                      | _          | 12.0                               | 0.083                                       | _    |
| 10                   | 29.6                               | 0.034                                      | 49.0       | 20.5                               | 0.049                                       | 41.5 |
| 50                   | 59.3                               | 0.017                                      | 74.5       | 34.8                               | 0.029                                       | 65.5 |
| 100                  | 83.2                               | 0.012                                      | 81.9       | 52.5                               | 0.019                                       | 77.1 |
| 250                  | 120.5                              | 0.008                                      | 87.5       | 77.0                               | 0.013                                       | 84.4 |
| 500                  | 175.2                              | 0.006                                      | 91.4       | 93.2                               | 0.011                                       | 87.1 |

| Table 5           |               |               |
|-------------------|---------------|---------------|
| Activation energy | for corrosion | of mild steel |

| Medium             | Activation energy (kJ mol <sup>-1</sup> ) |                |                |                |                |                |  |  |  |  |
|--------------------|---|----------------|----------------|----------------|----------------|----------------|--|--|--|--|
|                    | Inhibitor concentration                   |                |                |                |                |                |  |  |  |  |
|                    | 0 ppm                                     | 10 ppm         | 50 ppm         | 100 ppm        | 250 ppm        | 500 ppm        |  |  |  |  |
| 1 M HCl<br>2 M HCl | 21.83<br>20.30                            | 33.85<br>33.51 | 42.54<br>42.89 | 42.61<br>44.81 | 44.29<br>45.30 | 47.19<br>46.48 |  |  |  |  |

Table 6

Free energy of adsorption of inhibitor (QMQTPH) for corrosion of mild steel in HCl

| Medium  | Temp. (°C) | Free Energy of adsorption $(kJ mol^{-1})$ |        |         |         |         |  |  |  |
|---------|------------|---|--------|---------|---------|---------|--|--|--|
|         |            | Inhibitor concentration                   |        |         |         |         |  |  |  |
|         |            | 10 ppm                                    | 50 ppm | 100 ppm | 250 ppm | 500 ppm |  |  |  |
| 1 M HCl | 30         | -38.32                                    | -36.48 | -35.95  | -34.38  | -33.85  |  |  |  |
|         | 40         | -38.06                                    | -36.79 | -36.17  | -34.72  | -34.16  |  |  |  |
|         | 50         | -38.94                                    | -37.40 | -36.81  | -34.82  | -34.17  |  |  |  |
|         | 60         | -39.69                                    | -37.14 | -36.91  | -35.12  | -34.37  |  |  |  |
| 2 M HCl | 30         | -37.36                                    | -35.37 | -35.65  | -34.01  | -33.04  |  |  |  |
|         | 40         | -37.59                                    | -35.76 | -35.64  | -34.20  | -32.93  |  |  |  |
|         | 50         | -38.15                                    | -35.72 | -34.88  | -33.78  | -33.16  |  |  |  |
|         | 60         | -37.54                                    | -34.79 | -35.85  | -34.25  | -33.22  |  |  |  |



Fig. 4. SEM image of surface of mild steel after immersion for 24 h in 1 M HCl at 30  $^\circ C$  . Magnification X500.

# 3.6. Scanning electron microscopy

In order to evaluate the conditions of the mild steel surfaces in contact with hydrochloric acid solution, a superficial analysis was carried out. The SEM micrograph of the specimen in the presence of 1 M HCl solution is shown in Fig. 4. The faceting seen in the figure was a result of pits formed due to exposure of mild steel to acid. The influence of the inhibitor addition (500 ppm) on the mild steel in 1 M HCl solution is shown in Fig. 5. The faceting observed in the Fig. 4 was gone and the surface was free from pits and it was smooth. It can be concluded from Figs. 4 and 5 that corrosion does not occur in presence of inhibitor



Fig. 5. SEM image of surface of mild steel after immersion for 24 h in 1 M HCl at 30 °C in presence of 500 ppm QMQTPH. Magnification X500.

and hence corrosion was inhibited strongly when the inhibitor was present in the acid medium.

# 4. Conclusions

- (1) QMQTPH behaves as an excellent inhibitor for the mild steel corrosion in 1 M and 2 M HCl.
- (2) The QMQTPH inhibited the corrosion of mild steel in acid medium by chemisorptions and the adsorption of the compound on the metal surface obeyed the Langmuir adsorption isotherm.
- (3) QMQTPH behaves as anodic type inhibitor.



(4) Even at higher temperature also QMQTPH is an effective corrosion inhibitor.

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