



## Inhibition of C38 steel corrosion in hydrochloric acid solution by 4,5-Diphenyl-1H-Imidazole-2-Thiol: Gravimetric and temperature effects treatments

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### ABSTRACT

4,5-Diphenyl-1H-Imidazole-2-Thiol (**DIT**) has been evaluated as a corrosion inhibitor for C38 steel in 1 M HCl by gravimetric method. The effect of **DIT** on the corrosion rate was determined at various concentrations. The effect of the temperature on the corrosion behavior with addition of the optimal concentration of **DIT** was studied in the temperature range 298 – 328 K. The **DIT** acts as an effective corrosion inhibitor for C38 in hydrochloric acid medium. The inhibition process is attributed to the formation of an adsorbed film of **DIT** on the metal surface which protects the metal against corrosion. The protection efficiency increased with increase in temperature. Adsorption of **DIT** on the C38 steel surface is found to obey the Langmuir adsorption isotherm. Some thermodynamic functions of dissolution processes were also determined.

**Keywords:** C38 steel, 4,5-Diphenyl-1H-Imidazole-2-Thiol, hydrochloric acid, adsorption.

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### INTRODUCTION

The use of chemical inhibitors to decrease the rate of corrosion processes has been the focus of very many efforts within the chemical process industry [1]. In recent years, there is a considerable amount of effort devoted to find novel and efficient corrosion inhibitors and sulphur and/or nitrogen containing molecules have been found to be effective corrosion inhibitors [2 –8]. The corrosion inhibition of steel is a subject of large-scale technological importance, due to the fundamental economical implications of this material in the industrial medium [9-13].

In this work, a 4,5-Diphenyl-1H-Imidazole-2-Thiol (**DIT**) had been studied on the corrosion inhibition of C38 steel in 1M HCl solutions by weight loss and electrochemical methods studies. The chemical structure of the studied compound was given in Fig 1.

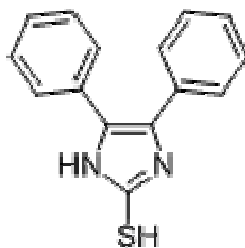


Figure 1. The chemical structure of the 4,5-Diphenyl-1H-Imidazole-2-Thiol

## EXPERIMENTAL SECTION

### *Weight loss measurements*

Coupons were cut into  $2 \times 2 \times 0.08 \text{ cm}^3$  dimensions having composition (0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance) are used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is  $80 \text{ cm}^3$ . The immersion time for the weight loss is 6 h at 298 K.

### *Electrochemical tests*

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte is  $0.094 \text{ cm}^2$ . Potentiodynamic polarization curves were plotted at a polarization scan rate of  $0.5 \text{ mV/s}$ . Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from  $-800 \text{ mV}$  to  $-400 \text{ mV}$  at 298 K. The solution test is there after de-aerated by bubbling nitrogen. Gas bubbling is maintained prior and through the experiments. In order to investigate the effects of temperature and immersion time on the inhibitor performance, some test were carried out in a temperature range 298–328 K.

### *Solutions preparation*

The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37 % HCl with double-distilled water. The organic compound tested was 4,5-Diphenyl-1H-Imidazole-2-Thiol. The concentration range of this compound was  $10^{-2}$  to  $10^{-6} \text{ M}$ . The studied organic compound was synthesized as described elsewhere [14-15].

## RESULTS AND DISCUSSION

### *Weight loss, corrosion rates and inhibition efficiency*

The value of corrosion rate was calculated from the following equation [16]:

$$V_{\text{corr}} = \frac{m_1 - m_2}{S t} \quad (1)$$

where  $m_1$  is the mass of the C38 steel coupon before immersion in (mg),  $m_2$  the mass of the C38 steel coupon after immersion in (mg),  $S$  is the total area of the C38 steel coupon in ( $\text{cm}^2$ ),  $t$  is the corrosion time in hours (h) and  $V$  is the corrosion rate in ( $\text{mg cm}^{-2} \text{ h}^{-1}$ ). The calculated corrosion rate ( $V_{\text{corr}}$ ) in equation (1) is an average corrosion rate.

From the corrosion rate, the percentage inhibition efficiency IE% and the degree of surface coverage ( $\theta$ ) were calculated using equations (2) and (3), respectively [16]:

$$\text{IE\%} = \frac{(V_{\text{corr}0} - V_{\text{corr}})}{V_{\text{corr}0}} \times 100 \quad (2)$$

$$\theta = \frac{(V_{\text{corr}0} - V_{\text{corr}})}{V_{\text{corr}0}} \quad (3)$$

where  $V_{\text{corr}0}$  and  $V_{\text{corr}}$  are the corrosion rates of the C38 steel coupon in 1 M HCl in the absence and presence of DIT. Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of C38 steel for different concentrations of DIT in 1 M HCl at 298 K after 6 h of immersion are given in Table 1.

This shows that the inhibition efficiency increases with the increasing inhibitor concentration. At this purpose, one observes that the optimum concentration of inhibitor required to achieve the efficiency is found to be  $10^{-2}$  M. The increase in the inhibition efficiency may be due to the adsorption of **DIT** to form an adherent film on the metal surface and suggests that the coverage of the metal surface with this film decreases the double layer thickness. The augmentation in the inhibition efficiency values may be due to the gradual replacement of water molecules by the adsorption of the **DIT** molecules on the metal surface, decreasing the extent of dissolution reaction [17-19]. The inhibition of corrosion of C38 steel by **DIT** can be explained in terms of adsorption on the metal surface. This compound can be adsorbed on the metal surface by the interaction between lone pairs of electrons of nitrogen and sulfur atoms of the inhibitor and the metal surface or via interaction of **DIT** with already adsorbed sulfate ions [16, 20]. This process is facilitated by the presence of vacant orbitals of low energy in iron atom, as observed in the transition group metals.

**Table 1. Effect of DIT concentration on corrosion data of C38 steel in 1M HCl**

Conc. (Mol/L)	$W_{\text{corr}}$ (mg. cm <sup>-2</sup> )	IE (%)
Blank	1.2614	----
$10^{-2}$	0.1106	<b>91.23</b>
$10^{-3}$	0.2694	<b>78.64</b>
$10^{-4}$	0.4122	<b>67.32</b>
$10^{-5}$	0.5282	<b>58.12</b>
$10^{-6}$	0.6795	<b>46.13</b>

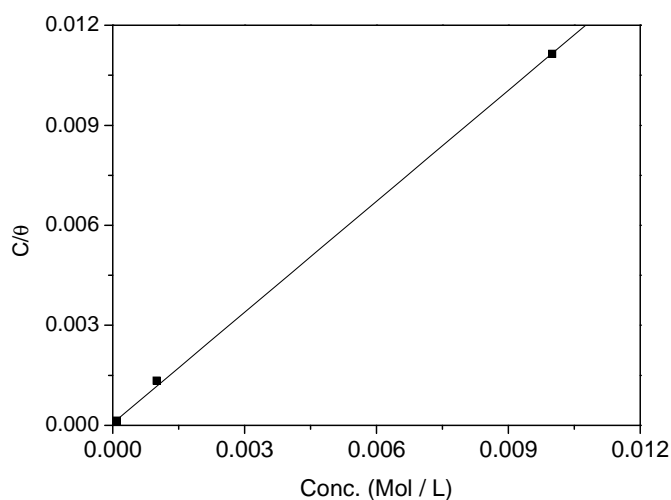
On the other hand, the inhibitor efficiency depends on the type and number of active sites at metal surface, the charge density, the molecular size of the inhibitor, the metal-inhibitor interaction, and the metallic complex formation. The adsorption isotherm can give information on the metal-inhibitor interaction. The adsorption isotherm can be derived from the curve surface coverage against inhibitor concentration. Surface coverage was estimated as Eq. 3. The  $\theta$  values for different inhibitor concentrations at different immersion times were tested by fitting to various isotherms. By far the best fit was obtained with the Langmuir isotherm. According to this isotherm  $\theta$  is related to concentration inhibitor C via

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (4)$$

with

$$K = \frac{1}{55,5} \exp\left(-\frac{\Delta G^{\circ}_{\text{ads}}}{RT}\right) \quad (5)$$

where K is the adsorptive equilibrium constant and  $\Delta G^{\circ}_{\text{ads}}$  the free energy of adsorption.



**Figure 2. Plot of Langmuir adsorption isotherm of DIT on the C38 steel surface at 298K.**

It was found that Fig. 2 (plot of  $\frac{\theta}{C}$  versus  $C$ ) gives straight lines with slope equal or nearly equal to 1.00 and the calculated value of  $\Delta G_{ads}^{\circ}$  is -33.94 kJ/mol.

The negative value of  $\Delta G_{ads}$  show that the adsorption of **DIT** is a spontaneous process under the experimental conditions described [21] and also the strong interaction between inhibitor molecules and the metal surface [22]. The value of  $\Delta G_{ads}$  is less than 40 kJ mol<sup>-1</sup> is commonly interpreted with the presence of physical adsorption by the formation of an adsorptive film with an electrostatic character [23-24]. In the other, the calculated  $-\Delta G_{ads}$  values in the range 30–40 kJ/mol indicate, therefore, that the adsorption mechanism of the **DIT** on C38 steel in 1 M HCl solution was both electrostatic-adsorption and chemisorption [25-26]. **DIT** possess aromatic  $\pi$ -electrons as well as unshared electrons pairs on the nitrogen and sulphur atoms, which can interact with d-orbitals of iron to provide a protective film [19, 22].

#### Effect of temperature

To investigate the mechanism of inhibition and to calculate the activation energies of the corrosion process, polarization measurements were taken at various temperatures in the absence and the presence of the optimal concentration of DIT. Corresponding data are given in Table 2, figures 3 and 4.

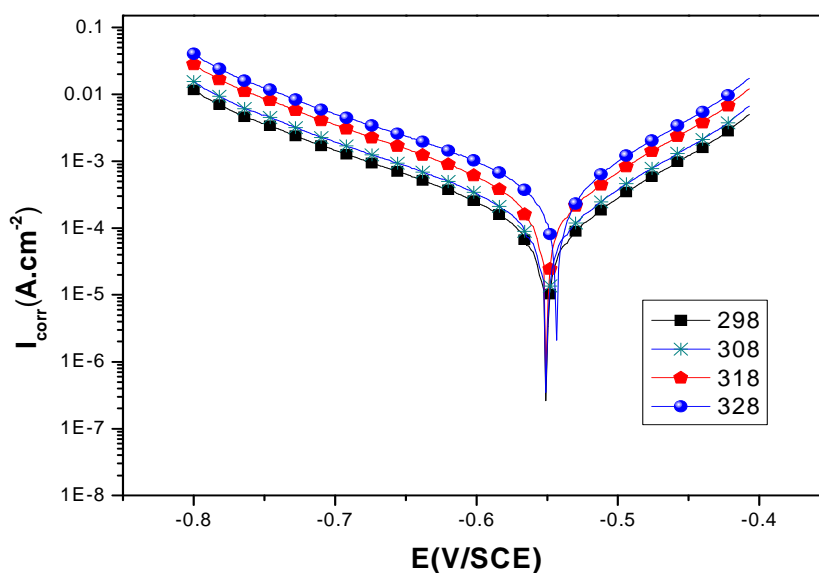


Figure 3. Potentiodynamic polarisation curves of C38 steel in 1M HCl at different temperatures

Table 2. The influence of temperature on the electrochemical parameters and inhibition efficiency for C38 steel electrode immersed in 1 M HCl and at 10<sup>-2</sup> M of DIT.

	Temp. (K)	E <sub>corr</sub> (mV/SCE)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	-b <sub>c</sub> (mV/dec)	E (%)
Blank	298	-612	124	149	----
	308	-544	177	132	----
	318	-545	280	133	----
	328	-537	435	140	---
<b>DIT</b>	298	-532	09	221	<b>92.74</b>
	308	-553	10	154	<b>94.35</b>
	318	-515	12	160	<b>95.71</b>
	328	-526	15	163	<b>96.55</b>

Corresponding data are given in Table 2. In the studied temperature range (298 - 328 K) the corrosion current density increases with increasing temperature both in uninhibited and inhibited solutions and the values of the inhibition efficiency of DIT increases with increasing temperature. The corrosion current density of C38 steel increases more rapidly with temperature in the absence of the inhibitor, these results confirm that DIT acts as an efficient inhibitor in the range of temperature studied. The DIT inhibitor efficiency was temperature dependent.

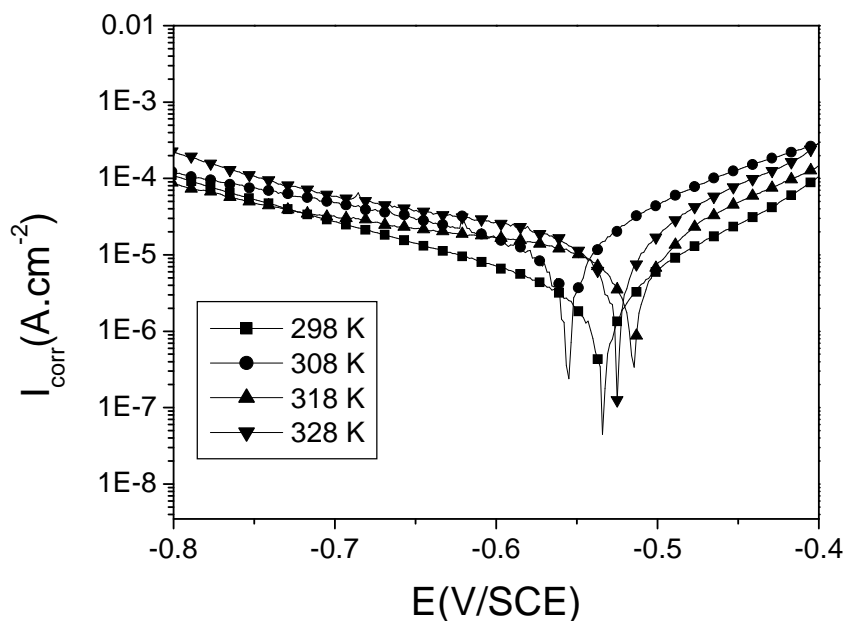


Figure4. Effect of temperature on the cathodic and anodic responses for C38 steel in 1 M HCl +  $10^{-2}$  M of DIT.

The activation parameters for the corrosion process were calculated from Arrhenius type plot according to the following equation:

$$\ln(I_{\text{corr}}) = -\frac{E_a}{RT} + \log A \quad (6)$$

and from transition state plot according to the following equation:

$$\log \frac{I_{\text{corr}}}{T} = -\frac{\Delta H_a^0}{RT} + B \quad (7)$$

where  $E_a$  is the apparent activation energy,  $A$  the pre-exponential factor,  $R$  the universal gas constant,  $\Delta H_a$  the enthalpy of activation and  $T$  the absolute temperature.

The variations of logarithm of the corrosion rate of C38 steel ( $\log I$ ) in hydrochloric acid containing  $10^{-2}$  M of DIT and  $\log(I/T)$  with reciprocal of the absolute temperature are presented in Figs. 5 and 6, respectively.

Straight lines with coefficients of correlation ( $cc$ ) higher to 0.99 are obtained. The  $E_a$  and  $\Delta H_a$  values were determined from the slopes of these plots. The calculated values of  $E_a$  and  $\Delta H_a$  in the absence and the presence of the optimal concentration of DIT are given in Table 3.

Table 3. The value of activation parameters  $E_a$ ,  $\Delta H_a$  and  $\Delta S_a$  for C38 steel in 1M HCl in the absence and presence of DIT

Inhibitor	$E_a$ (kJ/mol)	$\Delta H_a$ (kJ/mol)	$\Delta S_a$ (J/mol)	$E_a - \Delta H_a$ (KJ/mol)
Blank	37.22	34.63	-164.35	34.74
DIT	13.85	11.26	-189.02	11.37

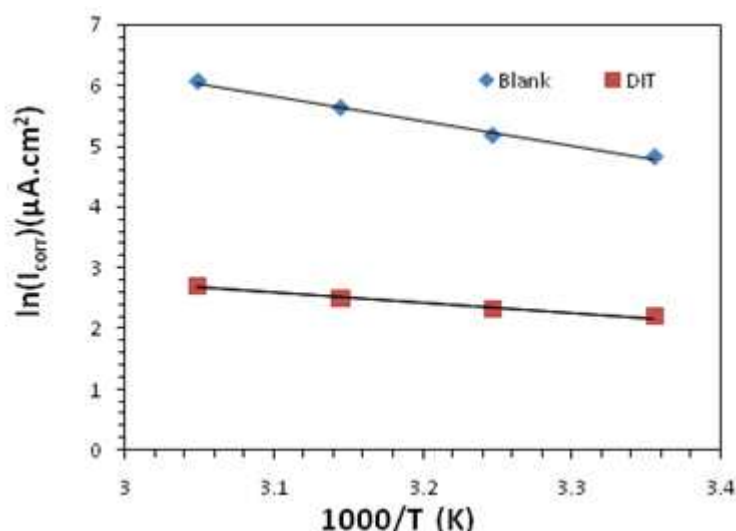


Figure 5. Arrhenius plots of C38 steel in 1 M HCl with and without  $10^{-2}$  M of DIT.

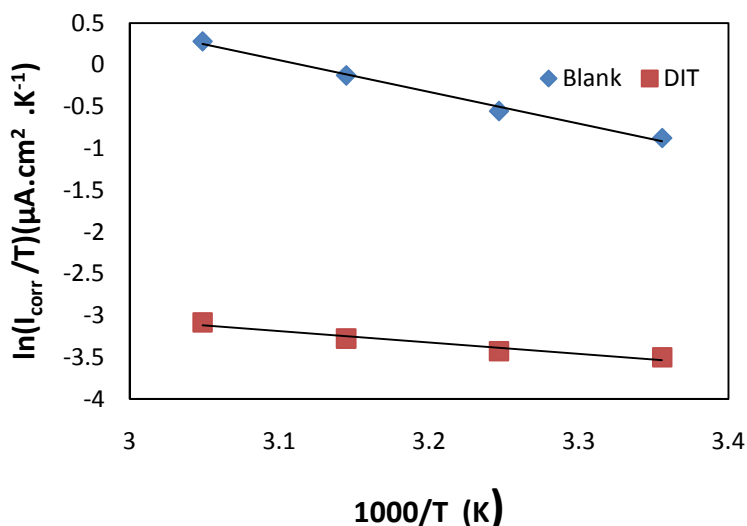


Figure 6 .  $\log(I_{\text{corr}}/T)$  vs.  $1/T$  for C38 steel dissolution in 1 M HCl in the absence and the presence of  $10^{-2}$  M of DIT.

The positive sign of enthalpies ( $\Delta H_a$ ) reflect the endothermic nature of the steel dissolution.

Inspection of these data reveals that the apparent activation energy  $E_a$  in HCl solution in the absence of the **DIT** was 37.22 kJ / mol. The addition of DIT to the acid solution decreases the activation energy. Note that the reduction of the activation energy in the presence of DIT may be attributed to the chemisorption of the DIT inhibitor on steel surface [27, 28].

Moreover one remark that the  $\Delta H_a$  values obtained from the slopes of plots  $\log(I_{\text{corr}}/T)$  vs  $f(1/T)$  and those determined from the equation (8) are in good agreement.

$$\Delta H_a = E_a - RT \quad (8)$$

## CONCLUSION

In this study, the inhibition property of 4,5-Diphenyl-1H-Imidazole-2-Thiol (**DIT**) was tested by using weight loss measurements. According to the results, 4,5-Diphenyl-1H-Imidazole-2-Thiol (**DIT**) is a good inhibitor in 1 M HCl. The optimum concentration of the inhibitor is  $10^{-2}$  M for an inhibition efficiency of  $\geq 92\%$ . The protection efficiency increased with increasing inhibitor concentration, but decreased slightly with the rise of temperature. The calculated activation energy value indicated that adsorbed inhibitor molecules create a physical and or chemical

barrier to charge, and mass transfer for metal dissolution and hydrogen reduction reaction. Adsorption of the inhibitor molecule onto mild steel surface obeys the Langmuir isotherm.

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