Study of 1,2,4-Triazole As Effective Corrosion Inhibitor For Mild Steel Used In Oil And Gas Industries In 1M HCl

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ABSTRACT

The corrosion inhibition effect of 1,2,4-triazole on mild steel in 1 M HCl solution has been investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization methods. The experimental results revealed that the compound having significant inhibiting effect on the corrosion of mild steel in 1M HCl solution. The inhibition efficiency was found to increase with increasing concentration of inhibitor and attain maximum value of 93% at 500 ppm concentration. Potentiodynamic polarization studies have shown that the compound acted as mixed-type inhibitor retarding the corrosion of mild steel by blocking the active sites of metal surface. The values of inhibition efficiency obtained from weight loss and polarization measurements are in good agreement. The adsorption of the inhibitor on mild steel surface followed Langmuir adsorption isotherm with negative value of the free energy of adsorption $\Delta G^0_{ads.}$ The surface morphology of the mild steel specimen was evaluated by using scanning electron microscopy(SEM)and energy dispersive x-ray analysis(EDAX) techniques.

Keywords: Triazole, Mild Steel, Inhibitor, Surface Morphology.

I. INTRODUCTION

Mild steel is an important category of material due to wide range of industrial applications[1-4]. Hydrochloric acid solutions are widely used for pickling, descaling, acid cleaning and oil well acidizing industry which leads to electrochemical corrosion. Among the various methods available, use of corrosion inhibitor is one of the most practical and economical method for corrosion protection of steel especially in acid media[4-8].An organic corrosion inhibitor is a chemical material applied to a liquid or gas within industrial processes to decrease the corrosion rate of metal or its alloy[9].Organic inhibitors containing heteroatom such as O,N,S and P are frequently used in order to minimize the corrosion attack on metal in acid media [10-15]. Organic inhibitors are generally adsorbed on metal surface and forms protective film which acts as barrier between the metal and aggressive solutions. The efficiency of organic compounds as an inhibitor depends on its ability to get adsorbed on the metal surface by replacing water molecule from metal surface. Nitrogen containing heterocyclic compounds are found very effective and efficient corrosion inhibitor of mild steel in acidic media. Persual of literature reveals that many N-heterocyclic compounds such as pyrazole, bipyrazole, benzimidazole, triazole, tetrazole, quinoline, isoquinoline,indole and quinoxaline have been used for corrosion inhibition of mild steel in acidic media [16-20]. Triazole and its derivatives are important constituents of pharmacologically active compounds. They possess wide spectrum of activities ranging from antibacterial, anti-inflammatory, anticonvulsant and

anti-neoplastic[21].A few triazole have been reported as corrosion inhibitor in different corrosive environment.

The present study was undertaken to investigate the inhibition of corrosion of mild steel in 1M hydrochloric acid by 1,2,4-triazole.The study was conducted by using weight loss, electrochemical technique, Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques.

II.   METHODS AND MATERIAL
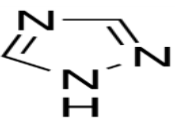
2.1. Material and sample preparation

The weight loss and electrochemical experiments were performed on mild steel specimen having chemical composition, C-0.16%, Si-0.10%, Mn-0.40%, P-0.013%, S-0.02% and remaining iron. The exposed dimensions were 1cm x 3cm x 0.025cm and 1cm^2 for the weight loss and electrochemical experiment respectively. Before exposure to test solution exposed areas were polished successively with different grades of metallographic emery paper,1/0,2/0,3/0 and 4/0, washed with doubled distilled water, degreased with acetone and finally dried and stored in desiccators.

2.2. Test solution

1 M HCl was prepared by dilution of 36% HCl (analytical grades) in bi-distilled water.

The characterization data, IUPAC name, structure and abbreviation used for the studied compound are given below in Table 1.

Table 1. IUPAC name, molecular structure, melting point and analytical data of studied inhibitor.

Inhibitor	Molecular Structure	Analytical data
1,2,4-Triazole		**MP-** 120-122 °C

2.3. Weight loss measurement:

The weight loss experiment was performed by immersing mild steel specimen in 50 ml of test solution with and without different concentration of inhibitors. After 24 h immersion time, the mild steel specimens were taken out, cleaned with distilled water, dried and accurately weighed. Each experiment was performed in triplicate to obtain good result and the mean value is reported. The inhibition efficiency was calculated by using the following relation:

$$\eta\% = \frac{W_o - W_{corr}}{W_o}$$

Where W_o and W_{corr} are the weight loss in absence and presence of inhibitors .The surface coverage is given by following relation
$\theta = \eta\%/100$.

2.4 Electrochemical measurement:

Polarization studies were carried out using electrochemical measurement system, DC 105, containing software of DC corrosion technique from M/S Gamry instrument, 734, Louis Drive, Warminster, PA, USA. For polarization studies, mild steel specimens having surface area of 1cm^2 were exposed to acid solution .Mild steel as working electrode, saturated calomel (SCE) as reference electrode and graphite as auxiliary electrode were used for all electrochemical measurement. Before each measurement the specimen were allowed to corrode freely, and their OCPs were measured as a function of time to obtain a steady-state potential. The anodic and cathodic Tafel curves were obtained by changing the electrode potential automatically from - 0.5 to 0.5 V at the scan rate of 5mv/s. Polarization study was done with and without inhibitors in 1M HCI.

2.5 Surface measurement:

The surface film formed on the metal specimen was evaluated by SEM-EDX analysis. This was carried out by using SEM/EDX model PHENOM PROX from the

Netherlands. The spectra were recorded for a sample exposed for 24 hours in 1M HCl in the absence and presence of 500 ppm inhibitor. The energy of acceleration beam employed was 20 kV.

III. RESULTS AND DISCUSSION

3.1 Weight loss measurement:

Weight loss data of mild steel in 1 M HCl in the absence and presence of various concentrations of inhibitor were obtained and given in table 2. Inhibition efficiencies were calculated according to following equation:

$$\%IE = \frac{W_0 - W_{corr}}{W_{corr}}$$

W_{corr} and W_0 are weight loss of mild steel in presence and absence of inhibitors respectively. The results showed that the inhibition efficiency increases with increasing the concentration of inhibitors. The results obtained from the weight loss measurement were in good agreement with those obtained from electrochemical measurements.

Table 2. The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of 1, 2, 4-triazole.

Inhibitor	Concentration (ppm)	Weight loss (mg)	Surface coverage	Inhibition efficiency (%E)
Blank	-	235	-	-
1,2,4-triazole.	100	42	0.8212	82.12
	200	30	0.8723	87.23
	300	28	0.8808	88.08
	400	21	0.9106	91.06
	500	16	0.9319	93.19

3.2 Adsorption isotherm

The surface coverage values θ, (defined as θ = %IE/100), increased with increasing inhibitor concentration as a result of adsorption of more inhibitor molecules on the steel surface (Table-2). If molecular adsorption at the metal/solution interface is the mechanism through which the corrosion inhibition occurs, several adsorption isotherms can be tested. The simplest, being the Langmuir isotherm, is based on the assumption that all adsorption sites are equivalent and that molecular binding occurs independently from nearby sites being occupied or not. Under these circumstances, the proportionality $\overline{=} \overline{=} \overline{=}$ (1) between surface coverage θ and bulk concentration C of the adsorbing compound is as follows [22]:

$$KC = \theta / (1-\theta) \qquad ----- (2)$$

Here K is the equilibrium constant. It is convenient to rearrange the equation, yielding:

$$C / \theta = C + 1/K \qquad ----- (3)$$

The graph of C/θ vs C obtained straight line with R^2 value obtained varied close to unity confirming the validity of this approach. The slope of the straight line was almost close to unity, suggesting that adsorbed molecule formed monolayer on mild steel surface.

Free energy of the adsorption (ΔG^0_{ads}) can be calculated by using the following equation:

$$\Delta G^0_{ads} = -RT \ln (55.5 \ k_{ads}) \qquad ----- (4)$$
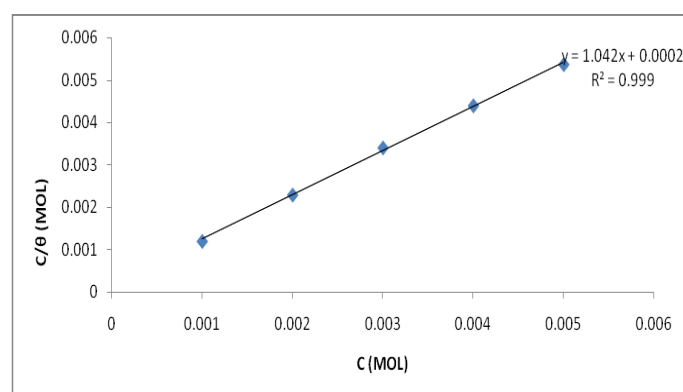

y = 1.042x + 0.0002
R² = 0.999

Figure 1. Langmuir isotherm plot for adsorption of 1,2,4-triazole on mild steel surface in 1 M HCl.

Generally, value of ΔG^0_{ads} up to -20 kjmol^{-1} are associated with physisorption while those around -40 kjmol^{-1} or higher are associated with chemisorptions. In present case the value was -31.05. This was lower than -40 kJ mol^{-1} but higher than -20 KJmol-1 indicating that the adsorption was neither typical physisorption nor chemisorption but it is mixed type. Thus in the present case adsorption of inhibitor molecule on the mild steel involved both physisorption and chemisorptions but physisorption was the predominant mode of adsorption. The negative value of ΔG^0_{ads} indicated the spontaneous adsorption of inhibitors on the surface of the metal [23,24]

3.3 Open circuit potential (OCP) measurement

The electrochemical behaviour of mild steel in 1M HCl was studied by monitoring change in corrosion potential (Ecorr.) with time. The change in open circuit potential of mild steel in absence and presence of various concentrations of inhibitors is shown in Figure 2.
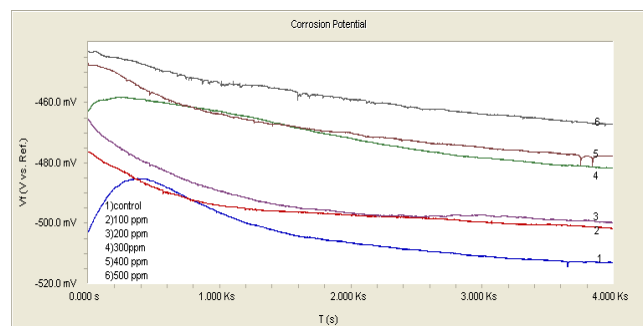

Figure 2. Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of 1,2 , 4-Triazole.

The change in OCP of mild steel in absence and presence of inhibitors were measured for period of one hour with sample period of one data per second. The potential attains steady state after exposure of approximately 30 minutes. The steady state potential is an equilibrium state at which Iox. equal to Ired. It has been observed that OCP of mild steel from moment of immersion in 1M HCl tends towards more

negative value in absence of inhibitor. This shows corrosiveness of medium which is due to breakdown of pre-immersion, air formed oxide film on the metal surface. In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more towards positive value. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal.

3.4 Potentiodynamic polarisation studies

The polarization behaviour of mild steel in 1 M HCl in the absence and presence of different concentration of inhibitors are shown in Figure 3.
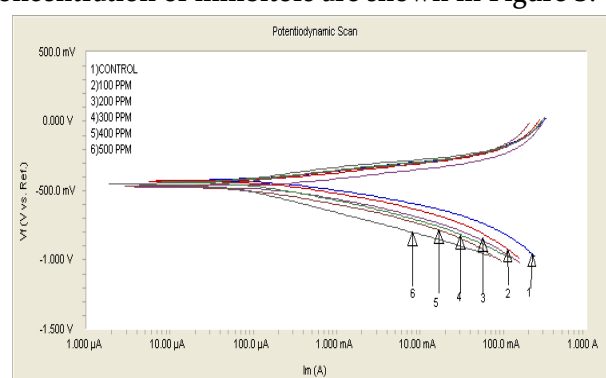

Figure 3. Polarization curve of mild steel in the absence and presence of 1,2,4-Triazole.

Electrochemical parameters such as corrosion current (I$_{corr}$), corrosion potential (E$_{corr}$), and Tafel slopes constant β_a and β_c calculated from Tafel plots are given in table 3. From the evaluated I$_{corr}$ value, η% can be calculated using the relation $\eta\% = \frac{i_0 - i_{corr}}{i_0}$ .where i$_0$ and i$_{corr}$ are the corrosion current densities in the absence and presence of inhibitors. From the data of table3 and figure 2, it is clear that in the presence of tetrazole there was remarkable decrease in i$_{corr}$ value by shifting both anodic and cathodic Tafel slopes towards low current densities [25]. It was further confirmed that the shape of polarization curves were similar in absence and presence of inhibitors, suggesting that 1,2,4-triazole inhibited mild steel corrosion by simply adsorbing on the mild steel surface without changing the mechanism

of mild steel dissolution[26]. An inhibitor can be classified as anodic, cathodic or mix type depending upon the displacement in E_{corr} value. If the displacement in E_{corr} for the inhibited and uninhibited solution is more than 85mV it can be classified as cathodic or anodic type. But the displacement in E_{corr} is less than 85 mV then it can be classified as mixed-type. Since the maximum displacement for studied compound was 23 mV indicating that tetrazole is mixed type of inhibitor [27].

Table 3. Tafel polarization parameters for mild steel in 1 M HCl in absence and presence of 1,2,4-triazole.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	-470.0	704.0	103.3 e^{-3}	196.4 e^{-3}	-
	100	-475.0	128.0	71.50 e^{-3}	144.3 e^{-3}	81.81
	200	-473.0	90.90	68.30 e^{-3}	133.6 e^{-3}	87.08
	300	-475.0	84.00	69.70 e^{-3}	164.5 e^{-3}	88.06
	400	-483.0	63.40	83.00 e^{-3}	169.3 e^{-3}	90.99
	500	-	36.90	93.1 e^{-3}	154.6	93.

IV. SURFACE STUDIES

4.1 SEM studies

To support our conclusion that the 1, 2, 4-triazole form protective surface film, SEM micrograph of the mild steel surface were recorded in the absence and presence of 500 ppm concentration of triazole. The result shows that the surface of polished mild steel

coupon (Figure 4a) was considerably smoother with minimum undulation or pitting. (Fig-4b) shows the surface of coupon immersed in 1 M HCl solution which is strongly damaged due to acid corrosion. However the coupon immersed in the solution containing 500 ppm of 1,2,4-triazole was relatively smooth compared to free acid solution(Figure 4c).
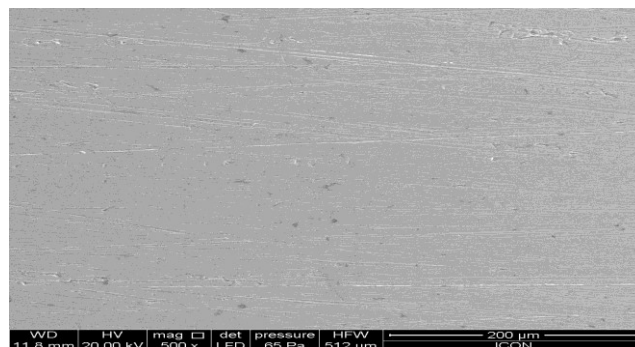

Figure 4(a). SEM micro graphs of mild steel surface before immersionin 1 M HCl
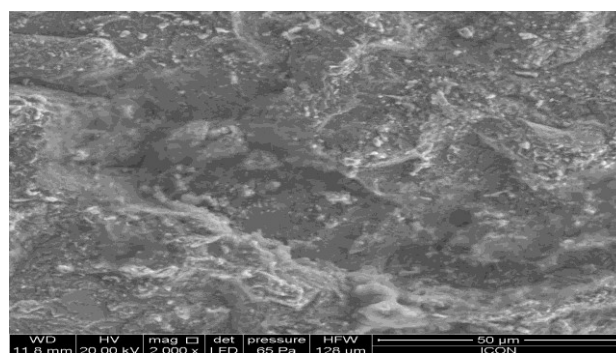

Figure 4(b). SEM micro graphs of mild steel surface after one day immersion in 1 M HCl
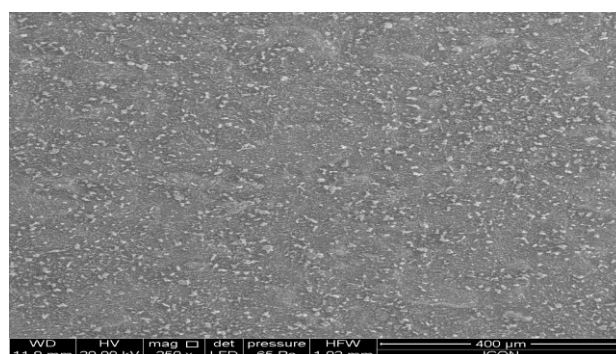

Figure 4(c). SEM micro graphs of mild steel surface after one day of immersion in 1 M HCl+500 ppm of 1,2,4-Triazole.

4.2 EDX studies

To further support our weight loss and electrochemical finding that 1, 2, 4-triazole inhibit mild steel corrosion by forming a protective film on surface, we recorded a the EDX spectra in absence and presence of 500 ppm of 1, 2,4-triazole.

The spectral profile of the polished mild steel sample before immersion in 1M HCl shows the signal for Fe, C and O. On immersion in 1M HCl, the signal for O is disappeared due to breaking of preimmersion air formed oxide film. Signal for Fe and carbon also slightly decreased. The profile in presence of 1, 2, 4-triazole shows additional signal for nitrogen atoms. This is due to adsorption of inhibitor on the mild steel surface.
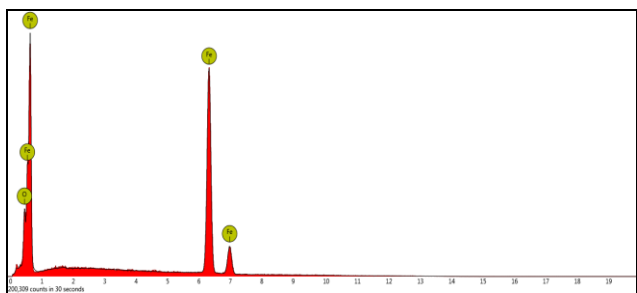

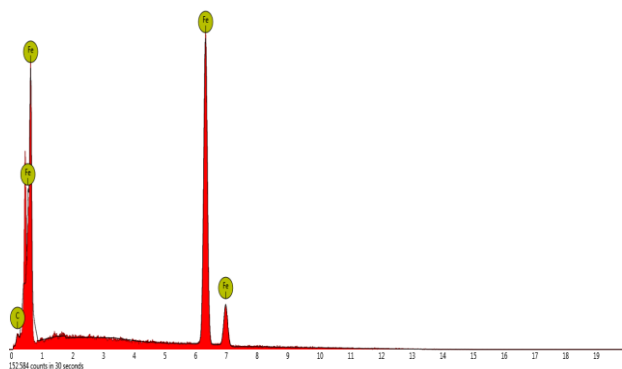**Figure 5.** EDX of (a) polished mild steel surface

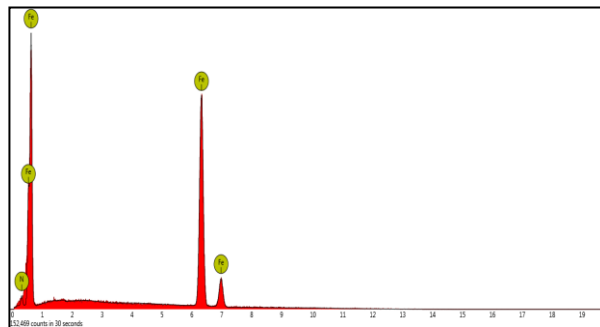**Figure 5.** EDX of (b) after one day immersion in 1 M HCl

Figure 5. EDX of (c) after one day of immersion in 1 M HCl +500 ppm of 1,2,4-Triazole.

V. MECHANISM OF INHIBITION

Corrosion inhibitors are believed to act by adsorption on metal surface by either physical or chemical means. The physical adsorption occurs via electrostatic interaction between the oppositely charged inhibitor molecule and metal surface, whereas chemical adsorption take place via donor acceptor interaction between lone pair electrons of heteroatom (N,S,O),π electrons of aromatic rings and polar functional groups with vacant d orbital of metal. The compound inhibits corrosion by controlling both anodic as well as cathodic reactions. In acid solution, inhibitor can exist as protonated species. The nitrogen atom present in the molecule can be easily protonated in acidic solution which can get adsorbed onto the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on the anodic sites occurs through pi electrons of triazole ring and lone pairs of electrons of nitrogen atoms which decrease the anodic dissolution of mild steel.

VI. CONCLUSION

The corrosion behaviour of mild steel in 1 M HCl in absence and presence of tetrazole compound was investigated using the weight loss, open circuit potential and potentiodynamic polarization technique and surface analytical techniques. From the result obtained the following conclusion can be drawn:

1. 1, 2, 4-Triazole acted as a good and efficient corrosion inhibitor for the corrosion of mild steel in 1M HCl solution.
2. The inhibition efficiency increased with an increase in the concentration of inhibitor.
3. The adsorption of the inhibitor on mild steel surface obeyed Langmuir adsorption isotherm. The negative Gibbs free energy value indicated that the adsorption of inhibitor on surface is spontaneous process.
4. Polarization studies showed that 1,2,4-triazole acts as mixed inhibitor
5. The surface morphology techniques revealed the formation of smooth uniform surface on mild steel in presence of inhibitor.

VII.   REFERENCES

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