

## Corrosion Inhibition Property of Some 1, 3, 4- Thiadiazolines on Mild Steel in Acidic Medium

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Received 9 July 2009; Accepted 5 September 2009

**Abstract:** The present work deals with the corrosion behavior of mild steel in acidic medium. The inhibitive effect of substituted 1, 3, 4-Thiadiazol-2-amines on the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> has been studied by weight loss and electrochemical methods. The electrochemical parameters for mild steel in acidic solution with and without inhibitor were calculated. The effect of temperature on the corrosion rate, activation energy and free energy of adsorption were also calculated. The synergistic effect has been studied by weight loss and electrochemical methods. The electrochemical parameters for mild steel in acidic solution were also calculated.

**Keywords:** Corrosion, Inhibition, Mild steel, 1,3,4-Thiadiazolines.

### Introduction

Most of the acid inhibitors are organic compounds 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. The influence of such organic compounds, on the corrosion of mild steel in acidic solution has been investigated by several authors. The inhibition property of these compounds is attributed to their molecular structure. The planarity and 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 there by reduce the corrosion rate.

The aim of this work is to investigate the role played by newly synthesized substituted 1, 3, 4-thiadiazol-2-amines on the corrosion behaviour of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub>. Using thiadiazolines only biological activities were carried out. Moreover using other *N*-heterocyclic compounds like thiadiazoles, triazoles, thiosemicarbazones *etc.* various corrosion studies

were carried. Hence a corrosion study using substituted 1, 3, 4-thiadiazol-2-amines is a new methodology though its synthesis already exists. Since the work on the corrosion inhibition of mild steel is not expensive, an attempt was made to examine the inhibitive action of mild steel in acidic solutions.

## Experimental

Mild steel specimens having the size of  $3.5 \times 1.5 \text{ cm}^2$  (C: 0.07%, S: Nil, P: 0.008 %, Si: Nil, Mn: 0.34, Rest: Fe) were used for the weight loss measurement.

### Synthesis of inhibitor

Substituted 1,3,4-thiadiazol-2-amines [(01TD),(02TD)(03TD)] have been chosen as inhibitors for the present investigation. The chemicals used were of Analar grade. 1,3,4-Thiadiazol-2-amines was synthesized in three stages as follows.

#### Stage I: Preparation of *N*- aryl thiosemicarbazide

About 0.1 mole of the aromatic primary amine was dissolved in 50 mL of 95% ethanol and 20 mL of ammonium hydroxide was added. After cooling the reaction mixture below  $30^\circ\text{C}$ , 8 mL of carbon disulphide was added slowly for 15 minutes with shaking. After the complete addition of carbon disulphide the solution was allowed to stand for an hour. About 0.1 mole of sodium chloroacetate solution was added to it. During this addition, the reaction was found to be exothermic and colour change was observed from red to yellowish green. About 20 mL of 50% solution of hydrazine hydrate was added. The mixture was warmed gently and kept overnight. The product thiosemicarbazide was filtered and recrystallised from ethanol. The purity of the compound was checked using TLC.

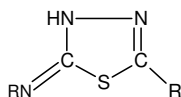
#### Stage II: Preparation of *N*-arylthiosemicarbazones

About 0.01 mole of the aromatic aldehyde and 0.01 mole of thiosemicarbazide were dissolved in 50 mL of ethanol and the solution was taken in a round bottomed flask. The mixture was refluxed for 3 to 4 h on a water bath. The product was cooled, filtered and recrystallised from ethanol.

#### Stage III: Preparation of thiadiazolines

The thiosemicarbazone in ethanol and sodium hydroxide with a little water was warmed on a water bath for 5 minutes and a solution of 10 % potassium ferricyanide was added drop wise until precipitation just appeared. The contents were warmed for about 1-2 h on a water bath and mixture was poured into a beaker, containing water. The product was filtered and recrystallised from ethanol. The compounds synthesized in this present study were (01TD), (02TD) and (03TD).

#### Structure and melting point of the Inhibitors



Inhibitors	R	R'	Melting Point
01TD	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	287.4° C
02TD	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	317.4° C
03TD	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>4</sub> OH	303° C

#### Weight loss measurement

Mild steel specimen was polished using 1/0, 2/0, 3/0 and 4/0 emery papers and finally degreased with the organic solvent trichloroethylene. The specimens were weighed. After

weighing the specimens were immersed in 1 M sulphuric acid with and without inhibitor. After 2 h, the specimens were washed with distilled water, dried and again weighed. The weight loss was noted. From this weight loss value, corrosion rate and inhibition efficiency were determined.

Corrosion rate has been determined from the following relationship.

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Weight loss in mg}}{\text{Density in g/cc} \times \text{Area in sq.inches} \times \text{Time in h}}$$

Inhibitor efficiency has been determined by using the following relationship.

$$\text{Inhibitor efficiency (\%)} = \frac{W_0 - W_e}{W_0}$$

Where,  $W_0$  is the weight loss without inhibitor and  $W_e$  is the weight loss with inhibitor.

### *Temperature studies*

The inhibition efficiencies of substituted thiadiazolines at room temperature and higher temperatures (313, 318, 323 and 328 K) have been determined for optimum inhibitor concentration of their inhibitors by using weight loss experiments. This study gives details about the nature of adsorption and activation energy.

### **Electrochemical studies**

#### *Electrode surface preparation*

The mild steel rod with an exposed area of 0.785 cm<sup>2</sup> was polished using 1/0, 2/0, 3/0 and 4/0 emery papers and finally degreased with the organic solvent trichloroethylene and immediately used for the experiments.

#### *Electrode cell assembly*

Electrochemical measurements were carried out in a glass cell with a capacity of 100 mL. A platinum electrode and a saturated calomel electrode were used as a counter electrode and reference electrode respectively. The mild steel electrode was then placed in the test solution (uninhibited and inhibited solutions) for 10-15 minutes before electrochemical measurements.

#### *Electrochemical study*

Electrochemical impedance spectroscopy (EIS) and Tafel polarization studies were conducted in an electrochemical measurement unit (Model 1280 B Solartron, UK). The EIS measurements were made at corrosion potentials over a frequency range of 10 kHz to 0.01 Hz with signal amplitude of 10 mV. The Tafel polarization measurements were made after EIS for a potential range of -200 mV to + 200 mV with respect to open circuit potential, at a scan rate of 1mV/sec. The  $I_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $R_{\text{ct}}$  and  $C_{\text{dl}}$  values were obtained from the data using the corresponding ‘‘Corr view’’ and ‘‘Zview’’ softwares. The inhibition efficiency from potentiodynamic polarization was calculated from the value  $I_{\text{corr}}$  by using the formula.

$$\text{Inhibition efficiency (\%)} = \frac{I_{\text{corr(Blank)}} - I_{\text{corr(inh)}}}{I_{\text{corr(Blank)}}} \times 100$$

Where,  $I_{\text{corr(Blank)}}$  is the corrosion current in the absence of inhibitor.

$I_{\text{corr(inh)}}$  is the corrosion current in the presence of inhibitor.

The inhibition efficiency from impedance measurements was calculated using the formula

$$\text{Inhibition efficiency (\%)} = \frac{R_{\text{ct(inh)}} - R_{\text{ct(Blank)}}}{R_{\text{ct(inh)}}} \times 100$$

Where,  $R_{\text{ct(inh)}}$  is the charge transfer resistance in the presence of inhibitor.

$R_{\text{ct(Blank)}}$  is the charge transfer resistance in the absence of inhibitor.

### Synergistic effect

The synergistic effect was also studied by electrochemical techniques in the presence of 1 M KCl, KBr and KI to the steel specimen immersed in 1 M sulphuric acid containing various concentrations of inhibitors for duration of 2 h. From the weight loss data the corrosion rate and inhibition efficiency was calculated.

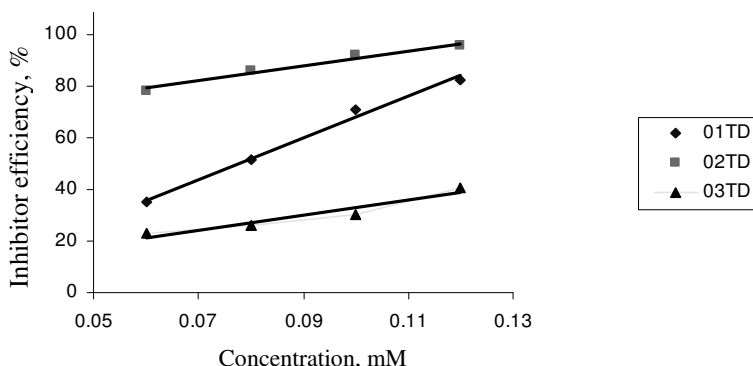
## Results and Discussion

### Weight loss measurements

The inhibiting efficiencies and corrosion rate with different concentrations (0.04, 0.06, 0.08 and 0.1 mM) of the inhibitors [(01TD) and (02TD)] and with the concentrations (0.04, 0.06, 0.08, 0.1, 0.2, 0.4 and 0.6 mM) of the inhibitor (03TD) on mild steel in 1 M sulphuric acid have been evaluated by weight loss measurements and results were summarized in Table 1. The effect of concentration on inhibition efficiencies and corrosion rate were shown in Figure 1. The synergetic effects caused by halide ions were also included in Table 2. The inhibition efficiencies and corrosion rate of the inhibitors at higher temperature were given in Table 3.

**Table 1.** Corrosion parameters of (01TD),(02TD) & (03TD) on mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> from weight loss measurements

S.No	Inhibition concentration, mM	Inhibition efficiency, %		
		01TD	02TD	03TD
1	Blank	-	-	-
2	0.04	8.88	6.55	16.63
3	0.06	35.22	78.12	22.77
4	0.08	51.53	86.12	26.13
5	0.1	70.92	91.82	30.09
6	0.12	82.54	95.52	40.5



**Figure 1.** Inhibition efficiency vs. concentration of compounds [(01TD), (02TD) and (03TD)] on the surface of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub>.

**Table 2.** Corrosion parameters of variously substituted thiadiazolines on mild steel at various halides in 1 M H<sub>2</sub>SO<sub>4</sub>

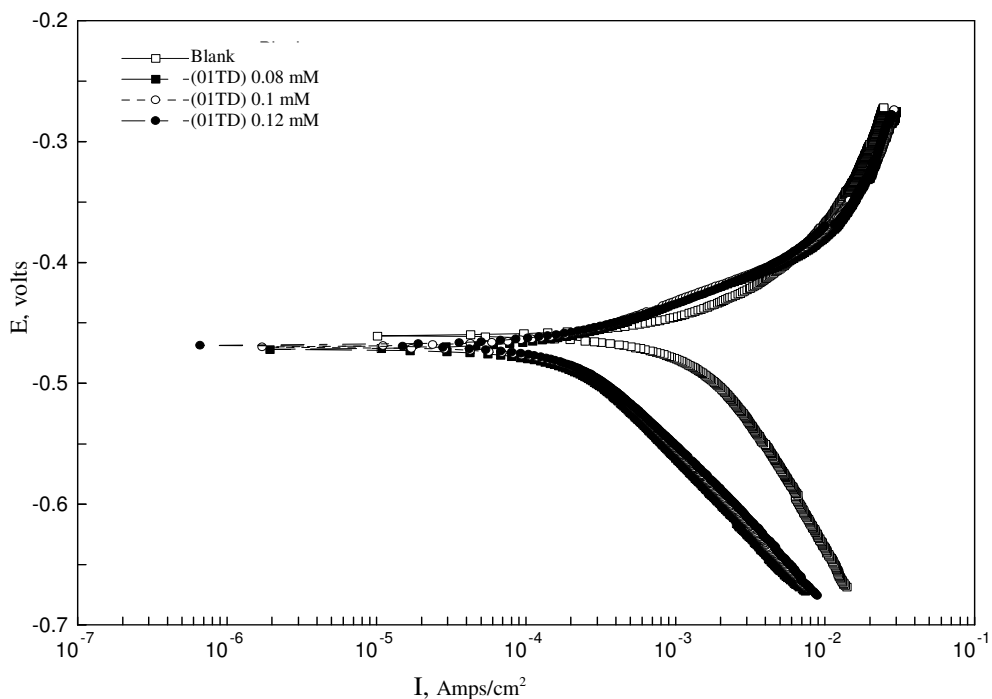
S.No	Compound	Concentration, mM	Inhibition efficiency, %		
			1 M KCl	1 M KBr	1 M KI
1	01TD	0.1	76.93	82.61	89.36
2	02TD	0.06	86.57	92.80	96.34
3	03TD	0.2	84.32	90.76	95.16

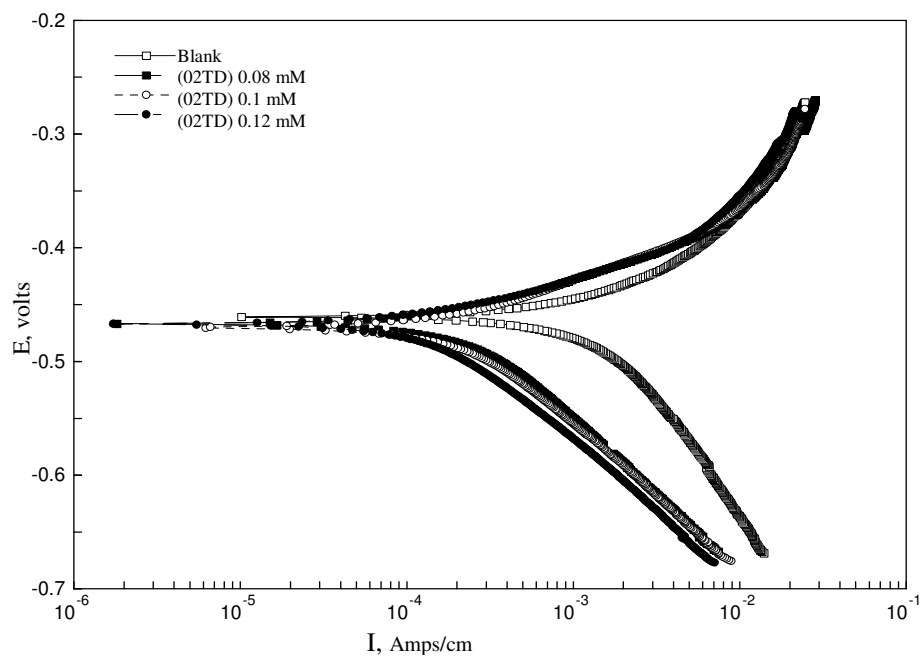
**Table 3.** Corrosion parameters of variously substituted thiadiazolines on mild steel at various temperatures in 1 M H<sub>2</sub>SO<sub>4</sub>.

S. No	Temperature, K	Inhibition efficiency, %		
		01TD	02TD	03TD
1	313	47.60	81.80	71.33
2	318	41.29	75.23	66.98
3	323	35.07	65.18	58.69
4	328	32.18	54.19	54.84

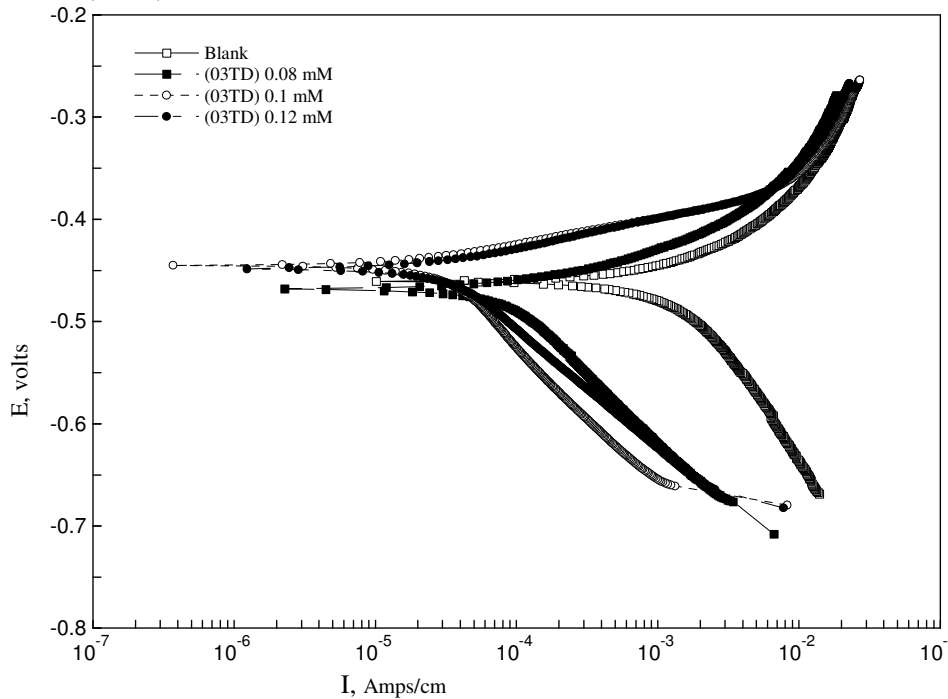
*Potentiodynamic polarization studies*

Potentiodynamic polarization studies were carried out for the corrosion of mild steel in 1 M sulphuric acid solution with and without inhibitors. The experiments were carried out at  $30 \pm 1^\circ\text{C}$  with a fine Luggin capillary to avoid ohmic polarization. The working electrode was prepared from a cylindrical mild steel rod insulated with polytetrafluoroethylene tube such that the area exposed to the solution was  $0.785 \text{ cm}^2$ . A saturated calomel electrode was used as the reference and platinum electrode ( $1 \text{ cm}^2$ ) was used as the counter electrode. The electrochemical parameters  $E_{\text{corr}}$  (corrosion potential) and  $I_{\text{corr}}$  (corrosion current) were obtained by the extrapolation of anodic and cathodic slopes. Tafel constants  $b_a$  and  $b_c$  were obtained from the anodic and cathodic polarization curves, respectively. These parameters are listed in Tables 4-6 and the representative curves are given in Figures 2-4. Addition of the inhibitors lowers the  $I_{\text{corr}}$  value significantly and this indicates the inhibiting nature. The inhibition efficiencies and corrosion rate have also been calculated and the results are included in Tables 4-6.

**Figure 2.** Potentiodynamic Polarization curves for mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of (01TD).



**Figure 3.** Potentiodynamic Polarization curves for mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of (O2TD).



**Figure 4.** Potentiodynamic Polarization curves for mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of (O3TD).

**Table 4.** Potentiodynamic polarization parameters for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without (01TD)

S.No	Inhibition Concentration mM	I <sub>corr</sub> mA/cm <sup>2</sup> ×10 <sup>-2</sup>	E <sub>corr</sub> mV vs. SCE	b <sub>a</sub> mV/dec	b <sub>c</sub> mV/dec	Corrosion Rate, mpy	Inhibition efficiency %
1	Blank	10.91	-460	162	-191	9777.31	-
2	0.08	3.55	-467	45	-126	3186.67	67.40
3	0.1	3.47	-464	44	-123	3109.84	68.19
4	0.12	3.30	-466	43	-119	2962.81	69.69
5	0.1 inhibitor +1M KCl	3.33	-464	51	-129	2983.04	69.49
6	0.1 inhibitor +1M KBr	2.43	-474	67	-126	2178.92	77.72
7	0.1 inhibitor +1M KI	2.42	-455	69	-115	2169.49	77.81

**Table 5.** Potentiodynamic polarization parameters for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without (02TD).

S.No	Inhibition Concentration mM	I <sub>corr</sub> mA/cm <sup>2</sup> ×10 <sup>-2</sup>	E <sub>corr</sub> mV vs. SCE	b <sub>a</sub> mV/dec	b <sub>c</sub> mV/dec	Corrosion rate, mpy	Inhibition efficiency %
1	Blank	10.91	-460	162	-191	9777.31	-
2	0.06	3.70	-460	47	-128	3315.62	66.08
3	0.08	3.24	-464	48	-119	2910.06	70.23
4	0.12	2.36	-465	42	-115	2121.85	78.29
5	0.06 inhibitor +1M KCl	2.90	-454	46	-124	2597.30	73.43
6	0.06 inhibitor +1M KBr	2.87	-453	71	-130	2577.51	73.63
7	0.06 inhibitor +1M KI	2.39	-443	70	-114	2143.37	78.07

**Table 6.** Potentiodynamic polarization parameters for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without (03TD).

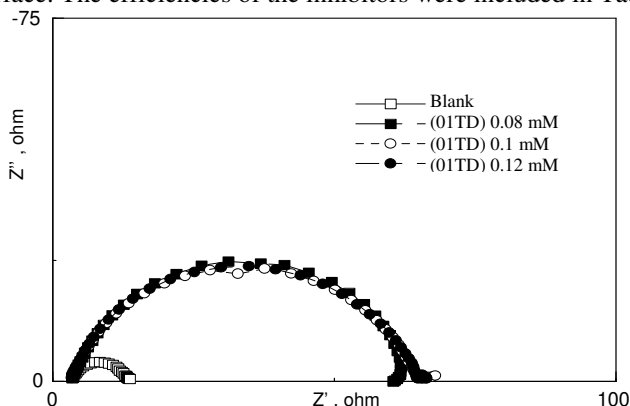
S.No	Inhibition Concentration mM	I <sub>corr</sub> mA/cm <sup>2</sup> ×10 <sup>-2</sup>	E <sub>corr</sub> mV vs. SCE	b <sub>a</sub> mV/dec	b <sub>c</sub> mV/dec	Corrosion Rate, mpy	Inhibition efficiency %
1	Blank	10.91	-460	162	-191	9777.31	-
2	0.2	1.92	-480	50	-133	1723.00	82.37
3	0.4	1.67	-439	25	-142	1498.95	84.67
4	0.6	1.47	-445	30	-115	1318.24	86.51
5	0.2 inhibitor +1M KCl	1.69	-461	60	-138	1515.00	84.50
6	0.2 inhibitor +1M KBr	1.57	-459	45	-99	1407.27	85.60
7	0.2 inhibitor +1M KI	1.50	-443	63	-116	1350.94	86.18

#### *Electrochemical impedance spectroscopic studies*

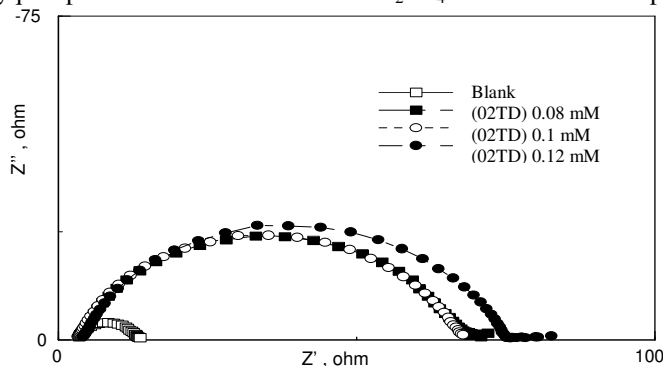
The corrosion behaviour of mild steel in acidic solution in inhibitors has been investigated by EIS method at 30 °C. Nyquists plots were recorded and typical plots are given in Figures 5-7. Impedance parameters like charge transfer resistance (R<sub>ct</sub>), double layer capacitance (C<sub>dl</sub>) are given in Tables 7-9. The impedance diagrams are almost semicircular. The charge transfer resistance values are calculated from the differences in impedance at lower and higher frequencies. The double layer capacitance values are obtained from the frequency at which imaginary components of the impedance f (-Z''<sub>max</sub>) is maximum. The relationship used is

$$f(-Z''_{\max}) = \frac{1}{2\pi C_{dl} R_{ct}(inh)}$$

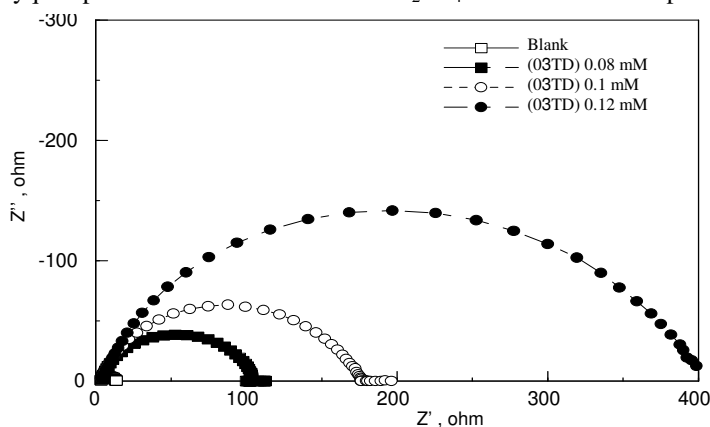
It is evident from the Tables 10-12 that  $R_{ct}$  value increases with increase in concentration and reaches a limiting value at 0.1 mM for the inhibitors [(01TD) and (02TD)] and at 0.6 mM for the inhibitor (03TD). The data also indicate that  $C_{dl}$  value increases with increase in concentration of the inhibitor. The increase is due to the adsorption of inhibitors on the metal surface. The efficiencies of the inhibitors were included in Tables 7-9.



**Figure 5.** Nyquist plots for the mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of (01TD).



**Figure 6.** Nyquist plots for the mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of (02TD).



**Figure 7.** Nyquist plots for the mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of (03TD).

**Table 7.** Impedance parameters for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without (01TD).

S. No	Inhibition Concentration, mM	R <sub>ct</sub> ohms	C <sub>dl</sub> ×10 <sup>-4</sup> μ Farads	Inhibition efficiency, %
1	Blank	10.05	1.27	-
2	0.08	58.79	1.62	82.88
3	0.1	60.57	1.75	83.39
4	0.12	61.50	2.04	83.64
5	0.1 inhibitor +1M KCl	69.36	1.53	85.49
6	0.1 inhibitor +1M KBr	79.68	1.93	87.38
7	0.1 inhibitor +1M KI	105.06	2.52	90.43

*Adsorption isotherm*

Organic molecules are used to inhibit corrosion as they get adsorbed on the metal-solution interface. The adsorption depends on the chemical structure of the inhibitor, chemical composition of the solution, nature of the metal surface, temperature and electrochemical potential at the metal-solution interface. The adsorption provides information about the adsorbed molecules themselves as well as their interaction with the metal surface. The values of surface coverage ( $\theta$ ) corresponding to different concentration of inhibitor (C) are used to obtain the best adsorption isotherm. The  $\theta$  values have been calculated using the following relationships.

$$\theta = \frac{1-W_{inh}}{W} \text{ (from weight loss measurements) and } \theta = \frac{1-C_{dl(inh)}}{C_{dl}} \text{ (from impedance measurements).}$$

**Table 8.** Impedance parameters for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without (02TD).

S. No	Inhibition Concentration, mM	R <sub>ct</sub> ohms	C <sub>dl</sub> ×10 <sup>-4</sup> μ Farads	Inhibition efficiency, %
1	Blank	10.05	1.27	-
2	0.06	64.24	1.76	84.34
3	0.08	64.29	1.98	84.35
4	0.12	71.12	1.85	85.85
5	0.06 inhibitor +1M KCl	64.25	1.92	85.49
6	0.06 inhibitor +1M KBr	67.78	2.40	87.38
7	0.06 inhibitor +1M KI	95.09	3.25	90.43

**Table 9.** Impedance parameters for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without (03TD)

S. No	Inhibition Concentration, mM	R <sub>ct</sub> ohms	C <sub>dl</sub> ×10 <sup>-4</sup> μ Farads	Inhibition efficiency, %
1	Blank	10.05	1.27	-
2	0.2	101.60	1.94	90.09
3	0.4	178.48	2.16	94.36
4	0.6	395.93	0.83	97.45
5	0.2 inhibitor +1M KCl	128.80	1.53	92.23
6	0.2 inhibitor +1M KBr	158.42	1.55	93.64
7	0.2 inhibitor +1M KI	198.52	1.58	94.93

Various adsorption isotherms were tested for the present experimental data and it has been found that data follow only Tempkin adsorption isotherm. The surface coverage ( $\theta$ ) for all the compounds when plotted against log concentration showed a linear plot, suggesting Tempkin adsorption isotherm<sup>1,2</sup>. The inhibition was essentially based on the coverage of the metal surface by the inhibitor molecules, thus preventing contact of the corroding species with acid<sup>3</sup>. The nitrogen, oxygen and sulphur atoms of the inhibitor molecules make it adsorbed readily on the metal surface forming an insoluble stable film on the metal surface thus decreasing metal dissolution.

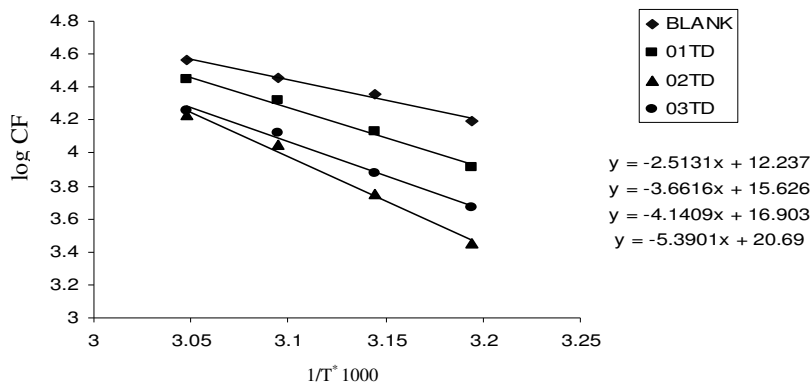
Adsorption of molecules on the metal surface is due to coordination of the  $\pi$  electron system and nonbonding electrons of the heterocyclic nitrogen and sulphur to the metal atom.  $\pi$  electron density would likely stabilize the complex. The involvement of the  $\pi$  electron density distinguishes the efficiencies of (02TD) and (03TD).

### Effect of temperature

To verify the nature of adsorption, the effect of temperature on the corrosion behavior of mild steel in presence of inhibitors was studied using weight loss technique. The data in Table 3 indicates that rate of corrosion increases with raise in temperature. This behaviour reveals that these inhibitors are efficient at optimum temperature. It has been reported by some authors that in acid solution, the logarithm of the corrosion rate is a linear function of  $1/T$  (Arrhenius equation).

$$\log(\text{Rate}) = -E_a$$

Where,  $E_a$  is the apparent effective activation energy,  $R$  is the general gas constant and  $A$  the Arrhenius preexponential factor. A plot of log of corrosion rate obtained by weight loss measurement *versus*  $1/T$  gave a straight line as shown in Figure 8. The values of activation energy  $E_a$  obtained from the slope of the lines are given in Table 10a. The data shows that activation energy ( $E_a$ ) values for inhibited system are higher than those of uninhibited system and are more effective at room temperature.



**Figure 8.** Arrhenius plots of the compounds [(01TD), (02TD) and (03TD)] on the surface of mild steel in 1 M  $\text{H}_2\text{SO}_4$ .

**Table 10(a).** The activation energy ( $E_a$ ) of the inhibitors.

Inhibitor	$E_a$ , $\text{kJ mol}^{-1}$
Blank	48.1186
01TD	70.1090
02TD	103.2048
03TD	79.2862

Free energy of adsorption ( $\Delta G_{\text{ads}}^0$ ) was calculated using the following equation<sup>4</sup>.

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5 K), \text{ where, } K = [\theta / (C (1-\theta))]$$

Where  $\theta$  is degree of coverage on the metal surface,  $C$  is the concentration of the inhibitor,  $K$  is equilibrium constant,  $R$  is gas constant and  $T$  is temperature. The obtained values of  $\Delta G_{\text{ads}}^0$  point out the spontaneity of the adsorption process in the experimental conditions. Generally, values of  $\Delta G_{\text{ads}}$  until  $-20$  kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal surface (physical adsorption). Those more negative than  $-40$  kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption)<sup>5-7</sup>. Radovici<sup>8</sup> classifies the inhibitors into 3 groups according to temperature effects:

1. Inhibitors whose I.E decreases with temperature increase and  $E_a$  is greater than that in the uninhibited solution. This is an indication of physisorption.
2. Inhibitors whose I.E does not change with temperature. The  $E_a$  does not change with the presence or absence of inhibitors.
3. Inhibitors whose IE increases with temperature and  $E_a$  is smaller for the inhibited solution, which is characteristic of chemisorption.

Popova *et al.*<sup>9</sup> also interpreted the decrease of I.E value with temperature increase as an indication for a physical or columbic type of adsorption. Therefore it can be concluded that thiadiazolines are adsorbed on the mild steel surface by physisorption

In the present study the low and negative value of  $\Delta G_{\text{ads}}^0$  shown in Table 10(b) indicated the spontaneous adsorption of inhibitor on the surface of the mild steel.  $\Delta G_{\text{ads}}^0$  values are less than  $-20$  kJ/mol, which show physical adsorption of inhibitors on the metal surface.

**Table 10 (b).** The free energy of adsorption ( $\Delta G^0$ ) of the Inhibitors at various temperatures.

Inhibitor	$\Delta G_{\text{ads}}^0$ at various temperatures, kJ mol <sup>-1</sup>			
	313 K	318 K	323 K	328 K
01TD	-16.775	-16.363	-15.916	-15.805
02TD	-20.927	-20.235	-19.247	-18.301
03TD	-17.011	-16.743	-16.049	-15.870

#### Nature of inhibitor

Shift in the values of Tafel constants  $b_a$  and  $b_c$  determines the nature of the inhibitor. In general, an increase in the  $b_c$  values with the concentration of the inhibitor is a characteristic phenomenon of a cathodic inhibitor which indicates an increase in the energy barrier for proton discharge leading to less gas evolution. On the other hand, an increase in  $b_a$  value with the concentration of the inhibitor is an indication of anodic type inhibitor. This type of inhibitor prevents anodic dissolution. The variation of  $b_a$  and  $b_c$  values with the concentration of inhibitor in 1 M H<sub>2</sub>SO<sub>4</sub> are given in Table 4-6. Analysis of the data reveals that both  $b_a$  and  $b_c$  values do not change appreciably with the concentration of thiadiazolines and only a slight variation is observed. Thus, thiadiazolines may be considered as mixed type inhibitors in H<sub>2</sub>SO<sub>4</sub>. It is observed that presence of inhibitors decrease  $I_{\text{corr}}$  values. Maximum decrease in  $I_{\text{corr}}$  was observed in case of (03TD).

#### Nature of anchoring site of the inhibitor

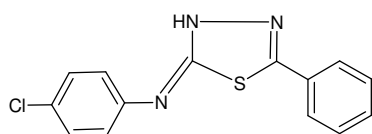
Inhibition of corrosion of mild steel in the acidic solutions by (01TD), (02TD) and (03TD) compounds can be explained on the basis of molecular adsorption. In acidic solution these compounds exists as protonated species. These protonated species may adsorb on the cathodic sites of mild steel and decrease the evolution of hydrogen. It is apparent from the

molecular structures that these compounds are able to get adsorbed on the metal surface through  $\pi$  electrons of aromatic ring and lone pair of electrons of N,O and S atoms.

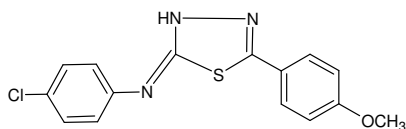
In this study the hetero atoms in five membered ring participates maximum. The  $\pi$  electrons of aromatic ring also participates for the same. This ring is assumed to be parallel to the mild steel surface in all the three cases. Electron donating groups generally increases the availability of the  $\pi$  electrons for the inhibition.

In the case of (03TD) OH group is in the *ortho* position. Probably this OH group forms H-bonding with the lone pair of electrons of the five membered ring which excludes the participation of the N-atom in five membered ring which in turn decreases the efficiency.

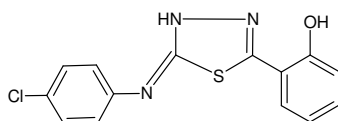
In (02TD) OCH<sub>3</sub> group is in the *para* position which completely makes the  $\pi$  electrons of aromatic ring for the inhibition. The nature of the adsorption may be shown as follows



(01TD)



(02TD)



(03TD)

Among the compounds investigated in the presence study, the order of inhibition efficiency has been found as follows,



#### *Synergistic influence of halide ions*

The mechanism of the reaction can be explained as follows. The synergistic effect brought about by the combination of inhibitor and halide ions for corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> can be explained as follows. The strong chemisorption of iodide ions on the metal surface is responsible for the synergistic effect of halide ions in combination with inhibitor cation. The positively charged inhibitor ion are then adsorbed by coulometric attraction at the metal surface, where iodide ions already adsorbed by chemisorption. Stabilization of adsorbed iodide ions by means of electrostatic interaction with positively charged inhibitor leads to greater surface coverage and there by greater inhibition. The order of reactivity of halide ions are as follows



#### **Conclusion**

1. Variously substituted thiadiazolines exhibits maximum efficiency towards corrosion inhibition of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> media even at a very low concentration.
2. The inhibition of corrosion by thiadiazolines is due to the physical adsorption on the metal surface.

3. It is apparent from the molecular structures that these compounds are able to get adsorbed on the metal surface through  $\pi$  electrons of aromatic ring and lone pair of electrons of N, O, and S atoms. S and O atoms are present both in the five membered rings and in the side chain but variation of the substitution in the side chain varies the inhibition efficiency.
4. The trend in the inhibition efficiency of thiadiazolines within the series has been found in the order (01TZ) > (02TZ) > (03TZ).
5. These compounds act as mixed type with more cathodic character and obeys Tempkin adsorption isotherm.

### References

1. Venkatachari G and Rajagopalan K S, *Chem Age India*, 1979, **30**, 475.
2. Vishnudevan M and Natesan M, *Bull Electrochem.*, 2000, **16**, 49.
3. Athar M, Ali H and Quraishi M A, *Br Corros J.*, 2002, **37**, 155.
4. Rafiquee M Z A, Nidhisexena, Sadaf Khan and Quraishi M A, *Indian J Chem Technol.*, 2000, **14**, 576.
5. Bastidas J M, Damborenea J De and Vazquez A J, *J Appl Electrochem.*, 1997, **27**, 345.
6. Kamis E, Belluci F, Lathanision R M and El Ashry E S H, *Corrosion*, 1991, **47**, 677.
7. Donahue F and Nobe K, *J Electrochem Soc.*, 1965, **112**, 886.
8. Radovici O, Proceedings of the 2<sup>nd</sup> European Symposium on Corrosion inhibitors, Ferrara, 1965, 178.
9. Popava A, Sokolova E, Raicheva S and Christov M, *Corros Sci.*, 2003, **45**, 33.