

## Synthesis, characterization and corrosion protective efficiency of some 1,3,4-thiadiazolines on mild steel in acid media

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### ABSTRACT

The Inhibition effect of corrosion of mild steel using Thiadiazolines in  $H_2SO_4$  medium by weight loss, electrochemical methods was investigated. The corrosion inhibition was studied in  $H_2SO_4$  by weight loss method for about 3hrs at room temperature and it was found that the corrosion inhibition behaviour of Thiadiazolines is greater in sulphuric acid. Results were fitted into suitable adsorption isotherm. The Electrochemical parameters for mild steel in  $H_2SO_4$  solution with and without inhibitor were calculated. The data revealed that Electrochemical polarization shows the Mixed Mode of inhibition and the results of Electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance with the change in concentration of the inhibitor is due to the adsorption of the molecules leading to the formation of a protective layer on the surface of mild steel. The Effect of Temperature on the corrosion rate, activation energy and free energy of adsorption were also calculated.

**Key words:** Thiadiazolines, mild steel, Langmuir adsorption isotherm, mixed type, physisorption.

### INTRODUCTION

Acids are used in many industries especially for cleaning, pickling and descaling. Many nitrogen containing heterocyclic compounds with polar groups or  $\delta$  electrons are employed as good corrosion inhibitor for mild steel in acid media<sup>1-4</sup>. This kind of organic molecules can adsorb on the metal surface because they form a bond between the N electron pair and/or the  $\pi$ -electron cloud and the metal thereby reducing the corrosive attack on metals in acid media<sup>5</sup>

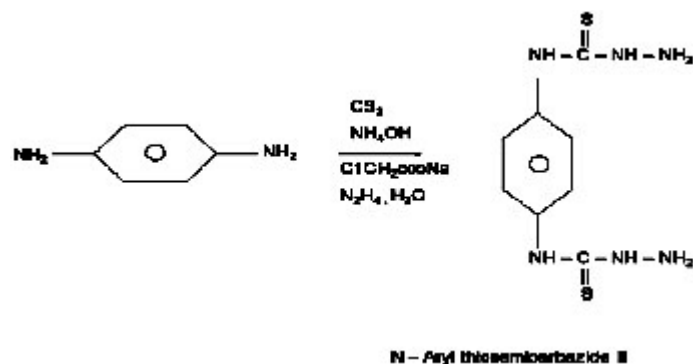
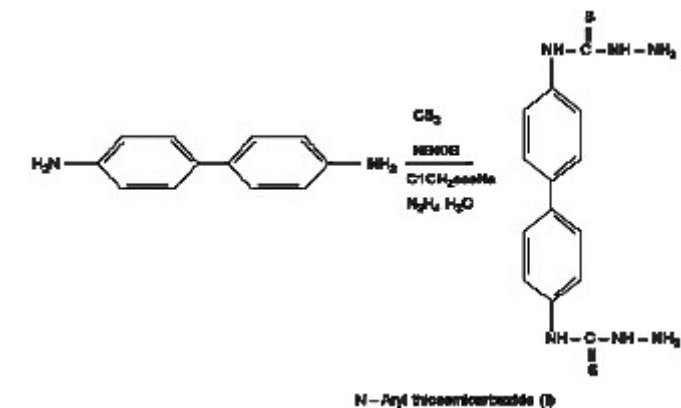
The aim of the present study is to synthesis various derivative of 1,3,4 thiadiazolines and to study the inhibition efficiency of these inhibitors on the corrosion process of mild steel in 1M sulphuric acid. The inhibition efficiency has been evaluated by weight loss, polarization and electrochemical techniques.

### EXPERIMENTAL

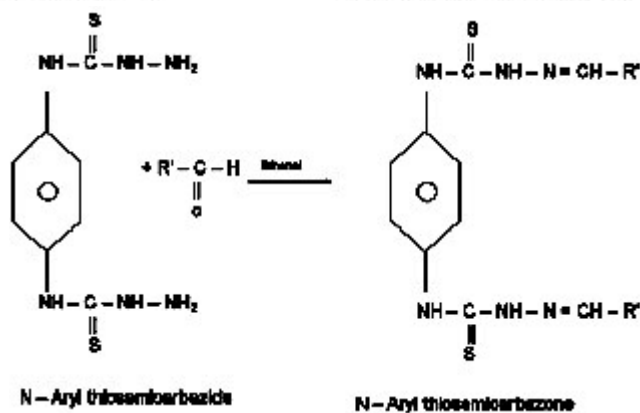
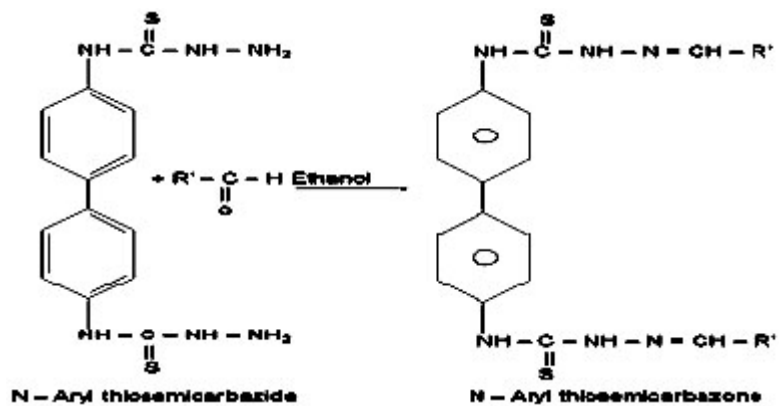
#### Synthesis of inhibitors

Substituted 1, 3, 4 – Thiadiazolines [(TD1),(TD2),(TD3),(TD4)] have been chosen as inhibitors for the present investigation. The substituted 1, 3, 4 – Thiadiazolines were synthesized in three stage. The first stage is the conventional method in which arylthiosemicarbazide were prepared by mixing aromatic amines with 95% ethanol and few ml of  $NH_4OH$ . After cooling the reaction mixture, few drops of  $CS_2$  and 0.1 mole of sodiumchloroacetate was added. Later few ml of hydrazine hydrate was added and the mixture was warmed and kept overnight. The product was filtered and dried. In the second stage the arylthiosemicarbazide is mixed with respective aldehydes and the reaction is carried over microwave oven. The produced formed was filtered, cooled and crystallized from ethanol.

## STAGE 1:

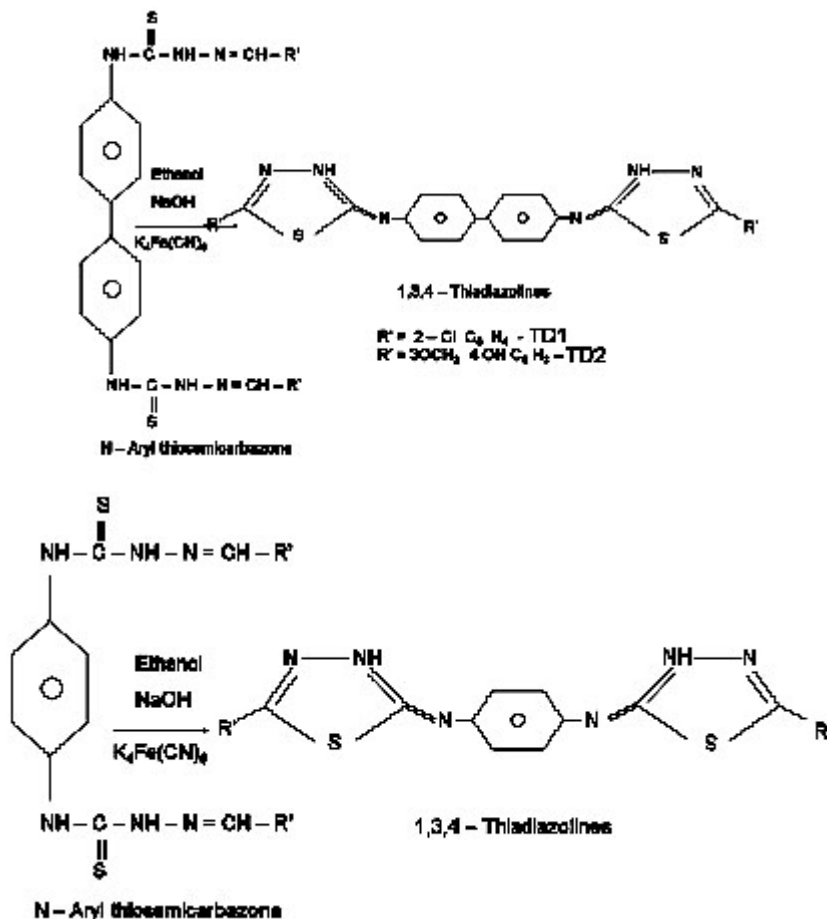


## STAGE 2:



R<sub>2</sub> = 2C<sub>6</sub>H<sub>4</sub>-  
= 3-OCH<sub>3</sub>, 4-OH, C<sub>6</sub>H<sub>3</sub>-

STAGE 3:



R<sup>1</sup> = 2 - Cl C<sub>6</sub>H<sub>4</sub> - TD3  
 = 3 - OCH<sub>3</sub>, 4 - OH, C<sub>6</sub>H<sub>3</sub> - TD4

In the third stage N-aryl thiosemicarbazone in ethanol and sodiumhydroxide was warmed and 10% potassium ferricyanide was added. The product formed was filtered and recrystallised from ethanol.

**Weight loss method**

The experiment was preceded with 1MH<sub>2</sub>SO<sub>4</sub>. First 1M H<sub>2</sub>SO<sub>4</sub> acid solutions was prepared with distilled water and then taken in a 100ml beaker and the specimens in triplicate were suspended in the solutions using glass hooks. After 3 hours, the specimens were removed washed with running water ,dried and weighed. From the initial and the final weights of the specimens, loss in weight was calculated .Duplicate experiments were performed in each case.

$$\% \text{Inhibition efficiency} = \frac{W_1 - W_2}{W_1} \times 100$$

Where W1 and W2 are the weight loss of mild steel in uninhibited and inhibited acid solutions.

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{weight loss in mgs}}{\text{Density} \times \text{Area in sq inches} \times \text{Time in hours}}$$

$$\text{Corrosion coverage, } \theta = \frac{W_1 - W_2}{W_1}$$

Where W1 and W2 are the weight loss of mild steel in uninhibited and inhibited acid solutions.

### Electrochemical methods

#### Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out for the corrosion of mild steel with various concentrations of inhibitors in  $1\text{M H}_2\text{SO}_4$ . The experiments were carried out at  $30 \pm 1^\circ \text{C}$  with a fine luggin capillary to avoid ohmic polarization. The working electrode is prepared from a cylindrical mild steel rod insulated with Teflon tube such that the area exposed to the solution was  $0.19625\text{cm}^2$ . A saturated calomel electrode was used as the reference and platinum electrode of  $1\text{cm}^2$  was used as counter electrode. A graph was plotted with potential,  $E$  vs  $\log I$  and Tafel constant  $b_a$  and  $b_c$ ,  $E_{\text{corr}}$  (corrosion potential) and  $I_{\text{corr}}$  (corrosion current) were calculated.

#### Impedance measurements

The electrochemical impedance measurements were carried out using mild steel in  $1\text{M H}_2\text{SO}_4$  with and without inhibitor at  $30^\circ\text{C}$ . A plot of  $Z_2$  (real part of impedance) and  $Z''$  (imaginary

part of impedance) were made from which  $R_t$  (charge transfer resistance),  $C_{dl}$  (double layer capacitance) and inhibition efficiency were calculated.

## RESULTS AND DISCUSSION

#### Weight loss measurement

The inhibition efficiencies and corrosion rate of 1,3,4-Thiadiazolines compound at different concentration (0.5ppm, 1ppm, 1.5ppm, 2ppm, and 2.5ppm) of the inhibitor on mild steel in  $1\text{M H}_2\text{SO}_4$  have been evaluated by weight loss measurement for about 3 hours and results were summarized in table 1. The effect of concentration on inhibition efficiencies and corrosion rate were shown in fig 1.

From Table 1, it was clear that the corrosion rate was decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the Inhibitor. In addition, the maximum corrosion inhibition

**Table 1: Inhibition efficiencies at various concentrations of inhibitors for the corrosion of mild steel in  $1\text{M H}_2\text{SO}_4$  obtained from weight loss at room temperature**

Name of the inhibitor	Inhibition Concentration (ppm)	Inhibition Efficiency (%)	Corrosion Rate (mpy)	Surface Coverage $\theta$
TD1	0.5	80.243	304.684	0.8024
	1	90.917	140.068	0.9091
	1.5	93.258	103.968	0.9325
	2	94.382	86.640	0.9438
	2.5	95.037	76.532	0.9503
TD2	0.5	61.551	644.024	0.6155
	1	89.655	173.28	0.8965
	1.5	94.655	89.528	0.9465
	2	96.551	57.76	0.9655
	2.5	97.155	47.652	0.9715
TD3	0.5	91.451	138.62	0.9145
	1	93.766	101.08	0.9376
	1.5	94.479	89.53	0.9447
	2	95.191	77.98	0.9519
	2.5	95.903	66.42	0.9590
TD4	0.5	18.012	1334.256	0.1801
	1	43.389	921.272	0.4338
	1.5	62.289	613.70	0.6228
	2	82.342	287.356	0.8234
	2.5	90.24	158.84	0.9024

efficiency of Thiadiazolines was >90% at 2.5ppm in  $1\text{M H}_2\text{SO}_4$  at about 3hours in room temperature. And also, it was concluded that the inhibitor was best inhibitor in mild steel corrosion in  $1\text{M H}_2\text{SO}_4$ . There by indicating the enhanced stability of the adsorbed constituents of the inhibitor on mild steel surface.

### Effect of Temperature

The Inhibition efficiency was increases suddenly with increase in temperature (in table 2) of the test solution up to 343k. This behaviour reveals that these inhibitors are efficient at optimum temperature. The marked changes in  $E_a$  suggest that the inhibitor may either participate in the

electrode process or may change the potential difference of the metal solution interface by adsorption. Results obtained indicate that the value of  $\Delta G$  are negative indicating the spontaneous adsorption of the inhibitor and it is strongly adsorbed on the mild steel surface<sup>6</sup>. Generally values of  $\Delta G$  upto -20kJ/mol are consistent with electrostatic interaction between charged molecules and charged metal (which indicates physisorption) while those more negative than -40kJ/mol involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicate chemisorptions)<sup>7,8,9</sup>. Therefore it can be concluded that Thiadiazolines are adsorbed on the mild steel surface by physisorption.

**Table 2: Corrosion parameters of Inhibitors on mild steel at various temperatures in  $1\text{M H}_2\text{SO}_4$**

Name of the Inhibitor	Temperature K	Weight Loss g	Corrosion Rate mpy	Inhibition Efficiency%
TD1	313	0.1623	2343.61	1.75
	323	0.0589	850.51	53.48
	333	0.0381	550.16	57.67
	343	0.0138	199.27	67.29
TD2	313	0.1559	2251.19	5.63
	323	0.0951	1373.24	24.88
	333	0.0613	885.17	31.89
	343	0.0144	207.94	65.88
TD3	313	0.1543	2228.09	9.24
	323	0.0277	399.98	78.12
	333	0.019	274.36	78.88
	343	0.0053	76.53	84.50
TD4	313	0.1331	1921.96	21.70
	323	0.0832	1201.40	34.28
	333	0.0528	762.43	41.33
	343	0.0155	223.82	54.68

**Table 3 : The Free Energy of Adsorption ( $\Delta G^\circ$ ), Activation Energy( $E_a$ ), Entropy and Enthalpy of adsorption of inhibitor at various temperature in  $1\text{M H}_2\text{SO}_4$**

INHIBITOR	$E_a$ (KJ/mol)	$\Delta G$ ads at various temperature (KJ/mol)				$\Delta S$	$\Delta H$
		313K	323K	333K	343K		
TD1	67.37	-6.394	-11.138	-11.95	-13.483	0.2207	-61.65
TD2	62.59	-11.086	-7.798	-8.996	-13.305	0.0785	-15.47
TD3	85.03	-16.930	-14.181	-14.741	-16.267	0.0143	-20.22
TD4	70.23	-7.090	-9.011	-10.125	-11.966	0.1574	-42.09

In the present study value of  $\Delta G_{ads}$  are less than  $-20\text{kJ/mol}$ , which show physical adsorption of inhibitor on the metal surface. The value of  $\Delta H$  and  $\Delta S$  are also presented in Table 3. The positive  $\Delta S$  values accompanied with endothermic adsorption process in  $\text{H}_2\text{SO}_4$  medium. The negative value of  $\Delta H$  shows adsorption of negatively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface in  $\text{H}_2\text{SO}_4$  medium.

### Adsorption Isotherm

The adsorption depends on the chemical structure of the inhibitor, nature of the metal surface, temperature, chemical composition of the solution and electrochemical potential at the metal-solution interface. The adsorption provides information about the adsorbed molecules and also their interaction with the metal surface. The  $\theta$  values have been calculated using the following relationship.

$$\theta = 1 - W_{inh} / W \quad (\text{from weight loss measurement and})$$

$$\theta = 1 - C_{dl} (inh) / C_{dl} \quad (\text{from impedance measurements})$$

Various adsorption isotherms were tested for the present experimental data and it has been found that data obey only Langmuir adsorption isotherm<sup>10</sup> and the data are plotted in fig 4. The inhibition was essentially based on the coverage of the metal surface by the inhibitor molecule, thus preventing contact of the corroding species with acid<sup>11</sup>.

Thiadiazolines compounds acted via simple adsorption model and exactly fit into the Langmuir adsorption isotherm by plotting  $\log(C)$  vs  $\log(C/\theta)$

### Potentiodynamic polarization studies

Potentiodynamic polarizing curve showing the inhibitory action of thiadiazolines for the  $\text{H}_2\text{SO}_4$  acid is given in fig 5. The corrosion parameters such

**Table 4: Potentiodynamic polarization parameters for the corrosion of mild steel**

Name of the Inhibitor	Inhibition Concentration (ppm)	In $1\text{M H}_2\text{SO}_4$ with and without (TD1), (TD2), (TD3), (TD4)				Inhibition efficiency (%)
		$i_{corr}$ ( $\text{mA/cm}^2$ ) $\times 10^3$	$E_{corr}$ (mV vs SCE)	$b_a$ (mV/dec)	$b_c$ (mV/dec)	
TD1	Blank	1.759	-470	202	330	-
	0.5	1.529	-442	133	365	13.07
	1	1.187	-441	138	344	32.52
	1.5	0.7229	-446	94.72	271.69	58.90
	2	0.7148	-443	115	317	59.36
	2.5	0.4804	-453	120	322	72.68
TD2	0.5	1.656	-444	155	360	5.85
	1	1.635	-443	135	346	7.05
	1.5	1.529	-442	133	365	13.07
	2	1.248	-441	184	420	29.05
	2.5	1.207	-440	228	476	31.38
TD3	0.5	1.759	-427	153	286	10.34
	1	0.7228	-420	94	249	58.91
	1.5	0.5700	-420	107	299	67.59
	2	0.5578	-420	96	268	68.29
	2.5	0.4564	-424	92	256	74.05
TD4	0.5	1.299	-436	120	291	26.15
	1	1.020	-436	150	431	42.01
	1.5	0.6571	-433	89	232	62.64
	2	0.4776	-432	76	216	72.85
	2.5	0.3623	-430	86.927	222	79.40

as  $E_{corr}$ ,  $I_{corr}$ , Tafel slopes constants ( $b_a$  and  $b_c$ ) obtained from these curves is presented in table 4.  $I_{corr}$  was found to decrease as the concentration of the inhibitor increases. This confirms the inhibitory action of the Thiadiazolines on metal surface. The  $E_{corr}$  value has not been shifted to any particular direction from the blank value, which also indicates that the inhibitor acts through Mixed Mode of inhibition<sup>12</sup>. Tafel slopes  $b_a$  and  $b_c$  obtained in the presence and absence of the inhibitor in  $H_2SO_4$  medium revealed that the inhibition of corrosion of mild steel is under Mixed control in both Anodic dissolution and cathodic hydrogen evolution mechanism are affected in presence of the inhibitor. Therefore, it can be concluded from the result that thiadiazolines act as a Mixed Type Inhibitor in  $H_2SO_4$  media. The Inhibition efficiency was found to be increases with increasing concentration in  $H_2SO_4$  media.

#### Electrochemical impedance spectroscopic studies

The behaviour of corrosion on mild steel

in  $H_2SO_4$  solution of inhibitors has been investigation by EIS method. Nyquist plots were recorded and typical plots are given in figure. Impedance parameters like charge transfer resistance ( $R_t$ ), double layer capacitance ( $C_{dl}$ ) are given in table 5. From the fig 6, the value of real impedance ( $Z_{re}$ ) was only 9.26 ohms, which indicates the least charge transfer resistance ( $R_t$ ) of the corrosion reaction. There was gradual increase in the diameter of each semicircle of the Nyquist plot when the concentration was increased from 0.5 to 2.5 ppm. This increase of the diameters clearly reflected that the  $R_t$  value also increased at the highest concentration of 2.5 ppm due to the formation and gradual improvement of the barrier layer of the inhibitor molecules. With the increase of inhibitor concentration  $R_t$  value increased. This can be understood by assuming that at the lower concentration of 0.5 ppm, the molecules was adsorbed on the metal surface partially and the major part of the surface remained unprotected, with an increase of the concentration the number of molecules adsorbed on the metal surface

**Table 5: Impedance Parameters for the corrosion of mild steel in  $1M H_2SO_4$  with and without (TD1), (TD2), (TD3), (TD4)**

Name of the Inhibitor	Inhibitor Concentration (mM)	$R_t$ (ohm $\cdot$ cm <sup>2</sup> )	$C_{dl} \times 10^5$ ( $\mu$ farads)	Inhibition efficiency (%)
TD1	Blank	9.26	1.84	-
	0.5	33.76	1.92	72.57
	1	38.97	1.05	76.24
	1.5	40.48	1.03	77.13
	2.5	58.38	0.87	84.14
TD2	0.5	19.54	1.367	52.61
	1	19.65	1.314	52.87
	1.5	19.7	1.347	52.99
	2	26.12	1.174	64.54
	2.5	28.33	1.240	67.32
TD3	0.5	19.58	5.867	52.70
	1	53.34	1.179	82.64
	1.5	61.63	1.137	84.97
	2	63.08	0.7608	85.32
	2.5	73.55	0.7869	87.41
TD4	0.5	21.89	1.065	57.69
	1	28.77	1.438	67.82
	1.5	33.83	0.968	72.63
	2	49.99	1.011	81.47
	2.5	73.89	0.847	87.47

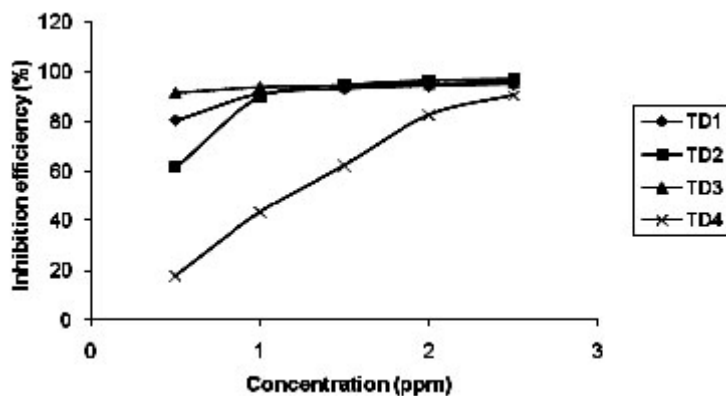


Fig. 1: Inhibition efficiency vs concentration of compounds (TD1), (TD2), (TD3), (TD4) on the surface of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>

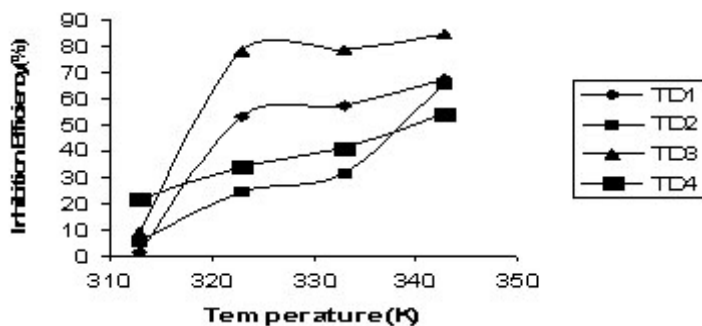


Fig. 2: Inhibition efficiency vs temperature of compounds (TD1), (TD2), (TD3), (TD4) on the surface of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>

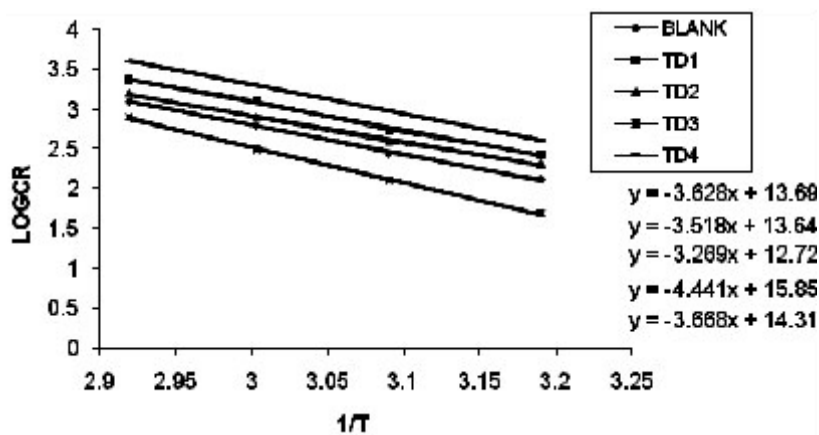


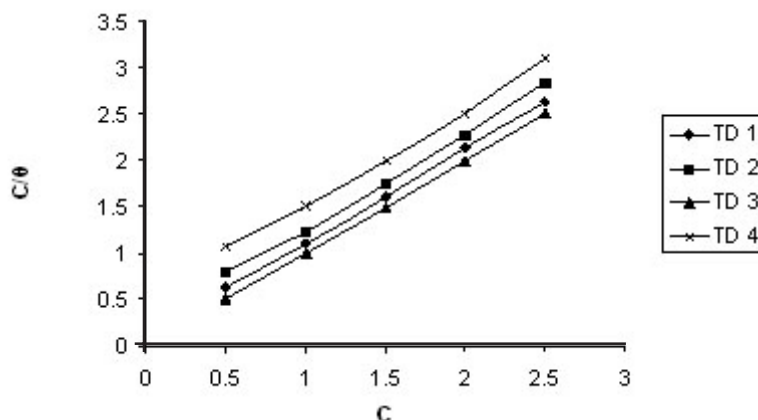
Fig. 3: Arrhenius plots of the compounds (TD1), (TD2), (TD3), (TD4) on the surface of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>



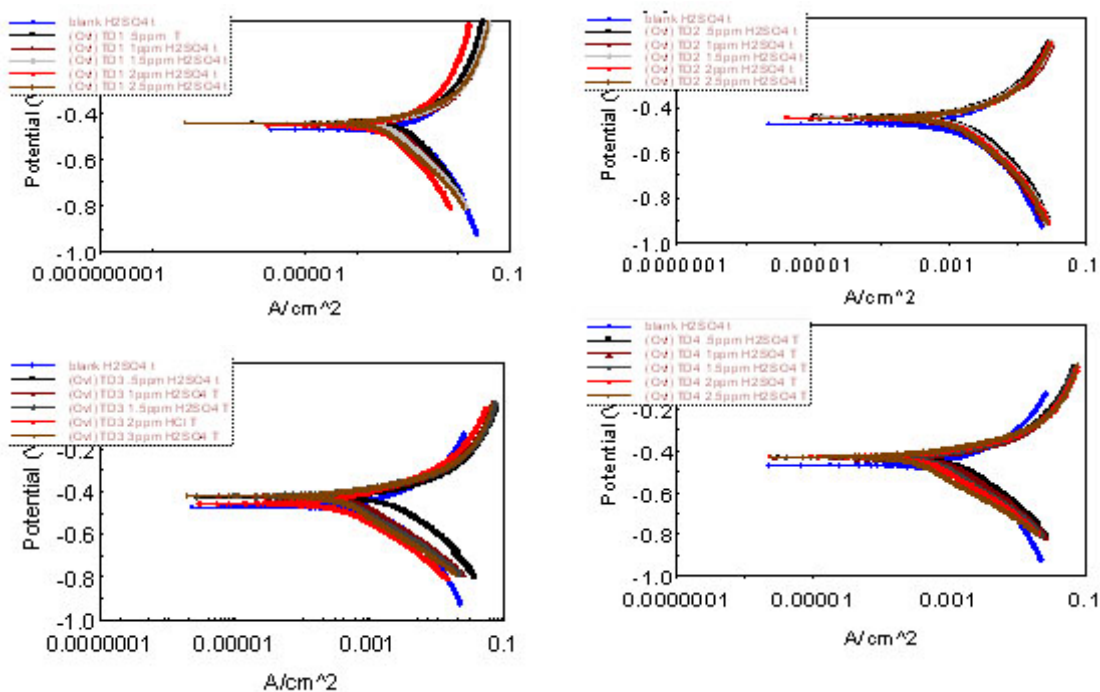
increased and at the maximum concentration ,the major part of the metal surface was covered<sup>13</sup>

There was a gradual decrease of the value of Cdl with the increase of the inhibitor concentration . The decrease of this capacity with the increasing

concentration may be associated with the formation of a protective layer at the electrode surface . Inhibition Efficiency was found to increase with increasing inhibitor concentration in H<sub>2</sub>SO<sub>4</sub> medium and results were summarized in table 5.



**Fig. 4:** Langmuir plot of the compounds (TD1), (TD2), (TD3), (TD4) on the surface of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>



**Fig. 5:** Potentiodynamic polarization curves for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in absence and presence of (TD1), (TD2), (TD3), (TD4)

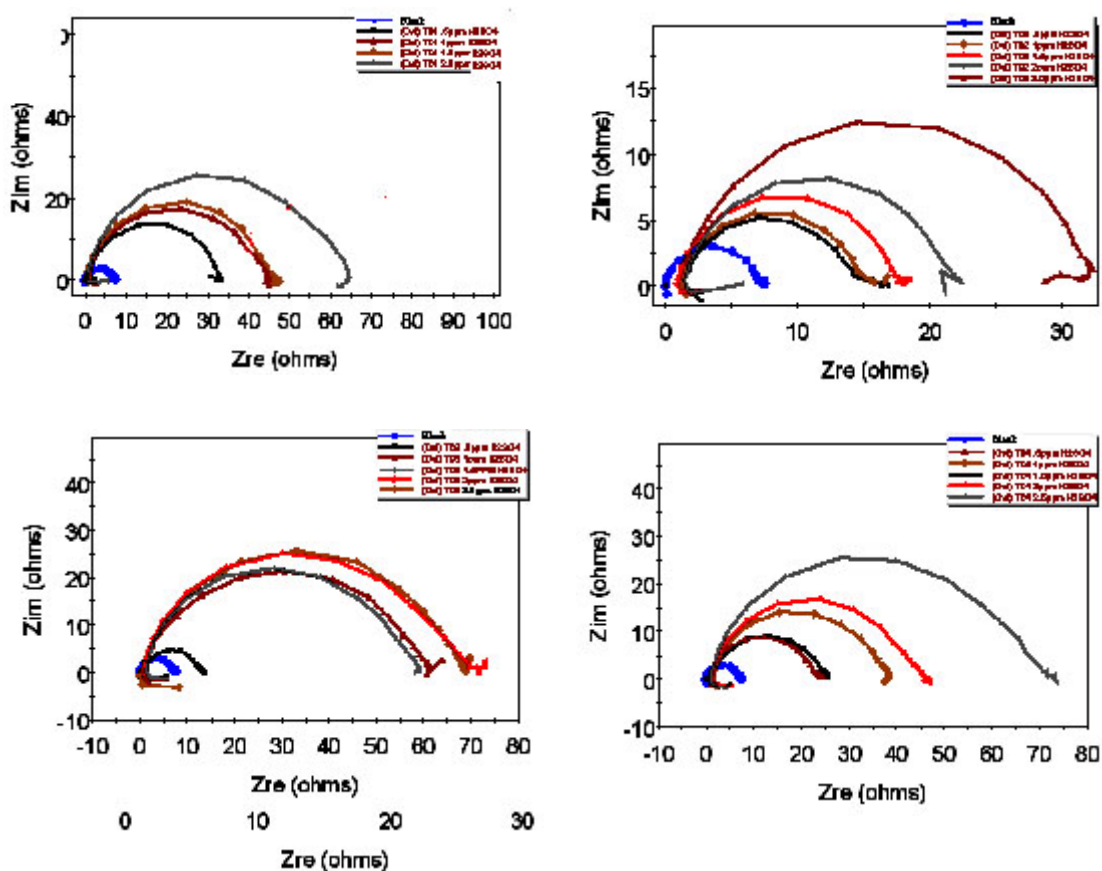


Fig. 6: Nyquist plots for mild steel in 1M  $H_2SO_4$  in absence and presence of (TD1), (TD2), (TD3), (TD4)

### CONCLUSION

- From the comparative studies, it was concluded that the inhibitor Efficiency is greater in  $H_2SO_4$ , because sulphuric acid is a dibasic acid, so it stimulated the corrosion rate of mild steel.
- The inhibition of corrosion by Thiadiazolines is due to the physical adsorption on the metal surface. The more Negative value of  $\Delta G^\circ$  ads support this conclusion.
- The adsorption of inhibitors on mild steel in  $1MH_2SO_4$  medium obeys Langmuir adsorption isotherm.
- Tafel slopes  $b_a$  and  $b_c$  obtained in the presence and absence of the inhibitor in  $H_2SO_4$  medium revealed that these compound acts as a Mixed mode of inhibition.
- Electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the inhibitor is due to the adsorption of the molecules leading to the formation of a protective layer on the surface of mild steel
- The Inhibition Efficiency increased suddenly with increase in temperature of the test solution upto 343k in  $1MH_2SO_4$ . This behaviour reveals that these inhibitors are efficient at optimum temperature.
- The value of  $\Delta G$  are Negative in  $H_2SO_4$  medium indicating the spontaneous adsorption of the inhibitor and it is strongly adsorbed on the mild steel surface.

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