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## INHIBITION OF CORROSION OF MILD STEEL IN 1M SULPHURIC ACID BY A NEW SCHIFF BASE

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### ABSTRACT

**Aim:** Corrosion is a serious problem faced by all the industries. The use of inhibitors is a simple and cost effective method to control corrosion. This paper reports the synthesis of a novel Schiff base and its application as corrosion inhibitor for mild steel.

**Methodology:** Inhibition behaviour of synthesized Schiff base for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> was studied by weight loss measurements, potentiodynamic polarization, and an electrochemical impedance spectra.

**Results:** The results revealed that the efficiency depends on concentration of the inhibitor and temperature. The inhibitor obeys Langmuir isotherm indicating monolayer adsorption on the mild steel surface. Thermodynamic parameters show that the adsorption of the inhibitor on mild steel surface occurs through electrostatic attraction. Polarization studies show that the inhibitor behaves as mixed type in 1M H<sub>2</sub>SO<sub>4</sub> affecting both anodic metal dissolution and cathodic hydrogen evolution. The formation of surface adsorptive film of the Schiff base on the mild steel surface was confirmed by SEM and EDX studies.

**Conclusion:** The prepared Schiff base is found to be a very good inhibitor for the mild steel corrosion in sulphuric acid media even at low concentration offers more than 90% inhibition efficiency.

**Keywords:** Inhibitors, Schiff base, Thiadiazoles, Potentiodynamic polarization, Langmuir isotherm, Impedance.

### INTRODUCTION

Corrosion is an electrochemical process by which metallic surfaces react with their environment causing the metal to lose its material properties due to surface deterioration. The use of inhibitors is one of the most practical methods for protection of metal against corrosion, especially in acidic media. Organic compounds contain mainly oxygen, sulfur, nitrogen atoms, and multiple bonds in the molecules that facilitate the adsorption of the molecules on the metal surface<sup>1,2</sup>. The polar unit is regarded as the reaction center for the adsorption

process. Thus, polar organic compounds are adsorbed on the metal surface, forming a charge transfer complex bond between their polar atoms and the metal. The size, orientation, shape and charge on the molecule determine the degree of adsorption and hence the effectiveness of the inhibitor. Various Schiff bases have been reported as effective corrosion inhibitors for steel.

In the present work, the efficiency of a new synthesized Schiff base (TDIQ) as inhibitor for the corrosion of mild steel in 1M sulphuric acid was evaluated on the basis of weight loss,

electrochemical impedance spectroscopy (EIS), Tafel polarization data and SEM- EDX studies.

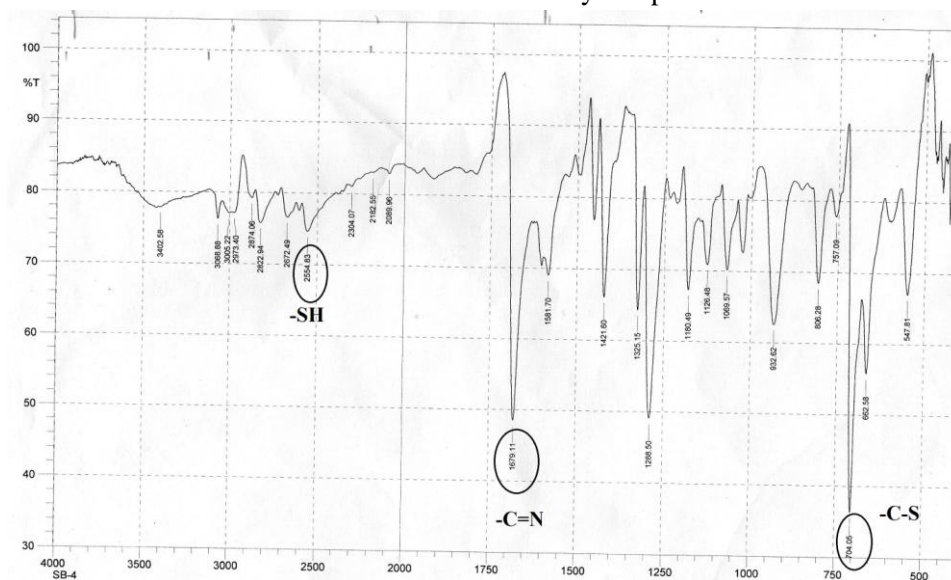
## MATERIALS AND METHODS

### Structure of the inhibitor (TDIQ)

### Chemical composition of the mild steel

The experiments were performed with cold rolled mild steel specimen of chemical composition (C=0.20%, Mn=1%, Si=0.05%, S=0.025%, P=0.25% and Fe=98%)

The structure is confirmed by IR spectra



**IR:** (KBr)  $\nu$   $\text{cm}^{-1}$ : 2554.83 (S-H str.), 1678.11 (C=N), 704.06 (C-S str.), 1288.50 (C-H bending)

### Corrosion monitoring methods

Weight loss measurements were carried out with rectangular mild steel plates of dimension  $3\text{cm} \times 1\text{cm} \times 0.1\text{cm}$ . The polished, preweighed plates were immersed in 1M  $\text{H}_2\text{SO}_4$  containing various concentrations of the inhibitor for 3 hrs, then reweighed. From the loss in mass, inhibition efficiency was calculated.

The effect of temperature on the inhibition efficiency was determined by carrying out the

weight loss measurements at higher temperatures (303K-333K)

The electrochemical studies were carried out with IVIUM Compactstat (potentiostat/galvanostat), using mild steel rod embedded in Teflon with exposed area  $0.785\text{ cm}^2$ . The potential range is -200 to +200 mV with respect to the open circuit potential at a scan rate of 1mV/sec. For impedance measurements, the sweep frequency is from 10Hz to 0.01KHz with a signal amplitude of 10mV.

SEM micrographs for the mild steel were recorded after 3 hrs of immersion in 1M H<sub>2</sub>SO<sub>4</sub> solution with and without inhibitor.

The synergistic effect was studied with 1mM KCl, KBr and KI in 1M H<sub>2</sub>SO<sub>4</sub> with various concentration of the inhibitor, where in the preweighed steel specimen were immersed for 3 hours. From the weight loss, inhibition efficiency was calculated.

## RESULTS

### Weight loss measurements

Table-1 gives the Inhibition efficiencies obtained from the weight loss measurements of mild steel for different concentrations of the inhibitor. It is clear that the inhibition efficiency increased as the concentration of the inhibitor increased from 0.1mM to 0.5mM.

### Effect of temperature and thermodynamic parameters

In order to study the effect of temperature on the inhibition efficiency and to determine the activation energy for the corrosion process, the weight loss studies were carried out at higher temperature (303K-333K). The results are given in the Table -2. It may be noted that the inhibition efficiency decreased with temperature.

The corrosion rate (CR) of the mild steel in acidic media is related to the temperature by the Arrhenius equation-

$$\text{Log CR} = \log A - Ea / 2.303 RT$$

Where CR is the corrosion rate, Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. The plot of log CR and 1/T gives linear plots (Fig.1) and the value of Ea is obtained from the slope of the straight line (Table -3) were calculated from the slope of the straight lines.

An alternative form of Arrhenius equation is  
Corrosion rate =  $RT/Nh \exp(\Delta S_{\text{ads}}^0/R) \exp(-\Delta H_{\text{ads}}^0/RT)$

Where h is Planck's constant, N is Avogadro number,  $\Delta S^0$  is the entropy of activation and  $\Delta H^0$  is the enthalpy of activation. Fig.2 shows a plot of

log corrosion rate against 1/T. A straight line is obtained with slope of  $\Delta H_{\text{ads}}^0/R$  and intercept  $\ln R/Nh + \Delta S_{\text{ads}}^0/R$  from which the values of  $\Delta H_{\text{ads}}^0$ ,  $\Delta G_{\text{ads}}^0$  and  $\Delta S_{\text{ads}}^0$  are calculated and are listed in Table -3.

### Langmuir Adsorption Isotherm

Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent<sup>3</sup>. A graph plotted between concentration vs C/θ gives a linear behaviour. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to the equation,

$$C/\theta = 1/K + C$$

Where 'K' is the equilibrium constant of adsorption.

### Potentiodynamic polarisation study

Potentiodynamic polarisation studies on the mild steel have been made for the inhibitor in 1M H<sub>2</sub>SO<sub>4</sub>. The electrochemical parameters such as I<sub>corr</sub> (corrosion current) and E<sub>corr</sub> (corrosion potential) obtained from Tafel plot for the inhibitor (Fig. 4) is given in Table 4. The I<sub>corr</sub> value decreases as compared to the blank value and at 0.5mM of inhibitor, the E<sub>corr</sub> value is slightly shifted towards negative direction. Tafel constants b<sub>a</sub> and b<sub>c</sub> are affected with increase in concentration of the inhibitor.

### Electrochemical impedance spectroscopy

Nyquist plot of mild steel in uninhibited and inhibited acidic solutions containing various concentrations of TDIQ are given in Fig-5. The impedance parameters derived from Nyquist plots are given in Table -5. It was observed that there is a gradual decrease in C<sub>dl</sub> (double layer capacitance) value with increase in concentration from 0.05 to 0.5 mM, whereas the R<sub>ct</sub> (charge transfer resistance) increases with the concentration of the inhibitor.

### Effect of halide ions

The synergistic effect provided by the addition of halide ions such as I-, Br-, and Cl- to the solution containing 1M H<sub>2</sub>SO<sub>4</sub> and the inhibitor

was studied by weight loss method and the data is presented in Table-6. Analysis of the data reveals that the addition of halides to the inhibitor increases the inhibition at each concentration of the inhibitor used. It has been reported that the surface of iron is found to be positively charged in an inhibitor free sulphuric acid media<sup>4</sup>. When the inhibitor is added, the nitrogen atoms present get protonated to form a cation. Hence they would be less strongly adsorbed. However, when halide ions are added, they are strongly chemisorbed on the positively charged steel surface. This makes the organic cations to be adsorbed on the layer of the anions. This is called co-operative adsorption and is responsible for the increased IE of the inhibitor in presence of halide ions.

#### Scanning Electron Microscopy Studies

The surface morphology of carbon steel surface was evaluated by Scanning Electron Microscopy (SEM). Fig. 6, 7 & 8 show the SEM image of the polished mild steel surface, steel surface immersed in 1M H<sub>2</sub>SO<sub>4</sub> and with TDIQ. It is clear that in the absence of the inhibitor, the surface is highly corroded. However in the presence of inhibitor the rate of corrosion is suppressed.

#### EDX Studies

Energy-dispersive X-ray (EDX) spectroscopy was used to determine the elements present on the metal surface before and after exposure to the inhibitor solution. Fig. 9 & 10 show the EDX graph for the mild steel immersed in 1M H<sub>2</sub>SO<sub>4</sub> and with TDIQ. The EDX graph shows that the presence of nitrogen, sulphur, oxygen atoms present in the inhibitor, which is adsorbed on the mild steel surface.

#### DISCUSSION

The inhibition efficiency increased as the concentration of the inhibitor increased. The behavior may be attributed to an increase in surface coverage,  $\theta$  by the adsorption of inhibitor on the mild steel surface, in the aggressive

solution, which restricts the dissolution of the metal.

The inhibition efficiency decreased with temperature. This may be attributed to desorption of the inhibitor molecule from metal surface at higher temperature<sup>5</sup>. This is also supported by  $E_a$  (Activation energy) value, which is higher in the presence of inhibitor as compared with that in the absence which is characteristics of physisorption of the inhibitor and formation of an absorptive film of electrostatic nature<sup>6</sup>. Negative  $\Delta G_{ads}^0$  (change in Gibb's Free energy of adsorption) values indicate spontaneity of the adsorption process and the values are less than 40 kJ/mol showing that the inhibitor is adsorbed on mild steel by physisorption. The negative sign of enthalpy  $\Delta H_{ads}^0$  (change in enthalpy of adsorption) reflects the exothermic nature of steel dissolution. Negative entropy imply that the formation of activated complex is the rate determining step and represents an association rather than dissociation and that a decrease in disorder occurs<sup>7</sup>.

Applicability of Langmuir isotherm to the adsorption of inhibitor on mild steel confirms the formation of monolayer adsorption where there is interaction between the adsorbate and the adsorbent<sup>8</sup>.

In the electrochemical studies,  $I_{corr}$  is reduced in presence of Schiff base showing the efficiency of the inhibitor. Tafel constants  $b_a$  and  $b_c$  are affected with increase in concentration of the inhibitor suggests that the inhibitor is mixed type<sup>9</sup>. In the EIS study, the Nyquist plots are semicircular in appearance indicating that charge transfer process controls the corrosion of mild steel<sup>10</sup>. The decrease in Cdl value results from increase in surface coverage by the inhibitor, which lead to an increase in Inhibition Efficiency (IE).

The synergistic influence of halide ions is more for I- ion which may be attributed to the large size and ease of polarisability of I- ion which facilitates stronger chemisorption with iron surface.

The SEM image observations suggest that the inhibitor forms a protective layer on the surface

that prevents the attack of acid on the metal<sup>11</sup>. The EDX studies inferred that the molecule interacted strongly with the metal through sulphur atom<sup>12</sup>.

### Corrosion inhibition mechanism

From the obtained results of various experimental techniques used, it was concluded that the synthesized Schiff base inhibit the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> by adsorption at the metal–electrolyte interface. Two modes of adsorption can be considered. The physical adsorption requires the presence of charged metal surface and charged inhibitor species in the solution, while chemisorption involves charge sharing or charge transfer from the inhibitor to the metal surface. TDIQ, which possesses N & S atoms with lone pair of electrons and also  $\pi$  electrons of the aromatic rings. The thermodynamic parameters suggest a physisorption mechanism prevails with the studied Schiff base. The effective performance of the inhibitor may be due to the electrostatic interaction between the positively charged Fe surface and the  $\pi$  electron of aromatic rings and azomethine group and also the lone pair of the electron on N & S atoms.

### CONCLUSION

- The synthesized Schiff base is a very good inhibitor for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>.
- The inhibition efficiency increases with increase in concentration of the inhibitor and decrease with temperature.
- The inhibitor acts by adsorption on the mild steel surface and the adsorption obeys Langmuir isotherm.
- Electrochemical studies show that the inhibitor is mixed type but slightly cathodic.
- SEM and EDX studies revealed the formation of a protective film of the inhibitor on the steel surface.

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## TABLES

**Table-1: Inhibition efficiency at various concentrations of TDIQ for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> obtained by weight loss measurements at 30 ± 1°C**

Concentration (mM)	Weight loss in gm	Inhibition Efficiency (%)	Degree of surface coverage (IE/100)	Corrosion Rate, mpy
Blank	0.1793			
0.01	0.1403	21.75	0.2175	58,848.03
0.05	0.1293	27.88	0.2788	54,234.14
0.1	0.1034	40.71	0.4071	44,586.92
0.2	0.0552	69.21	0.6921	23,153.32
0.3	0.0149	91.68	0.9168	6,249.72
0.4	0.014	92.19	0.9219	5,872.22
0.5	0.0121	93.25	0.9325	5,075.27

**Table: 2 Inhibition efficiency at the 0.5mM concentration of the inhibitor TDIQ for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> at various temperatures (303K- 333K)**

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate (mpy)
Blank	303	0.0609	-	76627.43
	313	0.1152	-	144950.4
	323	0.1443	-	181565.5
	333	0.2486	-	312801
TDIQ	303	0.0037	96.78	4655.83
	313	0.0075	95.89	16484.16
	323	0.0102	94.80	31709.98
	333	0.0121	93.25	142624.76

**Table: 3 Kinetics/Thermodynamic Parameters for mild steel corrosion in 1M H<sub>2</sub>SO<sub>4</sub> containing TDIQ**

Name of the inhibitor in mM	Activation energy, E <sub>a</sub> (kJ/mole)	-ΔG <sup>0</sup> <sub>ads</sub> (kJ/mole)				-ΔH <sup>0</sup> kJ/mole	-ΔS <sup>0</sup> kJ/mole
		303 K	313 K	323K	333 K		
Blank	29.8889	-	-	-	-	-	-
TDIQ	35.2077	20.44	21.11	21.78	22.46	20.16	1.8903

**Table 4: Corrosion Kinetic parameters for mild steel with selected concentration of the inhibitors in 1M H<sub>2</sub>SO<sub>4</sub> by potentiodynamic polarization method at 30±1 °C**

Concentration, mM	Tafel slope, mV/decade		I <sub>corr</sub> , (μF/cm <sup>2</sup> )	E <sub>corr</sub> , mV	Inhibition Efficiency(%)
	b <sub>a</sub>	b <sub>c</sub>			
Blank	69	117	287.7	-494.5	
0.05mM	75	106	95.8	-511.9	66.70
0.3mM	62	104	89.9	-505.4	68.75
0.5mM	61	104	31.3	-504.4	89.12

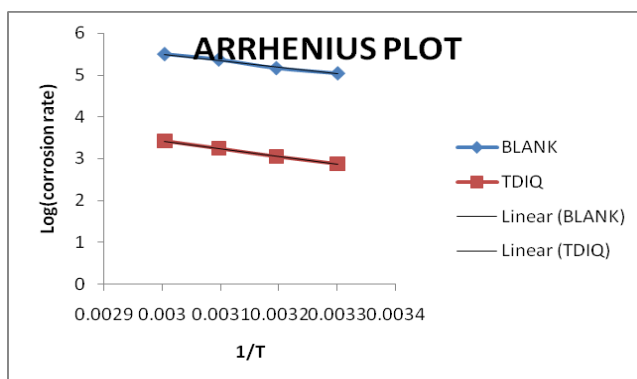
**Table 5: Impedance parameters for corrosion of mild steel for selected concentrations of the inhibitor TDIQ in 1M H<sub>2</sub>SO<sub>4</sub>**

Name of the compound	Concentration(mM)	R <sub>ct</sub> (ohm/ cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	Inhibition Efficiency(%)
Blank		6.98	31.7	
TDIQ	0.05	15.08	44.4	53.71
	0.3	17.73	28.2	58.20
	0.5	25.32	22.7	72.43

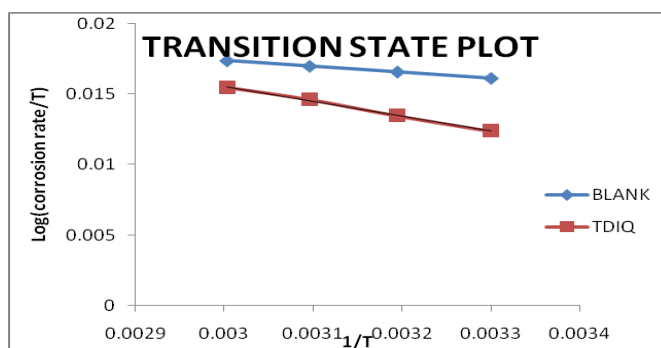
**Table 6: Effect of 1mM KCl / 1mM KBr / 1mM KI on the inhibition efficiency of the inhibitor TDIQ containing 1M H<sub>2</sub>SO<sub>4</sub>**

Name of the Inhibitor	Conc. (mM)	Inhibition efficiency (%)			
		Without KCl, KBr and KI	With 1mM KCl	With 1mM KBr	With 1mM KI
TDIQ	0.02	23.60	30.40	45.67	56.46
	0.04	25.83	37.58	51.83	65.12
	0.06	33.26	39.86	56.38	71.41
	0.08	36.36	50.48	59.65	72.46
	0.1	39.77	52.01	60.88	76.26

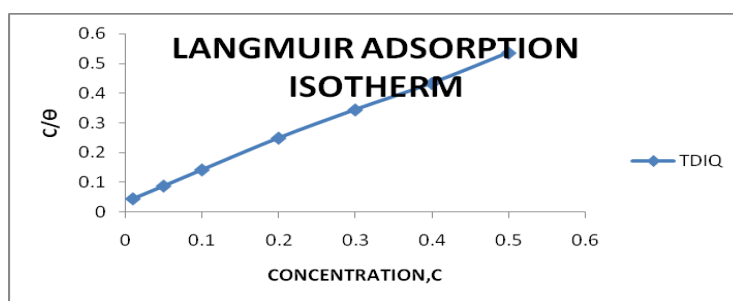
## FIGURES



**Fig-1** Arrhenius Plot of corrosion log corrosion rate vs  $1/T$  at different concentrations of the inhibitor TDIQ in  $1M H_2SO_4$



**Fig-2** Transition State plot of corrosion log corrosion rate /  $T$  vs  $1/T$  at different concentration of the inhibitor TDIQ in  $1M H_2SO_4$



**Fig-3** Langmuir Adsorption Isotherm for TDIQ on the mild steel surface in  $1M H_2SO_4$



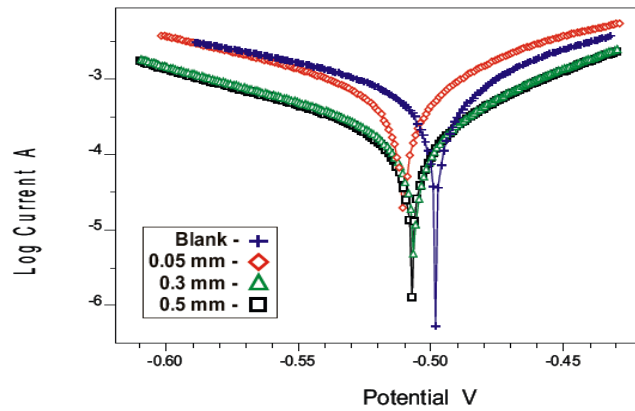


Fig-4: Polarisation plot for mild steel in 1M  $H_2SO_4$  containing various concentrations of the inhibitor TDIQ at  $30\pm 1^\circ C$

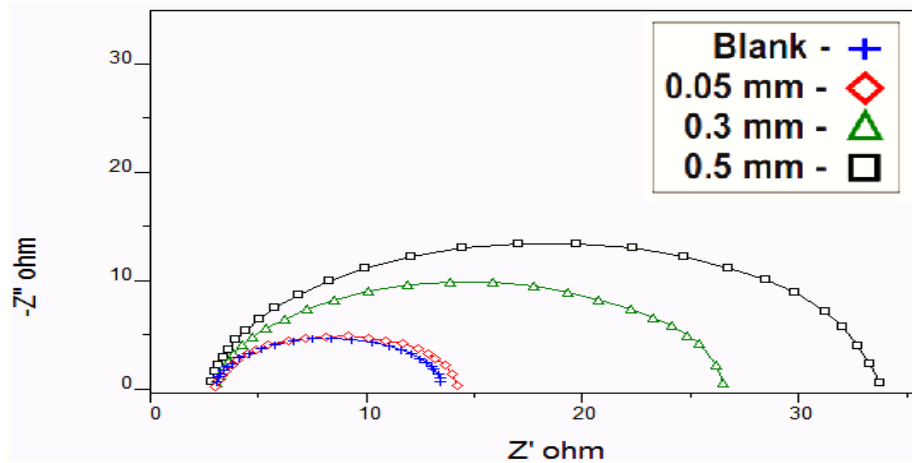


Fig-5: Nyquist plot for mild steel in 1M  $H_2SO_4$  containing various concentrations of the inhibitor TDIQ at  $30\pm 1^\circ C$

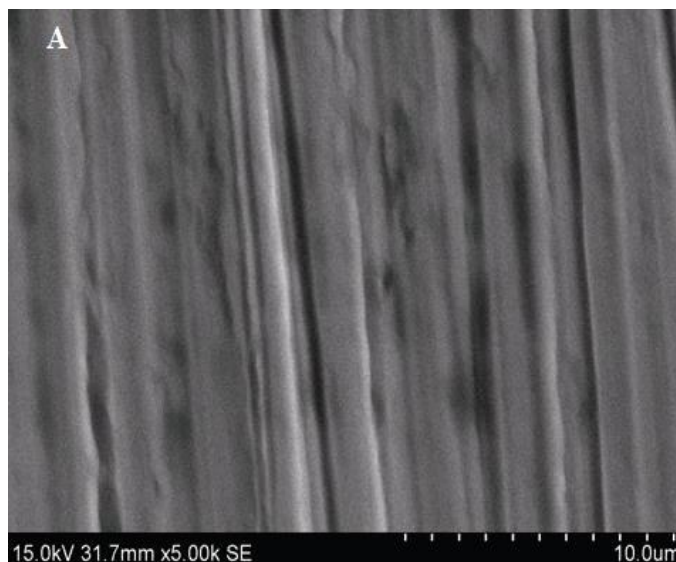
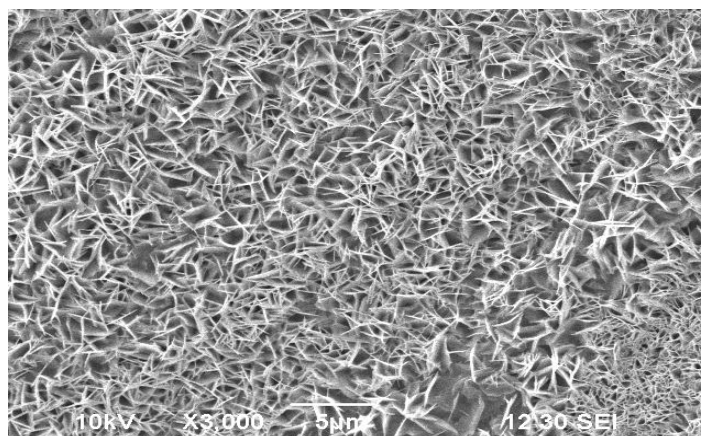
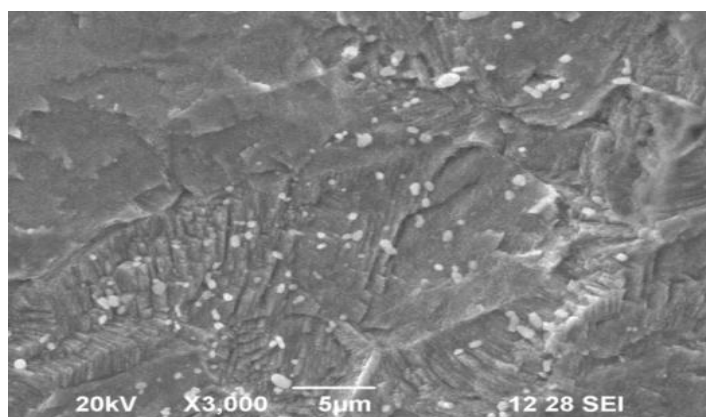


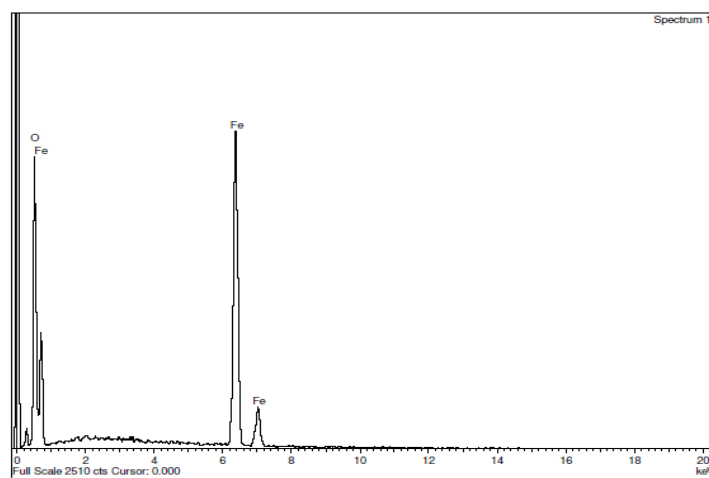
Fig-6 SEM image of Polished mild steel plate



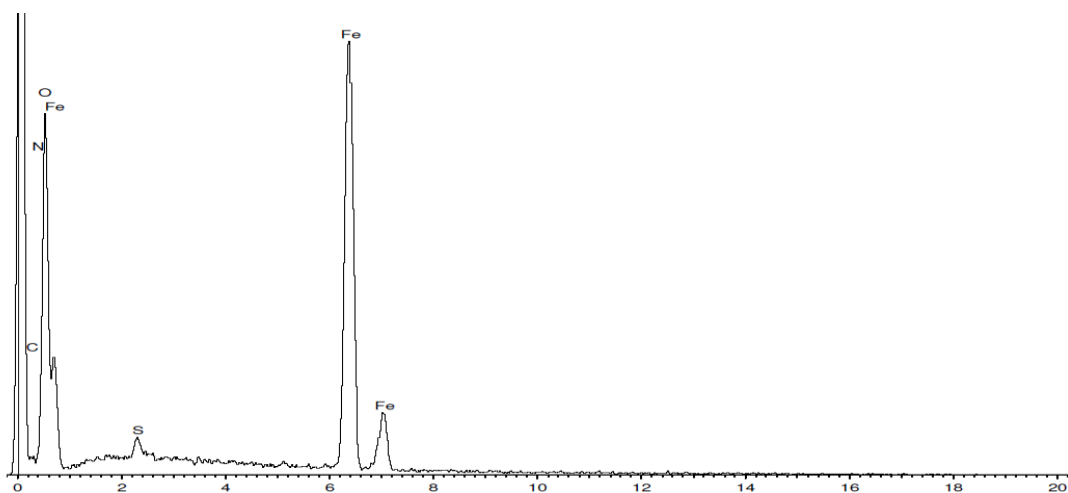
**Fig-7 SEM image of Mild steel plate after immersion for 3 hrs in 1M H<sub>2</sub>SO<sub>4</sub>**



**Fig-8 SEM image of Mild steel surface after immersion for 3 hrs in 1M H<sub>2</sub>SO<sub>4</sub> containing 0.5mM of the inhibitor TDIQ**



**Fig.9 EDX spectrum of the corrosion product on mild steel surface in 1M H<sub>2</sub>SO<sub>4</sub>**



**Fig.10 EDX spectrum of the corrosion product on mild steel surface in 1M H<sub>2</sub>SO<sub>4</sub> containing 0.5mM TDIQ**