



## Effect Of Polyethoxyethylene N, N, N` 1, 3 Diamino Propane On The Corrosion Of Mild Steel In Acidic Solutions

Namita K. Johar[a], K. Bhrara[b], R.Epshiba [c] and G. Singh[d]\*

The effect of polyethoxyethylene N,N,N` 1,3 daminopropane (POENNN) on the corrosion of mild steel (MS) in 0.5 mol L<sup>-1</sup> sulfuric acid has been studied at different concentrations and temperatures using polarization techniques and electrochemical impedance technique. The corrosion decreased considerably in presence of POENNN. An inhibition efficiency of 90% was evidenced in acidic solutions and was found to vary with the concentration of the inhibitor and the temperature. POENNN adsorbed on the mild steel surface according to the Temkin adsorption isotherm and the magnitude of activation energies confirms physisorption. The polymer acted as a mixed type of inhibitor. Scanning electron microscopic study was used to study the surface morphology of inhibited and uninhibited metal samples. The results were further supplemented by FT-IR spectroscopy.

**Keywords:** Adsorption, Corrosion inhibition; Electrochemical impedance technique; FTIR spectroscopy; Scanning electron microscopy; Temkin isotherm.

\*Corresponding Authors

[a] Department of Chemistry, Maharaja Agarsen Institute of Technology, Guru Gobind Singh Indraprastha University, Delhi, India. namita\_kh2002@yahoo.co.in.

[b] Department of Chemistry, Aditi Mahavidyalaya, University of Delhi, Delhi-110039, India. kbhrara@yahoo.com.

[c] Department of Chemistry, Sri Muthukumaran Institute of Technology, Chennai, Tamil Nadu, India 600026.

[d] Department of Chemistry, University of Delhi, Delhi-110007, India. gurmeet123@gmail.com.

### 1. INTRODUCTION

Corrosion is a severe material science problem. All structural metals corrode to some extent in chemical environments. Mild steel (MS) is highly versatile material and is used to produce many everyday objects as well as for commercial goods and projects. It is extensively used for structural purposes especially for buildings and bridges etc. Corrosion of structural grades of iron and steel however proceeds rapidly unless the metal is amply protected. Various inhibitors have been used to combat the problem of corrosion of MS but the polymers have proved to be excellent corrosion inhibitors [1-16]. Polymers due to their large surface area adsorb well even at the lowest concentrations on the metal surface leading to greater protection from corrosion. In the present study, polyethoxyethylene N, N, N` 1, 3 daminopropane (POENNN) has been used as an inhibitor to protect mild steel against acid corrosion. POENNN is a dark amber colored liquid and is water soluble tertiary diamine.

### 2. MATERIALS AND METHODOLOGY

#### 2.1 Materials

The mild steel (MS) used has the chemical composition (C=0.20%, Mn=1.00%, Si=0.05%, S=0.025%, P=0.25% and Fe=98%). 0.5 mol L<sup>-1</sup> sulfuric acid solution was prepared using AR grade H<sub>2</sub>SO<sub>4</sub> in double distilled water. POENNN was obtained from Sigma-Aldrich of AR grade. The solutions of POENNN were prepared at three different concentrations (C) of 0.25%, 0.5% and 1.00% in 0.5mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Square (1 cm x 1 cm) MS samples were prepared by grinding using 150, 320, 400, 600, 1000 grade emery papers. MS i.e. working electrode was soldered with insulated copper wire and was coated thoroughly with epoxy resin keeping some surface exposed for corrosion. The corrosion studies were carried out in a 3-electrode system comprising of working electrode i.e. MS electrode, reference electrode, i.e. saturated calomel electrode and the counter/auxiliary electrode i.e. platinum electrode.

## 2.2 Methodology

### 2.2.1 Potentiodynamic Polarization Measurements

The studies were carried out in a thermostat using the cell at three different concentrations of inhibitor i.e. 0.25%, 0.5% and 1% at different temperatures 308K, 318K, 328K, 338K. The reference electrode was connected through a Luggin's capillary to the cell. A constant distance of approximately 1-2 mm between the tip of luggin capillary and working electrode surface was maintained throughout the experiments. Steady state potentials took three hrs to stabilize. The current was passed through the cell at different predetermined values from a constant current generator through the counter electrode. The cathodic polarization curve was determined first and then after the re-establishment of the open circuit potential, anodic polarization curve was obtained. Corrosion current in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  ( $i_0$ ) and in the presence of inhibitor ( $i_{inh}$ ), corrosion potential ( $E_{corr}$ ) values and other parameters were determined.

### 2.2.2 Potentiostatic Polarization Measurements

Steady state potentiostatic polarization was done through the potentiostat by applying potentials of 40 mV increments after every one minute and the corresponding current values were recorded one minute after the potential was applied. Various electrochemical parameters of anodic dissolution of MS like passivating potential ( $E_{pp}$ ), passivating current ( $i_p$ ) and critical current density ( $i_c$ ) were obtained.

### 2.2.3 Impedance Measurements

An electrochemical impedance analyzer (Autolab PGSTAT 30; Ecochemie, Netherlands) was used for carrying out the impedance measurements. All the measurements were performed at the open circuit potential after immersing the MS electrode in the respective solution for about 90 minutes. The frequency sweep was applied from 10 mHz to 1MHz using 0.01V amplitude. The Nyquist plots were obtained from which charge transfer resistance ( $R_{ct}$ ) and double layer capacitance values ( $C_{dl}$ ) were obtained.

### 2.2.4 Infrared Spectroscopy

IR spectra of the pure inhibitor i.e. POENNN in KBr were obtained using Perkin Elmer FT-IR Spectrometer Spectrum 2000. The MS coupons were dipped in the lowest concentration of the inhibitors for about 4 hrs. The film formed on the surface of MS in the presence of the inhibitors was analyzed with a Perkin Elmer FTIR Spectrophotometer using reflectance mode.

### 2.2.5 Scanning Electron Microscopy

MS coupons were dipped into the solutions of 0.25% and 1% concentrations of the inhibitor (POENNN) and were subjected to scanning electron microscopic (SEM) examination.

## 3. RESULTS AND DISCUSSION

### 3.1 Potentiodynamic Polarization Studies

The representative polarization curves of the MS in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  in presence of POENNN at 308K are shown in Figure 1 in which the current densities ( $\text{mA cm}^{-2}$ ) are represented as CD. The anodic Tafel slope ( $b_a$ ), cathodic Tafel slope ( $b_c$ ) and corrosion current densities, determined from the extrapolation of the polarization curves, are given in table 1.

Inhibitor efficiencies ( $I$  %) are calculated using equation 1.

$$I \% = 100 [1 - (i_{inh} / i_0)] \quad (1)$$

Where  $i_0$  is the corrosion current in absence of the inhibitor and  $i_{inh}$  is the corrosion current in the presence of POENNN.

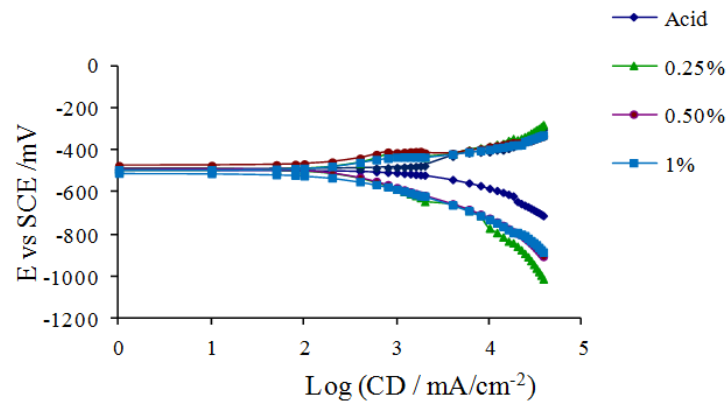


Figure 1. Potentiodynamic polarization curves for MS in  $H_2SO_4$  in the presence of POENNN at 308K

Table 1. Corrosion parameters of MS in  $H_2SO_4$  in the presence of POENNN.

C (%)	Temp. (K)	$-E_{corr}$ (mV)	$i_{inh} \times 10^{-3}$ ( $mA\ cm^{-2}$ )	$b_c$ ( $mV\ dec^{-1}$ )	$b_a$ ( $mV\ dec^{-1}$ )	I (%)
0.00	308	500	1.000	80	65	
0.25		480	0.100	150	50	90.0
0.50		485	0.112	160	50	88.8
1.00		450	0.126	120	35	87.4
0.00	318	510	1.412	80	75	
0.25		500	0.316	150	40	77.6
0.50		510	0.363	120	80	74.3
1.00		480	0.389	100	50	72.4
0.00	328	520	2.512	35	30	
0.25		490	0.631	100	40	74.9
0.50		510	0.794	140	40	68.4
1.00		480	1.000	65	30	60.2
0.00	338	520	3.162	40	20	
0.25		500	1.000	130	90	68.4
0.50		470	1.230	200	60	61.1
1.00		510	1.995	100	55	36.9

Table 1 clearly shows that the inhibitor efficiencies decrease with increase in concentration and temperature. The inhibitor shows no appreciable shift of  $E_{corr}$  towards any direction which indicates that this indicator acts as mixed type of indicator [19-22]. It shows irregular trends in Tafel slope values, suggesting that the inhibiting effect is not due to adsorption of inhibitor molecule alone but is assisted by various other species adsorbing on the metal surface. With the increase in temperature, the adsorption tends to weaken resulting in short time lag between adsorption and desorption thus leading to higher extent of corrosion. The decrease in the inhibition efficiency with increase in the concentration is probably due to steric hindrance which does not allow the proper adsorption on the metal surface.

### 3.2 Potentiostatic polarization studies

The steady state potentiostatic behavior of the anodic dissolution of MS in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  in the absence and presence of POENNN was studied. The representative polarization curves are shown in Figure 2 where CD represents current densities in  $\text{mA cm}^{-2}$ . The various passivating parameters ( $i_c$ -critical current,  $i_p$ -passivating current,  $E_{pp}$ - passivating potential) were determined and are given in Table 2.

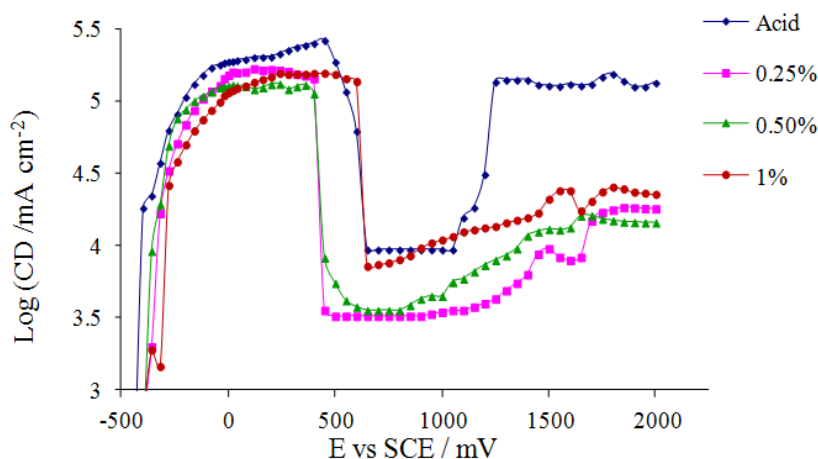


Figure 2. Potentiostatic polarization curves for MS in  $\text{H}_2\text{SO}_4$  in presence of POENNN at 308K

The data of Table 2 clearly indicates that the additive behaves as non-passivating type of inhibitor. Although it passivates slightly at the lowest concentration but this passivity is destroyed at higher concentrations. This may be due to considerable steric hindrance to the process of adsorption or to the formation of a passive layer. The passivity which primarily results due to the formation of  $[\text{M-In-OH}]_{\text{ads}}$  or  $[\text{M-OH-In}]_{\text{ads}}$  or  $[\text{M-In-X}]_{\text{ads}}$  where X are the other anions present in solutions, is not sustained in the present case due to non-uniform adsorption on the surface. Therefore, POENNN may be considered to be non-passivating type of inhibitor.

Table 2. Electrochemical parameters of MS in  $\text{H}_2\text{SO}_4$  in the presence of POENNN.

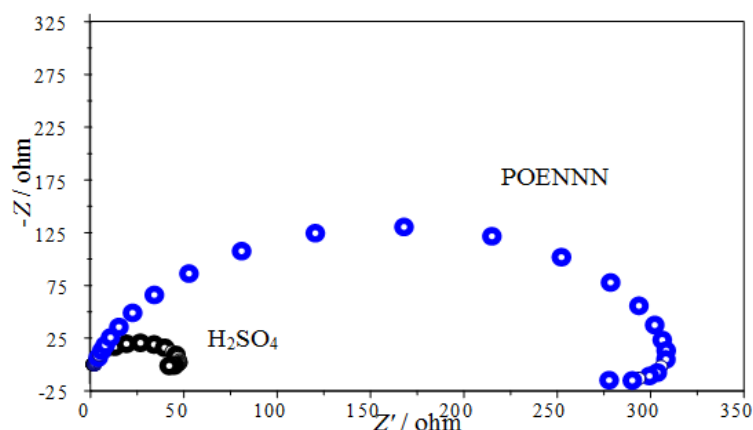
C (%)	$E_{pp}$ (mV)	$i_c$ ( $\text{mA cm}^{-2}$ )	$i_p$ ( $\text{mA cm}^{-2}$ )
0.00	590	251.180	10.000
0.25	380	158.480	3.162
0.50	495	158.480	3.981
1.00	460	158.480	6.309

### 3.3 Impedance measurements

Figure 3 shows electrochemical impedance (Nyquist) diagrams plotted for MS electrode in 0.25% of inhibitor solution i.e. POENNN. The impedance parameters namely the double layer capacitance ( $C_{dl}$ ), charge transfer resistance ( $R_{ct}$ ) and the inhibition efficiencies were calculated from the graphs and are given in Table 3. In the curve, the black points represent the corrosion in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  in the absence of the inhibitor and the blue points represent the corrosion in the presence of the inhibitor. Inhibition efficiency is also calculated using the equation (2)

$$I \% = 100 [1 - \{(R_{ct})_0 / (R_{ct})_{\text{inh}}\}] \quad (2)$$

Where  $(R_{ct})_{\text{inh}}$  and  $(R_{ct})_0$  are charge transfer resistances in presence and in the absence of the inhibitor.

Figure 3. Nyquist plots of MS in H<sub>2</sub>SO<sub>4</sub> and in the presence of POENNN.Table 3 Impedance parameters for MS in H<sub>2</sub>SO<sub>4</sub> in the presence of POENNN.

C (%)	R <sub>s</sub> (Ω cm <sup>2</sup> )	R <sub>ct</sub> (Ω cm <sup>2</sup> )	f(Hz)	C <sub>dl</sub> (F cm <sup>-2</sup> )	I (%)
0.00	1.97	47.39	7.44	4.55x10 <sup>-4</sup>	
0.25%	3.93	321.52	3.26	1.52x10 <sup>-4</sup>	85.3

The impedance diagram (Figure 3) for the solution examined has almost a semi-circular appearance. Knowing the value of  $R_{ct}$ , which is obtained by measuring the diameter of the semi-circle, electrochemical reaction rates, can be calculated [23-34]. In presence of POENNN, the diameter of the capacitive loop increases as compared to the acid, this is an indication of the inhibition of the corrosion process. The value of  $R_{ct}$  increases which in turn leads to a decrease in the  $i_{corr}$  for MS in the acidic solution. In the present case, the double layer capacitance ( $C_{dl}$ ) values decreases on addition of the inhibitor solution revealing that a complete film is formed on the metal surface when dipped in the lowest concentration of the inhibitor solution, which further indicates the adsorption of the inhibitor on the metal surface.

### 3.4 Temperature Kinetic Studies

Surface coverage ( $\theta$ ) is calculated using equation (3)

$$\theta = I\% / 100 \quad (3)$$

Different isotherms like Langmuir, Freundlich, Temkin, and Flory-Huggins were tried but Temkin isotherm was found to be the closest to the description of the adsorption behavior of the studied inhibitor. The correlation coefficient,  $R^2 = 1$  indicates the best fit line [17]. Temkin adsorption isotherm [18] is given by equation (4).

$$2a\theta = (-2.303 \log K) + (-2.303 \log C) \quad (4)$$

Therefore,  $\theta$  is plotted vs.  $\log(C)$  and from the slope and intercept, the values of  $K$  and 'a' are calculated. The graph is shown in Figure 4 and various parameters are given in Table 4.

Table 4 Parameters calculated from Temkin isotherm for POENNN.

Temp. (K)	Slope	a	Intercept	Log K	$-\Delta G_{ads}^0$ (kJ mol <sup>-1</sup> )	R <sup>2</sup>
338	-0.3239	3.5	0.470	-1.45	9.38	0.8795
328	-0.2442	4.7	0.603	-2.47	15.98	0.9956
318	-0.0864	13.3	0.721	-8.38	54.23	0.9694
308	-0.0432	26.7	0.874	-20.33	131.57	1.0000

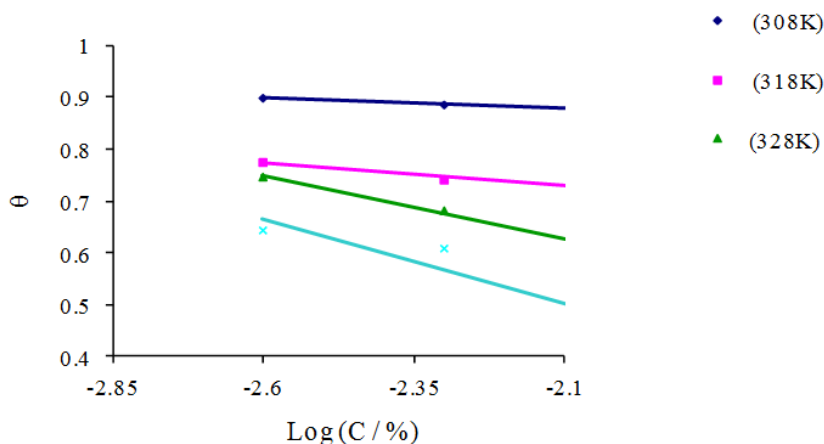


Figure 4.  $\theta$  vs.  $\log(C)$  for MS in  $H_2SO_4$  in the presence of POENNN.

The adsorption of the additive follows Temkin isotherm which is indicative of lateral interactions between the adsorbed molecules and the energetic surface homogeneity in adsorption. Table 4 shows that the value of 'a' is found to be in the range from 3.5 to 26.6 which shows good adsorption of the inhibitor molecule on the MS surface. The negative values of  $\Delta G^0_{ads}$  show the spontaneity of adsorption and the stability of adsorbed layer especially at lower temperatures.

The values of effective activation energy ( $E_{eff}$ ) were calculated by using equation (5)

$$i_{inh} = A \exp(-E_{eff} / RT) \tag{5}$$

where  $A$  is Arrhenius constant,  $R$ = Gas constant and  $T$  is the temperature in K. Plot between  $\log(i_{inh})$  against  $1/T$  for POENNN in  $0.5 \text{ mol L}^{-1}H_2SO_4$  at different temperatures have been shown in Figure 5. The values of  $E_{eff}$  are calculated and are given in table 5.

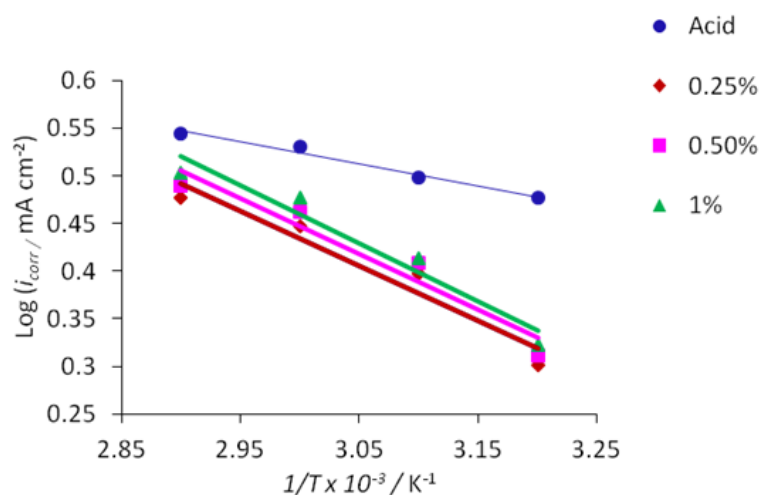


Figure 5.  $\log i_{corr}$  vs.  $1/T$  for MS in  $H_2SO_4$  in the presence of POENNN.

Table 5  $E_{eff}$  for corrosion of MS in  $H_2SO_4$  in the presence of POENNN.

C (%)	$E_{eff}$ (kJ mol <sup>-1</sup> )	$R^2$
0.00	34.90	0.9780
0.25	66.10	0.9690
0.50	69.31	0.9690
1.00	73.68	0.9750

The values of  $E_{eff}$  (Table 5) are found to be higher in presence of POENNN solution compared to sulfuric acid which suggests that the additive induces an energy barrier and slows the corrosion of MS in acidic medium.

### 3.5 Infra-red Spectroscopic Studies

IR Spectrum of pure POENNN in KBr medium and of POENNN adsorbed on the surface of metal are shown in Figures 6 and 7.

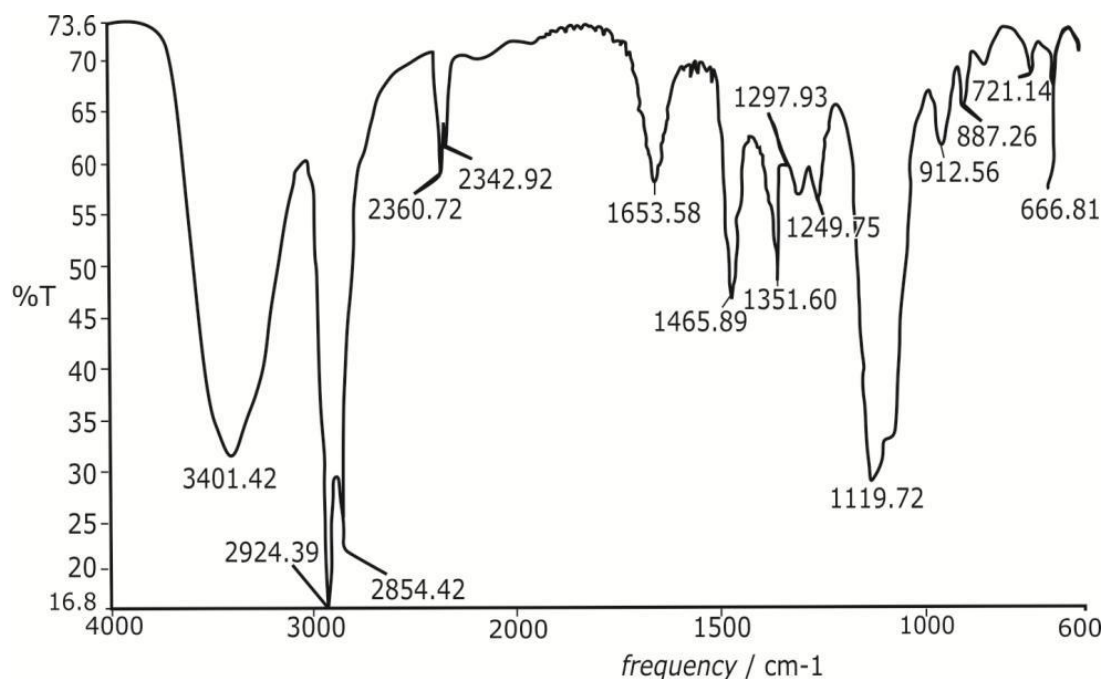


Figure 6. FTIR Spectrum of POENNN in KBr Medium

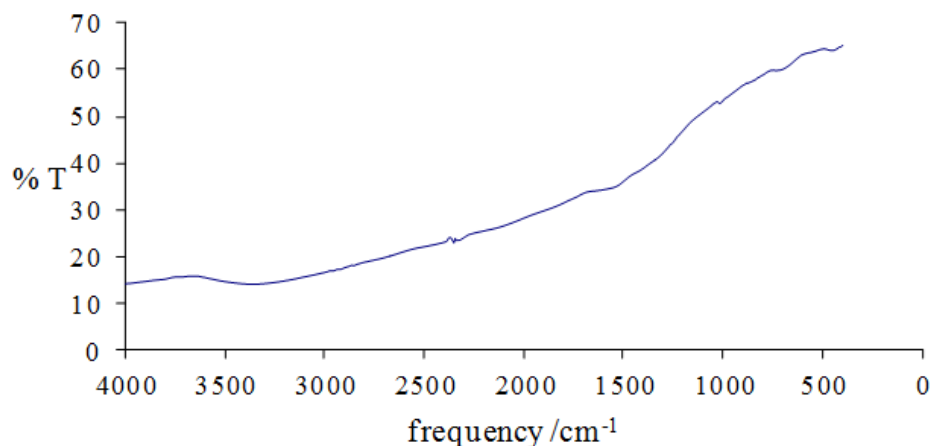


Figure 7. FTIR Spectrum of the film formed on MS in  $H_2SO_4$  in the presence of POENNN.

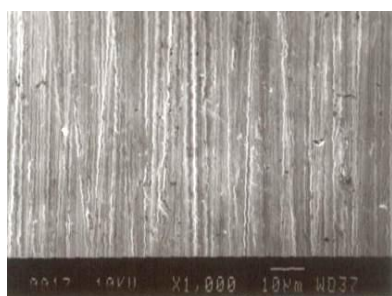
Spectrum of pure POENNN shows the following peaks:

- A band at  $3401.42\text{ cm}^{-1}$  is due to the N-H stretch of secondary amine, which is shifted to higher frequency side due to intermolecular hydrogen bonding.
- A peak at  $2854.42\text{ cm}^{-1}$  is due to the asymmetric C-H stretch of the  $CH_2$  group.
- A band at  $1653.58\text{ cm}^{-1}$  is due to C=C stretch of the un-conjugated olefin.
- The C-H bending vibrations of the  $CH_2$  are observed in the region of 1465 and  $1351.60\text{ cm}^{-1}$ .
- A weak band at  $1249\text{ cm}^{-1}$  is due to C-N stretching coupled with the stretching of adjacent bonds in the molecule.
- A peak at  $1119.72\text{ cm}^{-1}$  is due to the asymmetrical C-O-C stretching.

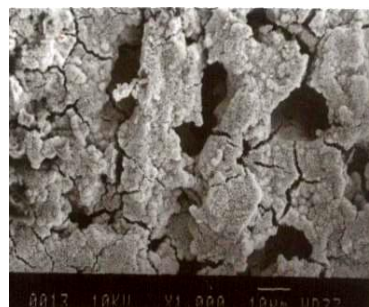
IR spectrum of POENNN adsorbed on the surface of metal shows a band at  $3401.42\text{ cm}^{-1}$  which is shifted to  $3389\text{ cm}^{-1}$  indicating that nitrogen is involved in adsorption on the metal surface. A new peak at  $2348\text{ cm}^{-1}$  is observed. The peak at  $1119.72\text{ cm}^{-1}$  is shifted to  $1094\text{ cm}^{-1}$  owing to some sort of involvement of C-O-C linkage in adsorption on the metal surface. The FTIR studies show that hetero-atoms like nitrogen and oxygen may be the most probable adsorption centers. There seems to be the involvement of C-O-C linkage in adsorption on the metal surface. Various other peaks also disappear suggesting that POENNN adsorbs on the metal surface and molecule as a whole is participating in the adsorption process.

### 3.6 Scanning Electron Microscopic Studies

Figures 8(a) and (b) show the micrographs of plain MS and MS in  $0.5\text{ mol L}^{-1} H_2SO_4$ . The micrographs of MS surface in 0.25% and 1% solutions of POENNN in sulfuric acid are as shown in Figures 8 (c) and (d).



(a)



(b)



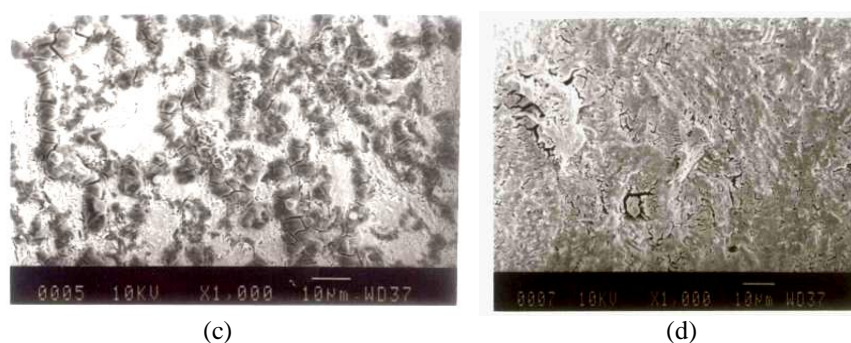


Figure 8. SEM of (a) Plain MS Surface, MS in presence of (b) 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, (c) Acid+0.25% and (d) Acid+ 1% POENNN at 1000 Magnification

On comparing the various micrographs, it can be concluded that the extent of corrosion is maximum in 0.5mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The corrosion reduced considerably in presence of 0.25% and 1% of the additive. The additive seems to have got adsorbed on the metal surface forming the film of the corrosion products. The results obtained from the SEM pictures are in direct agreement with the electrochemical results.

#### 4.CONCLUSIONS

From the studies above, it may be concluded that

- POENNN is found to be a good inhibitor for the corrosion of MS in sulfuric acid media.
- It is a mixed inhibitor inhibiting both cathodic and anodic processes to an equal extent.
- The inhibition efficiency decreased with the increase in the concentration and temperature. The inhibitor adsorbs on the MS surface according to Temkin adsorption isotherm.
- The values of  $E_{eff}$  show that the inhibitor is physically adsorbed on the MS surface in sulfuric acid.
- It is non-passivating type of inhibitor, although it passivates slightly at 0.25% concentration of POENNN but passivity is destroyed at higher concentrations.
- The impedance results supplement the results obtained from potentiodynamic polarization studies.  $R_{ct}$  value was found to be higher in the presence of the inhibitors. Higher the value of Charge transfer resistance ( $R_{ct}$ ), higher is the inhibition efficiency. The value of Double layer capacitance ( $C_{dl}$ ) was found to be lower suggesting the inhibitors adsorb well on the MS surface even at low concentrations.
- FTIR studies revealed that certain peaks have completely disappeared whereas some have shifted to lower frequency. It indicates that POENNN adsorbs on the metal surface and the molecule as a whole is participating in the adsorption process.
- The surface morphology as studied by SEM reveals that corrosion is considerably reduced in presence of conducting polymer solution. The results are in direct agreement with the electrochemical results.

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Received: (14-10-2014)  
Accepted: (17-11-2014)