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Corrosion Inhibition Study of Mild Steel by Benzodiazepine Derivative in 1M H₂SO₄

T.Sasikala¹, K.Parameswari²

Associate Professor, Department of Chemistry, Sri Ramakrishna College of Arts and Science, Coimbatore,
Tamilnadu, India. ¹

Controller of Examinations, P.S.G.R. Krishnammal College for Women, Coimbatore Tamilnadu, India².

ABSTRACT: 2-(3-methoxy-4-hydroxyphenyl) - 2-phenyl-2, 3 -dihydro-1H-1, 5-benzodiazepine (MEPBD) was synthesized by the condensation of o-phenylenediamine and ketone catalyzed by sulphated zirconia and characterized by FTIR spectra. Corrosion inhibition property of the benzodiazepine for mild steel in sulphuric acid medium was evaluated by weight loss, electrochemical methods and by Scanning electron microscopic studies (SEM). The results showed that the compound is an efficient inhibitor and the efficiency depends on concentration and temperature. The adsorption of the inhibitors is found to obey Langmuir adsorption isotherm Thermodynamic parameters such as ΔG , E_a , ΔH , ΔS for the corrosion inhibition process have been deduced and discussed.

KEYWORDS: Mild steel, benzodiazepine, corrosion inhibitors, adsorption

I. INTRODUCTION

Mild steel is widely used in petrochemical, chemical and metallurgical industries. It is also used as construction material owing to its excellent mechanical properties and cost effectiveness. However it easily undergoes corrosion in various environmental conditions especially in acid medium. Acids find various applications in industries as pickling, etching, descaling and cleaning agents but instigate corrosion of mild steel. Hence, in the industrial point of view, corrosion inhibition plays an important role nowadays.

The use of inhibitors was found to be the best practical method in reducing corrosion [1]. Addition of inhibitors to the acid solutions minimizes the acid attack on the metal. The corrosion inhibition efficiency of the inhibitors is related to their adsorption properties which depend on the presence of π -electrons of aromatic systems and heteroatoms which induce greater adsorption of the molecules on the metal surface. Many heterocyclic compounds containing nitrogen atom are proved to be efficient corrosion inhibitors [2-3]. Benzodiazepines have these requirements to act as corrosion inhibitors. A review of literature reveals that though many reports are available on the synthesis of benzodiazepines as biological agents, only limited studies are reported on their use as corrosion inhibitors [4-9]. In the present study, the effect of 2-(3-methoxy-4-hydroxyphenyl) - 2-phenyl-2,3 -dihydro-1H-1,5-benzodiazepine on the corrosion of mild steel in 1M H₂SO₄ was studied using mass loss and electrochemical studies. The kinetic and thermodynamic parameters were evaluated and discussed.

II. EXPERIMENTAL METHODS

SYNTHESIS OF BENZODIAZEPINE

2-(3-methoxy-4-hydroxyphenyl) - 2-phenyl 2, 3 -dihydro-1H-1, 5-benzodiazepine was synthesized by the condensation of o-phenylenediamine with chalcone under solvent free conditions catalyzed by sulphated zirconia [10]. The molecular structure and IUPAC nomenclature for the synthesized benzodiazepines are tabulated in table 1.

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Mild steel Preparation:

The mild steel specimens used for the corrosion experiments have the dimensions of 1cm X 3cm X 0.1cm with composition of C-0.084%, Mn-0.369%, Si-0.129%, S-0.025%, Cr-0.022%, Mo-0.01%, Ni-0.015% and rest of Fe. For electrochemical studies, mild steel specimen of the same composition embedded with Teflon with exposed area of 0.785cm² is used. The specimens were pretreated with emery papers of 100, 120 and 180 grades, rinsed with ethanol, water and air dried. It is then kept in a desicator to prevent moisture attack.

Corrosive medium

Analar grade sulphuric acid medium is used as the corrosive medium. Using deionized water, appropriate concentrations of the acid solutions were prepared with and without benzodiazepine MEPBD. The concentration of the inhibitor varied from 10-200 ppm.

Weight loss measurements

The polished mild steel specimens were weighed using Denver analytical balance (Precision ± 0.1 mg) and immersed in 100 mL of 1M H₂SO₄ containing various concentrations of the inhibitor using glass hooks. Care was taken to ensure the complete immersion of the specimen. After 3h of immersion the specimens were removed, washed with water, dried and weighed. From the initial and final weights of the specimen, the weight loss was calculated. The measurements were carried out with triplicate specimens and the average weight loss was recorded. The degree of surface coverage, inhibition efficiency and corrosion rate were calculated from the weight loss¹¹,

$$\text{Surface coverage } (\theta) = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}}$$

$$\text{IE (\%)} = \frac{(\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Weight loss in mgms}}{\text{Density} \times \text{Area in sq. inch} \times \text{Time in hours}}$$

The effect of temperature on corrosion and inhibition was studied at different temperatures in the range (303-333K). A digital thermostat (0.5°C accuracy) was used for maintaining the temperature. All experiments were carried out under static condition.

Electrochemical measurements

Electrochemical studies were performed on IVIUM compact stat/potentiostat with a three electrode cell assembly at room temperature. Platinum foil was used as counter electrode and saturated calomel electrode as the reference electrode and mild steel as the working electrode. The potential range was -200 mV to +200 mV with respect to the open circuit potential at a constant scan rate of 1mV/s. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), cathodic and anodic Tafel slopes (b_a and b_c) were calculated from the plot of potential vs. log current using IVIUM SOFT software installed in the instrument.

The inhibition efficiency was calculated from I_{corr} by using the formula¹²,

$$\text{IE (\%)} = \left(1 - \frac{I_{\text{corr}}}{I_{\text{corr}}^0}\right) \times 100$$

Where, I_{corr} and I_{corr}⁰ are the corrosion current densities in the absence and presence of benzodiazepine derivatives.

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The same cell setup employed for polarization study was used for EIS study also. The electrochemical impedance measurements were carried out using AC signal in the frequency range of 10 kHz to 0.01 Hz at the open circuit potential with peak to peak amplitude of 10 mV. The real (Z') and the imaginary (Z'') component of the cell impedance were measured in ohm cm^2 at various frequencies and plotted in the form of Nyquist plots. The impedance parameters such as charge transfer resistance R_t , double layer capacitance C_{dl} , were obtained by fitting the experimental results to a most appropriate equivalent circuit which was used to model the metal solution interface as shown below

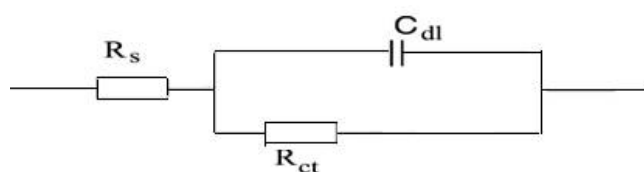


Fig.1. Equivalent circuit model

R_t values were calculated from the difference in impedance at lower and higher frequencies.

The percentage inhibition efficiency was calculated from R_t using the equation¹³,

$$IE (\%) = \frac{R_{t(\text{inh})} - R_{t(\text{blank})}}{R_{t(\text{inh})}} \times 100$$

Where $R_{t(\text{inh})}$ and $R_{t(\text{blank})}$ are the charge transfer resistances for mild steel immersed in 1M H_2SO_4 with inhibitor and without inhibitors respectively.

Surface morphology analysis

The surface of the mild steel after immersion in 1M H_2SO_4 in the absence and presence of inhibitors was examined by surface analysis techniques.

(i) SEM with EDX

The morphology of the mild steel surface was studied by scanning electron microscope CARL ZEISS UK. The polished mild steel coupons immersed in 1M H_2SO_4 and 1M H_2SO_4 containing 200 ppm of the inhibitor was examined. EDX spectra were used to determine the elements present on the surface.

(ii) Atomic force microscopy (AFM)

Atomic force microscopy is the high resolution scanning probe microscopy used to display the surface microstructures of the specimen in three dimensional model. The metal specimens were immersed in 1M H_2SO_4 with and without the inhibitor for 3 h, rinsed with double distilled water, dried and subjected to investigation. The surface morphology of the mild steel surface was examined using VEECO CP II Atomic force microscope. The scan size of the recorded AFM image is $15\mu\text{m} \times 15\mu\text{m}$.

III. RESULTS AND DISCUSSION

Weight loss measurements

Weight loss of mild steel specimens were measured after 3 h of immersion in 1M H_2SO_4 containing different concentrations of 1,5-benzodiazepine. The corrosion rate, degree of surface coverage and inhibition efficiency were calculated and recorded in Table 1. Corrosion rate of mild steel decreased with increasing concentration of the inhibitors. The degree of surface coverage θ increased as the concentration of the inhibitor increased. This shows that

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the inhibitor inhibit corrosion by adsorption on the steel surface. As concentration of the inhibitor increases more molecules get adsorbed and block the active sites for corrosion. The inhibitor MEPBD shows 90.3% inhibition efficiency at a maximum concentration of 200 ppm.

Table 1: Inhibition efficiency of the benzodiazepines for mild steel corrosion in 1M H₂SO₄ at 303 ± 1 K

| Inhibitor | Concentration (ppm) | Mass loss (mg/cm ²) | Inhibition Efficiency (%) | Degree of surface coverage(θ) | Corrosion rate (mpy) |
|-----------|---------------------|---------------------------------|---------------------------|-------------------------------|----------------------|
| BLANK | - | 44.26 | - | - | 17466.71 |
| MEPBD | 10 | 0.0888 | 66.56 | 0.6656 | 9121.35 |
| | 50 | 0.0779 | 70.67 | 0.7067 | 5122.95 |
| | 100 | 0.0585 | 77.97 | 0.7797 | 4715.22 |
| | 150 | 0.0425 | 83.99 | 0.8399 | 900.95 |
| | 200 | 0.0246 | 90.73 | 0.9073 | 526.10 |

The same study was carried out with the maximum concentration of the inhibitor at varied temperatures (303-333K) for a period of 1 hour. As the temperature increases, the corrosion rate increases and hence the inhibition efficiency of the benzodiazepine decrease (Table 2). Analysis of the data shows that, as the temperature is increased from 303K to 313K, the efficiency of the compound decreased by 10-14%. After that, the decrease in efficiency was less and about 5-9% decrease was noted.

Table 2: Variation of Inhibition efficiency of the benzodiazepines with temperature for mild steel corrosion in 1M H₂SO₄

| Name of the inhibitor | Temperature (K) | Mass loss (mg/cm ²) | Inhibition efficiency (%) | Corrosion rate(mpy) |
|-----------------------|-----------------|---------------------------------|---------------------------|---------------------|
| Blank | 303 | 0.0885 | - | 17466.71 |
| | 313 | 0.1152 | - | 22727.6 |
| | 323 | 0.1443 | - | 28468.69 |
| | 333 | 0.2486 | - | 49045.85 |
| MEPBD | 303 | 0.0082 | 90.73 | 1617.76 |
| | 313 | 0.0238 | 79.34 | 4695.45 |
| | 323 | 0.0388 | 73.11 | 7654.78 |
| | 333 | 0.0852 | 65.72 | 16808.96 |

A plot of log corrosion rate vs. 1/T was found to be linear (Figure 4.6). E_a was obtained from the slopes of the lines (E_a= slope * 2.303).

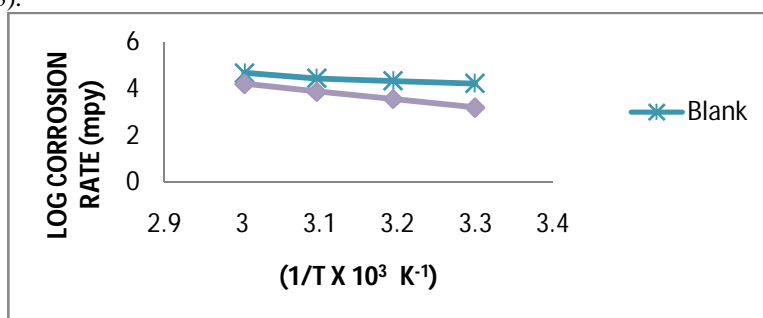


Fig. 2 Arrhenius plots for corrosion of mild steel in 1M H₂SO₄ solution in the absence and presence of benzodiazepine MEPBD

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Vol. 6, Issue 10, october 2017

The enthalpy of activation, ΔH^* is obtained from the equation,

$$\Delta H^* = E_a - RT$$

The change in free energy of activation ΔG^* is defined as the difference in the activation energies between the activated state and initial state of the reacting species¹¹ and is calculated using Eyrings equation,

$$r = \frac{kT}{h} e^{-\frac{\Delta G^*}{RT}}$$

Where r is the rate constant for corrosion process and is equated to corrosion rate. k = Boltzmann's constant, h = Planck's constant and T is the absolute temperature. The change in entropy of activation at any temperature is given by

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

The value of E_a , ΔH^* , ΔG^* and ΔS^* obtained are recorded in Table 3

Table 3 Thermodynamic parameters for the corrosion of mild steel in 1M H₂SO₄ without and with 200 ppm concentration of the benzodiazepine MEPBD

| Name of the inhibitor | E_a (kJ/mol) | ΔG^* (kJ/mol) | ΔH^* (kJ/mol) | ΔS^* (kJ mol ⁻¹ K ⁻¹) |
|-----------------------|----------------|-----------------------|-----------------------|--|
| BLANK | 27.7 | -21.56 | 25.18 | 0.15 |
| MEPBD | 64.94 | -25.39 | 62.42 | 0.28 |

From the table it is evident E_a is higher for the inhibited mild system compared to the uninhibited system against the blank acid value of 27.7 kJ/ mol. This shows that the presence of inhibitors increases the activation energy for corrosion and hence decreases the corrosion rate. The ΔH^* values are positive and increased in the presence of benzodiazepines by about 30 kJ/mol. This reveals that the dissolution of steel is endothermic. ΔG^* values are negative and are in the range of -20 kJ/mol indicating that the physisorption of the inhibitor's occur spontaneously. Change in entropy ΔS^* of the uninhibited and inhibited systems is positive, but the values are more for inhibited mild steel compared to uninhibited mild steel ($\Delta S^* = 0.15$ kJ mol⁻¹K⁻¹) which may be attributed to an increase in disorder due to adsorption of the compounds on steel surface.

Adsorption isotherm

The interaction between the inhibitor and mild steel surface can be understood from the adsorption isotherms. The degree of surface coverage obtained from mass loss measurements at different concentrations of the benzodiazepines were fitted graphically to various adsorption isotherms

A plot of C_{inh}/θ vs. C_{inh} gives a straight line with a regression coefficient R^2 closer to unity suggesting that the adsorbed benzodiazepine MEPBD obeys Langmuir adsorption isotherm.

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Vol. 6, Issue 10, october 2017

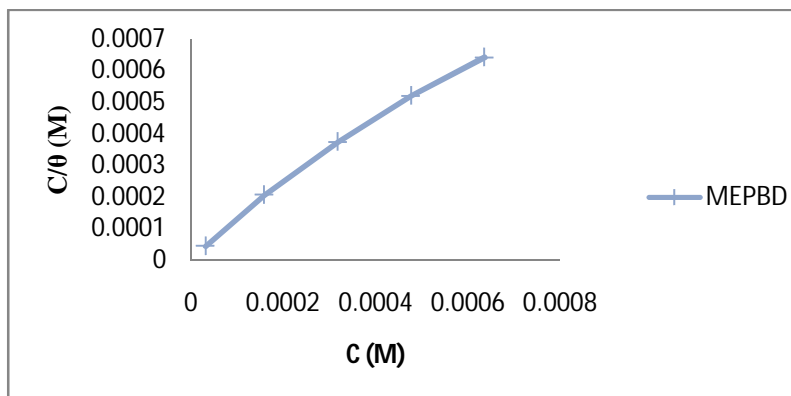


Fig. 3 Langmuir plots for benzodiazepine in 1M H₂SO₄

K_{ads} and free energy change of adsorption are related as,

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5 K_{ads})$$

Where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in Kelvin. The calculated ΔG°_{ads} values are tabulated table 4.

Table 4 Langmuir adsorption isotherm parameters for benzodiazepine MEPBD at 303 ± 1 K

| Compound | K _{ads} (M ⁻¹) X 10 ⁴ | R ² | -ΔG ^o _{ads} (kJ/mol) |
|--------------|---|----------------|--|
| MEPBD | 2.5 | 0.9915 | 35.63 |

The values are negative and the absolute values approach than 40 kJ/mol. This indicates spontaneous adsorption of the benzodiazepine MEPBD through electrostatic attraction between the metal ions and the inhibitor species. Afterwards there may be formation of chemical bonds via electron transfer reaction. The value of equilibrium constant is high suggesting strong adsorption.

Electrochemical measurements

Fig.4 shows the anodic and cathodic polarization curve of mild steel in 1M sulphuric acid solution without and with benzodiazepine derivative at 303 ± 1 K.

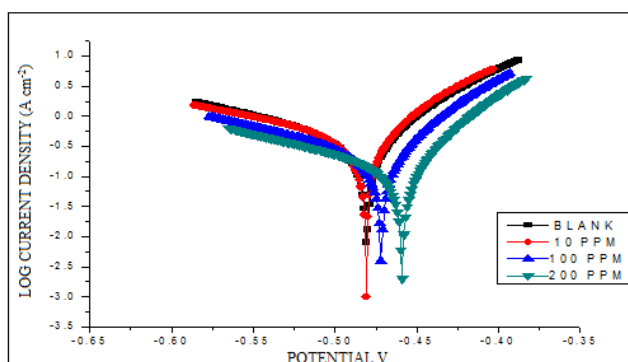


Fig. 4 Polarization curves for mild steel in 1M H₂SO₄ for selected concentrations of benzodiazepine MEPBD

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 10, october 2017

The electrochemical parameters derived from the Tafel polarization curves such as corrosion current density I_{corr} , corrosion potential E_{corr} , anodic and cathodic Tafel constants b_a and b_c (obtained by extrapolation of the linear parts of Tafel lines to E_{corr} are recorded in Table 5. Inhibition efficiency was calculated using the equation,

$$IE (\%) = \left(1 - \frac{I_{corr}}{I_{corr}^0} \right) \times 100$$

Where, I_{corr} and I_{corr}^0 are the corrosion current densities in the absence and presence of benzodiazepine derivatives.

Table 5 Corrosion parameters for corrosion of mild steel in 1M H_2SO_4 with selected concentrations of benzodiazepines (series II) by potentiodynamic polarization method at 303 ± 1 K.

| Name of the inhibitor | Concentration (ppm) | Tafel slopes (mV/dec) | | E_{corr} (mV) | I_{corr} ($\mu A/cm^2$) | Inhibition efficiency (%) |
|-----------------------|---------------------|-----------------------|--------|-----------------|-----------------------------|---------------------------|
| | | b_a | $-b_c$ | | | |
| BLANK | - | 68 | 167 | -480.0 | 414.0 | - |
| MEPBD | 10 | 54 | 152 | -478.0 | 150.0 | 63.76 |
| | 100 | 56 | 167 | -470.0 | 130.00 | 68.59 |
| | 200 | 43 | 134 | -460.0 | 66.5 | 83.93 |

The inhibitor MEPBD remarkably decreased the corrosion current density of mild steel to $66 \mu A/cm^2$ with a percent inhibition efficiency of 83%. The significant reduction in corrosion current density indicated the effective corrosion protection performance of the compound. The E_{corr} values are shifted slightly towards less negative direction by about 20mV. It has been reported that, if the displacement in E_{corr} is more than ± 85 mV vs. saturated calomel electrode compared to the corrosion potential of the blank, the inhibitor acts as pure cathodic or anodic type¹⁴. If the change is less than 85 mV vs. SCE, the inhibitor is classified as mixed type. Maximum shift of E_{corr} in the present study was found to be 20 mV for MEPBD indicating that the benzodiazepine is mixed type. The anodic and cathodic slopes b_a and b_c are both affected confirming that the tested compound behave as mixed type inhibitor.

Electrochemical impedance spectroscopy (EIS)

The kinetics of the electrode processes and the surface properties of the investigated systems was studied by EIS techniques. The technique is based on the measurement of the impedance of the double layer at the metal/solution interface.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 10, october 2017

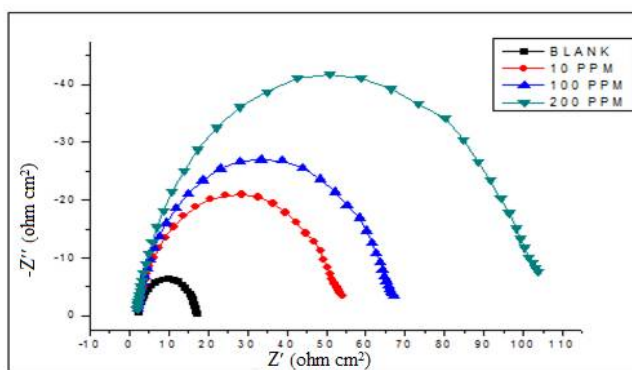


Fig.5 Nyquist diagram for mild steel in 1M H₂SO₄ for selected concentrations of benzodiazepine MEPBD

Fig.5 represents the Nyquist plots of mild steel specimens in 1M H₂SO₄ without and with various concentrations of the inhibitor MEPBD. These plots are semicircles which intersect the real axis at higher and lower frequencies. The charge transfer resistance values R_t are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance C_{dl} is used to characterize the double layer which is believed to be formed at the metal-solution interface of systems having non-ideal capacitive behaviors i.e., corroding metal in aqueous solution.

The values of R_t and C_{dl} obtained for mild steel in 1M H₂SO₄ (blank and inhibited) are given in Table 6.

Table 6 Impedance parameters for the corrosion of mild steel in 1M H₂SO₄ for selected concentrations of benzodiazepines (series II) at 303 ± 1 K.

| Name of the inhibitor | Concentration (ppm) | R _t (ohm.cm ²) | C _{dl} (μ F/cm ²) | Inhibition efficiency (%) |
|-----------------------|---------------------|---------------------------------------|--|---------------------------|
| BLANK | - | 18.00 | 46.7 | - |
| MEPBD | 10 | 55.00 | 32.2 | 67.27 |
| | 100 | 69.00 | 25.9 | 73.91 |
| | 200 | 105.00 | 17.7 | 82.85 |

The percentage inhibition efficiency is calculated from R_t values as,

$$IE (\%) = \frac{R_{t(inh)} - R_{t(blank)}}{R_{t(inh)}} \times 100$$

Where R_{t (inh)} and R_{t (blank)} are the charge transfer resistances for mild steel immersed in 1M H₂SO₄ with inhibitor and without inhibitors respectively. It is clear that addition of benzodiazepines into the sulphuric solution caused an increase in the charge transfer resistance R_t and a decrease in C_{dl} values. R_t is increased to a maximum value of 105 ohm.cm² for MEPBD which show the maximum inhibition efficiency of 82.85% at 200 ppm concentration.

Surface Morphology

The mild steel specimens immersed in the blank acid (1M H₂SO₄) and inhibited acid (1M H₂SO₄ + 200 ppm of MEPBD) were observed under a scanning electron microscope and the micro graphs are shown in (Fig.6a.) and

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 10, october 2017

(Fig.6b.). It is evident that the mild steel was heavily corroded in 1M H₂SO₄ (Fig. 6a.) where as in the presence of inhibitor the surface condition was comparatively better (Fig.6b.).

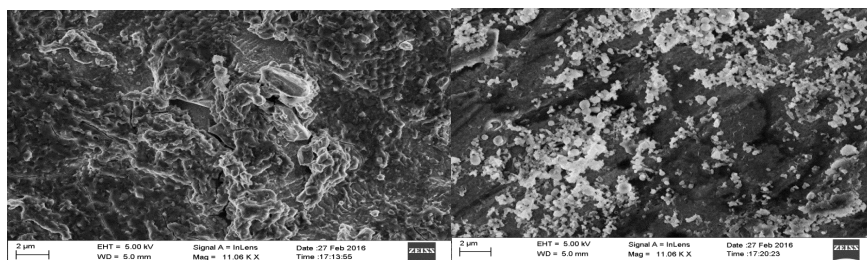


Fig.6a

Fig.6b

Fig. 6a. SEM image of the mild steel in presence of mild steel
Fig.6b. SEM image of the mild steel in presence of the inhibitor

Evaluation of the inhibitors

The inhibition efficiency is due to the presence of substituents on the phenyl group at position-2 of the benzodiazepine ring in MEPBD. In acid solution, the compounds get protonated at the N-atoms and the protonated species adsorb on the cathodic site of the mild steel and decrease the hydrogen evolution. Adsorption on anodic sites takes place through the π -electrons of the aromatic rings thereby decreasing the metal dissolution¹⁵. This is also due to the planar orientation of the phenyl group with respect to the mild steel surface.

IV. CONCLUSION

1. The synthesized benzodiazepine derivative MEPBD act as good corrosion inhibitor for mild steel in sulphuric acid medium with displaying 90% efficiency.
2. The adsorption of the inhibitor was found to obey Langmuir adsorption isotherm.
3. Electrochemical polarization method revealed the mixed mode of inhibition of the benzodiazepine.

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