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## ORIGINAL ARTICLE

# *N*-[Morpholin-4-yl(phenyl)methyl]acetamide as corrosion inhibitor for mild steel in hydrochloric acid medium



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## KEYWORDS

*N*-[Morpholin-4-yl(phenyl)methyl]acetamide;  
Mild steel;  
Langmuir adsorption isotherm;  
Electrochemical impedance;  
Potentiodynamic polarization;  
Scanning electron microscopy

**Abstract** The inhibiting effect and adsorption behavior of *N*-[morpholin-4-yl(phenyl)methyl]acetamide (MPA) on mild steel in hydrochloric acid solution were studied by weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy techniques. The inhibitor showed greater than 90% inhibition efficiency at 0.01 M. Potentiodynamic polarization studies showed that the inhibition action is concentration dependent, at low concentration anodic, higher concentration cathodic, inhibition predominant. Electrochemical impedance spectroscopy (EIS) confirmed that changes in the impedance parameters ( $R_i$  and  $C_{dl}$ ) are due to surface adsorption. The inhibition efficiencies obtained from weight loss measurements and electrochemical tests were in good agreement. The adsorption process of MPA at the mild steel/hydrochloric acid solution interface is described by Langmuir adsorption isotherm model. The negative value of standard free energy of adsorption in the presence of inhibitor suggests spontaneous adsorption of MPA molecule on the mild steel surface. The activation energy of corrosion and other thermodynamic parameters were calculated to elaborate the mechanism of corrosion inhibition.

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## 1. Introduction

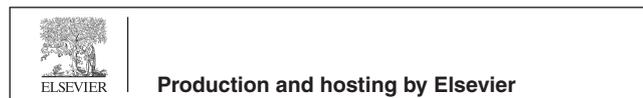
Mild steel is an industrially important material used in the fabrication of reaction vessels, storage tanks which either man-

ufacture or use hydrochloric acid as reactant. Moreover, hydrochloric acid solutions are widely used for the pickling, cleaning, descaling and etching of mild steel (James et al., 2007; Ekpe et al., 2001; Odoemelam and Eddy, 2008). Various methods are adopted to prevent corrosion but the use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media (Muralidharan et al., 1995a,b; Xiang-Hong et al., 2009). Most of the well known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms (Jamal Abdul Nasser et al., 2004, 2009; Abd El-Maksoud, 2008; Ramesh Saliyan and Airody, 2009; Benali et al., 2009). Sulfur and nitrogen con-

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taining heterocyclic compounds with various substituents are considered to be very effective corrosion inhibitors (Ramesh Saliyan and Airody, 2008; Jamal Abdul Nasser and Anwar Sathiq, 2007; Popova and Christov, 2008; Ousslim et al., 2009; Deana et al., 2008; Bentiss et al., 2009; Acharya and Upadhyay, 2004; Hammouti et al., 2005).

The role of inhibitor is to form a barrier against the acid attack. The protective action is often associated with chemical or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other.

In the present work, the corrosion inhibiting behavior of MPA was investigated on mild steel in HCl solutions by various methods.

The selection of the inhibitor is based on the following facts:

1. They contain two kinds of heteroatoms (two nitrogen and two oxygen for MPA) as reactive centers through which they can adsorb readily on the metal surface.
2. These compounds are readily soluble in medium.
3. They do not cause any health hazards like other sulfur containing derivatives, hence the use of MPA as corrosion inhibitor is safe.
4. Relatively inexpensive procedures for the preparation of MPA.

## 2. Materials and methods

### 2.1. Materials

Mild steel strips with the composition Carbon = 0.07%; Sulfur = 0%; Phosphorus = 0.008%; Manganese = 0.34% and Iron = Remainder and size of  $4 \times 1 \times 0.025$  cm were used for weight loss and effect of temperature studies. Mild steel cylindrical rods of the same composition embedded in polytetrafluoroethylene (PTFE) with exposed area of  $1 \text{ cm}^2$  were used for potentiodynamic polarization and impedance measurements. The electrode was polished using a sequence of emery papers of different grades and then degreased with acetone. *N*-[morpholin-4-yl(phenyl)methyl]acetamide was synthesized (Raman et al., 2004), and purified by recrystallization from ethanol to analytical purity grade. Its purity was confirmed by elemental analysis and characterized by IR and NMR spectroscopy. The name and molecular structure of the studied compound was given as Fig. 1.

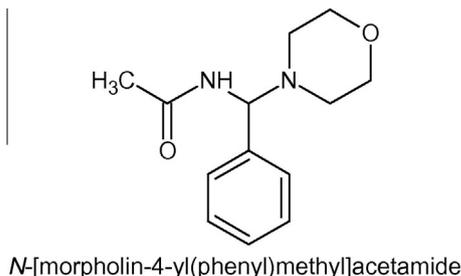


Figure 1 Molecular structure of MPA.

The acid solution (1.0 M HCl) was prepared by dilution of analytical grade HCl with double distilled water. All tests were conducted at different temperatures in magnetically stirred solutions.

### 2.2. Weight loss measurements

Weight loss measurements were done according to the method described previously (Jamal Abdul Nasser, 2005). Weight loss measurements were performed at  $303 \pm 1$  K for 2 h by immersing the mild steel cups into acid solution (100 mL) without and with various amounts of inhibitor. After the elapsed time, the specimen was taken out, washed, dried, and weighed accurately. All the tests were performed in triplicate and average values were reported. All the concentrations of inhibitor for weight loss and electrochemical study were taken in *M*.

The surface coverage ( $\theta$ ) and inhibition efficiency (I.E. %) was determined by using following equation:

$$\theta = \frac{W_0 - W_1}{W_0} \quad (1)$$

$$\text{I.E. (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

where,  $W_1$  and  $W_0$  are the weight loss values in presence and absence of inhibitors, respectively.

### 2.3. Effect of temperature

The loss in weights was calculated at different temperatures from 303 to 333 K. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in 1.0 M HCl with and without the addition of the inhibitor at their best inhibiting concentrations. Percentage inhibitions of the inhibitor at various temperatures were calculated.

### 2.4. Potentiodynamic polarization measurements

Both cathodic and anodic polarization curves were recorded ( $\text{mV s}^{-1}$ ) using the corrosion measurement system BAS (Model: 100 A) computerized electrochemical analyzer and PL-10 digital Plotter. A platinum foil and  $\text{Hg}|\text{Hg}_2\text{Cl}_2|1.0 \text{ M HCl}$  electrode was used as auxiliary and reference electrodes respectively. The Tafel polarization curves were obtained by changing the electrode potential automatically from  $\pm 0.2$  V at open circuit potential with a scan rate  $1.0 \text{ mV s}^{-1}$ .

### 2.5. Electrochemical impedance measurements

Electrochemical measurements were carried out in the conventional three-electrode, cylindrical Pyrex glass cell with a capacity of 1000 mL. A saturated calomel electrode (SCE) and a platinum disk electrode were used, respectively, as reference and auxiliary electrodes. The temperature was controlled at 303 K by thermostat. The working electrode was abraded with silicon carbide paper (grade P1200), degreased with AR grade ethanol and acetone, and rinsed with double distilled water before use. All potentials are reported versus SCE. EIS measurements were carried out in a frequency range of 100,000–0.01 Hz with amplitude of 10 mV using ac signals at open circuit potential.

**Table 1** Corrosion rate, inhibition efficiency and surface coverage of mild steel immersed in 1.0 M HCl for various concentrations of MPA obtained by weight loss method at  $303 \pm 1$  K.

| S. no. | Concentration of inhibitor (M) | Corrosion rate (mpy) | I.E. (%) | Surface coverage ( $\theta$ ) |
|--------|--------------------------------|----------------------|----------|-------------------------------|
| 1      | Blank                          | 0.8676               | –        | –                             |
| 2      | 0.000001                       | 0.4161               | 52.04    | 0.5204                        |
| 3      | 0.000001                       | 0.3364               | 61.22    | 0.6122                        |
| 4      | 0.000005                       | 0.3001               | 65.31    | 0.6531                        |
| 5      | 0.00001                        | 0.2390               | 72.45    | 0.7245                        |
| 6      | 0.00005                        | 0.2036               | 76.53    | 0.7653                        |
| 7      | 0.0001                         | 0.1771               | 79.60    | 0.7960                        |
| 8      | 0.0005                         | 0.1329               | 84.69    | 0.8469                        |
| 9      | 0.001                          | 0.1062               | 87.76    | 0.8776                        |
| 10     | 0.005                          | 0.0798               | 90.82    | 0.9082                        |
| 11     | 0.01                           | 0.0708               | 91.84    | 0.9184                        |

**Table 2** Values of corrosion rate, inhibition efficiency and surface coverage for different temperatures in the presence of 0.01 M concentration of MPA in 1.0 M HCl.

| S. no. | Temperature (K) | Corrosion rate (mpy) | I.E. (%) | Surface coverage ( $\theta$ ) |
|--------|-----------------|----------------------|----------|-------------------------------|
| 1      | 303             | 0.0708               | 91.84    | 0.9184                        |
| 2      | 308             | 0.0744               | 91.92    | 0.9192                        |
| 3      | 313             | 0.0850               | 91.94    | 0.9194                        |
| 4      | 318             | 0.1301               | 88.75    | 0.8875                        |
| 5      | 323             | 0.1753               | 85.86    | 0.8586                        |
| 6      | 328             | 0.3169               | 76.43    | 0.7643                        |
| 7      | 333             | 0.4409               | 69.23    | 0.6923                        |

## 2.6. Standard free energy of adsorption

The adsorption free energy changes in 0.01 M concentration (best inhibition) of MPA at different temperatures (313–333 K) were calculated using the equation  $\Delta G^0 = -RT \ln (K/55.5)$  kJ mol<sup>-1</sup>, (Quraishi and Singh, 2010). Where  $\Delta G^0$  = adsorption free energy,  $R$  = gas constant,  $T$  = temperature,  $K$  = adsorptive equilibrium constant. The value of 55.5 is the concentration of water in solution expressed in mol L<sup>-1</sup>. The value of  $K$  was calculated from  $K = \theta/C(1 - \theta)$ , where  $\theta$  = surface coverage (inhibition efficiency/100) and  $C$  = inhibitor concentration.

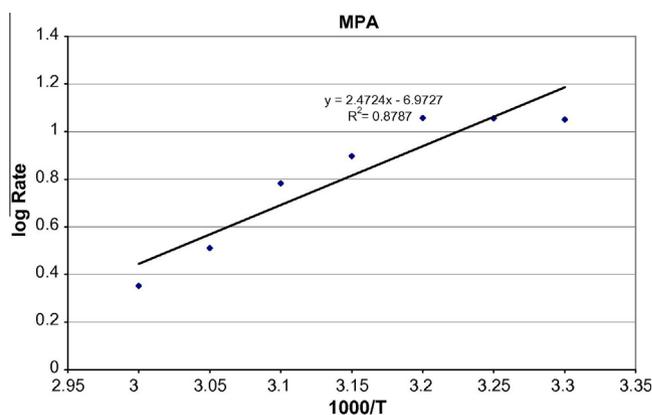
## 2.7. SEM analysis

The specimens used for surface morphological examination were immersed in acid containing various concentrations of inhibitor and blank for 2 h. Then they were removed, rinsed quickly with rectified spirit, and dried. The analysis was performed on HITACHI-model S-3000 H SEM.

## 3. Results and discussion

### 3.1. Weight loss measurements

The effect of concentration of MPA on the corrosion of mild steel in 1 M HCl is given in Table 1. It has been observed from the results that IE of MPA increases with increase in inhibitor concentration. The increase in efficiency may be due to the blocking effect of the surface by both adsorption and film

**Figure 2** The Arrhenius plots of log rate versus  $1000/T$  for the effect of temperature on the performance of the MPA at the optimum inhibition concentration of 0.01 M.

formation mechanism, which decreases the effective area of corrosion attack. The results confirm that MPA is an efficient corrosion inhibitor, which gives efficiency values as high as 91% in room temperature. The inhibiting performance exhibited by the compound may be due to the presence of protonated form of nitrogen and oxygen atoms of the compound which makes it adsorb quickly on the mild steel surface, thus forming an insoluble stable film on the surface of the mild steel. The greater extent of performance of MPA may be due to the presence of an amide moiety and one phenyl ring.

### 3.2. Effect of temperature

The temperature increases the rate of all electrochemical processes and influences adsorption equilibrium and kinetics as well (Popova and Christov, 2008). The effect of temperature on the corrosion inhibition with and without inhibitor is shown in Table 2. It can be seen that the weight loss increases with temperature in the absence and presence of inhibitor. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between two process at a particular temperature. With the increase of temperature, the equilibrium between the adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature (Chaudhary et al., 2007; Sanyal and Anil, 2010).

In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used (Quraishi and Singh, 2010)

$$\log(CR) = -E_a/2.303RT + \log \lambda \quad (3)$$

$$CR = RT/Nh \exp(-\Delta H_a^0/RT) \exp(\Delta S_a^0/R) \quad (4)$$

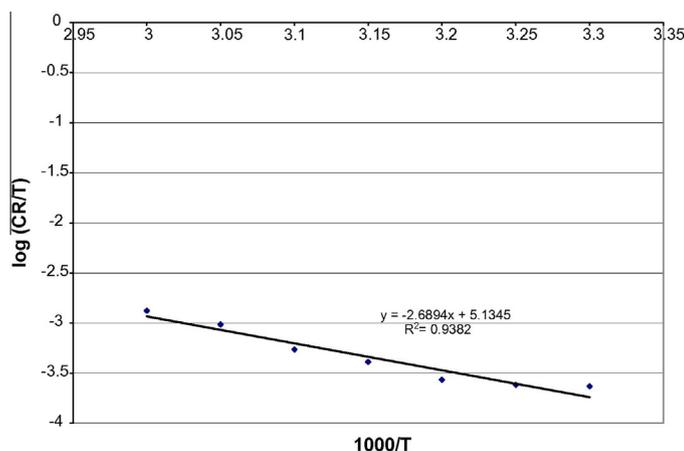
where  $E_a$  is the apparent activation energy,  $\lambda$  is the Arrhenius pre-exponential factor,  $CR$  is the corrosion rate,  $\Delta H_a^0$  the enthalpy of activation,  $\Delta S_a^0$  the entropy of activation,  $N$  the Avogadro's number,  $R$  the universal gas constant and  $T$  the absolute temperature.

The apparent activation energy ( $E_a$ ) at optimum concentration of MPA was determined by linear regression between  $\log(CR)$  versus  $1/T$  in 1 M HCl medium have been shown in Fig. 2. The results are shown in Table 3. Inspection of Table 3 showed that the values of  $E_a$  determined in 1.0 M HCl containing MPA is higher (47.34 kJ mol<sup>-1</sup>) than that for uninhibited solution (36.68). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage (Quraishi and Singh, 2010). Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature. As adsorption decreases more desorption of inhibitor molecules occurs because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of mild steel comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature (Szauer and Brand, 1981).

Fig. 3 showed a plot of  $\log(CR/T)$  versus  $1/T$ . The straight lines are obtained with a slope ( $\Delta H_a^0 = -\text{slope}/2.303R$ ) and an

**Table 3** The values of activation parameters  $E_a$ ,  $\Delta H_a^0$  and  $\Delta S_a^0$  for mild steel in 1.0 M HCl in the absence and presence of MPA.

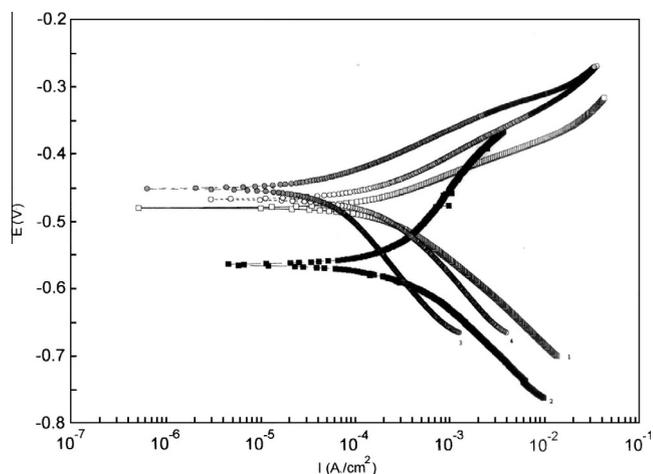
| S. no. | Inhibitor | $E_a$ (kJ mol <sup>-1</sup> ) | $\Delta H_a^0$ (kJ mol <sup>-1</sup> ) | $\Delta S_a^0$ (J mol <sup>-1</sup> K <sup>-1</sup> ) |
|--------|-----------|-------------------------------|--|---|
| 1      | Blank     | 36.68                         | 11.82                                  | -207.27   |
| 2      | MPA       | 47.34                         | 51.49                                  | -99.26  |



**Figure 3** The Arrhenius plots of  $\log(CR/T)$  versus  $1000/T$  for the effect of temperature on the performance of the MPA at the optimum inhibition concentration of 0.01 M.

**Table 4** Potentiodynamic polarization parameters and inhibition efficiency values for mild steel in 1.0 M HCl in absence and presence of different concentrations of MPA.

| S. no. | C (M)    | $E_{corr}$ (mV) | Tafel slope    |                | $I_{corr}$ (mA/cm <sup>2</sup> ) | I.E. (%) |
|--------|----------|-----------------|----------------|----------------|----------------------------------|----------|
|        |          |                 | $b_a$ (mV/dec) | $b_c$ (mV/dec) |                                  |          |
| 1      | Blank    | -475            | 45             | 120            | 5.10                             | -        |
| 2      | 0.000001 | -449            | 53             | 129            | 2.51                             | 50.78    |
| 3      | 0.0001   | -466            | 59             | 150            | 0.99                             | 80.59    |
| 4      | 0.01     | -564            | 64             | 174            | 0.42                             | 91.76    |



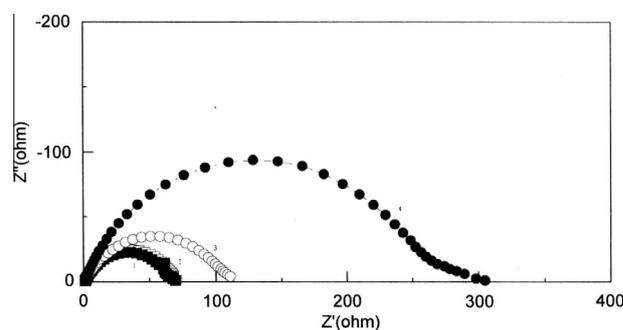
**Figure 4** Potentiodynamic polarization curve for mild steel in 1 M HCl in absence and presence of different concentration of MPA. (1) 1.0 M HCl; (2) 1.0 M HCl + 0.01 M MPA; (3) 1.0 M HCl + 0.0001 M MPA; (4) 1.0 M HCl + 0.000001 M MPA.

intercept of  $\log(R/Nh + \Delta S_a^0/2.303R)$  from which the values of  $\Delta H_a^0$  and  $\Delta S_a^0$  are calculated and are given in Table 3.

Inspection of Table 3 revealed that the enthalpy of activation parameters for dissolution reaction of mild steel in 1.0 M HCl in the presence of MPA is higher (51.49 kJ mol<sup>-1</sup>) than that of in the absence of inhibitors (11.82 kJ mol<sup>-1</sup>). The positive signs of  $\Delta H_a^0$  reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow (Guan et al., 2004) in the presence of inhibitors.

Furthermore, Table 3 showed that the negative entropy of activation is obtained in the presence of MPA, while high negative value is observed in the case of free 1.0 M HCl. Such variation is concerned with the phenomenon of ordering and disordering of the inhibitor molecules at the electrode surface and could be explained as follows.

The adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase and water molecules at the electrode surface (Sahin et al., 2002). The adsorption of inhibitors on the mild steel surface is accompanied by desorption of water molecules from the surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. The thermodynamic values obtained are the algebraic sum of the adsorption of organic molecules and desorption of water molecules (Branzoli et al., 2000). Hence, the gain in entropy is attributed to the increase in solvent entropy and to more positive water desorp-



**Figure 5** Nyquist plots of mild steel in 1 M HCl in absence and presence of various concentration of MPA. (1) 1.0 M HCl; (2) 1.0 M HCl + 0.01 M MPA; (3) 1.0 M HCl + 0.0001 M MPA; (4) 1.0 M HCl + 0.000001 M MPA.

tion enthalpy (Ateya et al., 1984). The less negative value (when compared to free acid) of entropy of activation for MPA also suggests that an increasing in disordering takes place in going from reactants to the metal/solution interface (Banerjee and Malhotra, 1992), which is the driving force for the adsorption of inhibitors onto the mild steel surface.

### 3.3. Potentiodynamic polarization studies

The inhibition effects of MPA on the corrosion of mild steel in 1 M hydrochloric acid solutions, studied by potentiodynamic polarization technique at different concentrations are shown in Table 4. The corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), and anodic ( $b_a$ ) and cathodic ( $b_c$ ) slopes are obtained by the anodic and cathodic regions of the Tafel plots. The corrosion current density ( $I_{corr}$ ) can be obtained by extrapolating the Tafel lines to the corrosion potential ( $E_{corr}$ ). It can be seen from the polarization curves (Fig. 4) and their fitted results that there is a large negative shift and smaller positive shift in the corrosion potential ( $E_{corr}$ ) and a drastic reduction in corrosion current density ( $I_{corr}$ ). The shift in corrosion potential in the negative direction indicates that MPA is a cathodic inhibitor. Potentiodynamic polarization studies showed that the inhibition action is concentration dependent, at low concentration anodic, higher concentration cathodic, inhibition predominant.

The inhibition efficiency was evaluated from the measured  $I_{corr}$  values using the relationship.

$$\text{Inhibition efficiency} = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100$$

where,  $I_{corr}^0$  and  $I_{corr}^i$  are values of corrosion current density in the absence and in presence of inhibitor, respectively.

**Table 5** Impedance parameters and inhibition efficiency values for mild steel in 1.0 M HCl in absence and presence of different concentrations of MPA.

| S. no. | C (M)    | $R_t$ (ohm cm <sup>2</sup> ) | $C_{dl}$ (μF/cm <sup>2</sup> ) | $I_{corr}$ (mA/cm <sup>2</sup> ) | I.E. (%) |
|--------|----------|------------------------------|--------------------------------|----------------------------------|----------|
| 1      | Blank    | 68.18                        | 9.92                           | 4.90                             | –        |
| 2      | 0.000001 | 69.35                        | 9.75                           | 2.40                             | 51.02    |
| 3      | 0.0001   | 106.12                       | 8.26                           | 0.94                             | 80.82    |
| 4      | 0.01     | 301.37                       | 4.76                           | 0.40                             | 91.84    |

### 3.4. Electrochemical impedance spectroscopy

Table 5 gives the values of  $R_t$ ,  $C_{dl}$  and  $I_{corr}$  were derived from Nyquist Plots as shown in Fig. 5.

The impedance response of mild steel in acid solution was significant after the addition of MPA. Furthermore, at 0.01 M concentration of MPA gives rise to a much larger semi circle diameter than the other two lower concentrations of MPA. Deviation from perfect circular shape, often known as frequency dispersion, was attributed to surface roughness and inhomogeneities of the solid surface (Lenderink et al., 1993).

The change of  $I_{corr}$  and  $R_t$  values can be related to the gradual replacement of water molecules and/or hydroxyl ions by MPA molecule on the mild steel surface and consequently to a decrease in the number of active sites necessary for the corrosion reaction. The increase in  $R_t$  and decrease in  $I_{corr}$  values is attributed to the formation of protective film on the metal/solution interface.

Moreover, the values of double layer capacitance ( $C_{dl}$ ) decreased with increasing MPA concentration. The decrease in  $C_{dl}$  is probably due to the decrease in local dielectric constant and/or an increase in the thickness of the protective layer at electrode surface, enhancing, therefore, the corrosion resistance of the studied mild steel.

The inhibition efficiency was evaluated from the measured  $I_{corr}$  values using the relationship.

$$\text{Inhibition efficiency} = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

where,  $I_{corr}^0$  and  $I_{corr}$  are values of corrosion current density in absence and in presence of inhibitor, respectively.

The results indicate good agreement between the values of corrosion inhibition efficiency from weight loss, potentiodynamic polarization and impedance measurements. It is concluded that the corrosion rate depends on the chemical nature of the electrolyte rather than the applied technique (Ostovari et al., 2009). The differences are sometime as high as >2–3% but the order of magnitude is the same for all the methods.

### 3.5. Adsorption isotherm

The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. When corrosion rate is sufficiently decreased in the presence of inhibitor, the adsorption steady state has a tendency to attain quasi-equilibrium state. Now, it is reasonable to consider quasi-equilibrium adsorption in a thermodynamic way using the appropriate adsorption isotherm. Langmuir, Temkin and Frumkin adsorption isotherms were tested to find the best suitable adsorption isotherm for adsorption of MPA on the surface of mild steel from 1 M HCl solution. Langmuir adsorption isotherm was found to fit.

With regard to the Langmuir adsorption isotherm the surface coverage ( $\theta$ ) of the inhibitor on the mild steel surface is related to the concentration ( $C_{inh}$ ) of the inhibitor in the bulk of the solution according to the following equation:

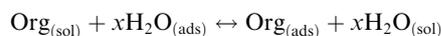
$$\theta = \frac{K_{ads} C_{inh}}{1 + K_{ads} C_{inh}} \quad (5)$$

where,  $K_{ads}$  is the equilibrium constant for the adsorption/desorption process. This equation can be rearranged to

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (6)$$

It is known fact that  $K_{ads}$  represents the strength between adsorbate and adsorbent. Large values of  $K_{ads}$  imply more efficient adsorption and hence better inhibition efficiency. The plot of  $\log C_{inh}/\theta$  versus  $\log C$  gave a straight line as shown in Fig. 6. The linear regression coefficients ( $R^2 = 0.9983$ ) are almost equal to 1, confirming that the adsorption of studied MPA in 1.0 M HCl solution follows the Langmuir's adsorption isotherm (Ahamed et al., 2010).

It is well recognized that the first step in the inhibition of metallic corrosion is the adsorption of organic inhibitor molecules at the metal/solution interface and that the adsorption depends on the molecule's chemical composition. In fact, the solvent  $H_2O$  molecules could also adsorb at metal/solution interface. So the adsorption of organic molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase  $[Org_{(sol)}]$  and water molecules at the metal surface  $[H_2O_{(ads)}]$  (Bockris and Reddy, 1976).



### 3.6. Standard free energy of adsorption

The negative values of  $\Delta G_{ads}^0$  ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface (Keles et al., 2008; Quraishi and Singh, 2010). It is usually accepted that the value of  $\Delta G_{ads}^0$  around  $-20 \text{ kJ mol}^{-1}$  or lower indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution while those around  $-40 \text{ kJ mol}^{-1}$  or higher involve charge sharing or charge transfer between the metal surface and organic molecules (Moretti et al., 1996). In the present study, the  $\Delta G_{ads}^0$  values obtained for the MPA on mild steel in 1 M HCl solution are ranging between  $-26$  and  $-28 \text{ kJ mol}^{-1}$ , which are higher than  $-20 \text{ kJ mol}^{-1}$  and lower than  $-40 \text{ kJ mol}^{-1}$  (Table 6); this indicates that the adsorption is neither typical physisorption nor typical chemisorption but it is complex mixed type that is the adsorption of inhibitor molecule on the mild steel surface in present study involves both physisorption and chemisorption and chemisorption is the predominant mode of adsorption.

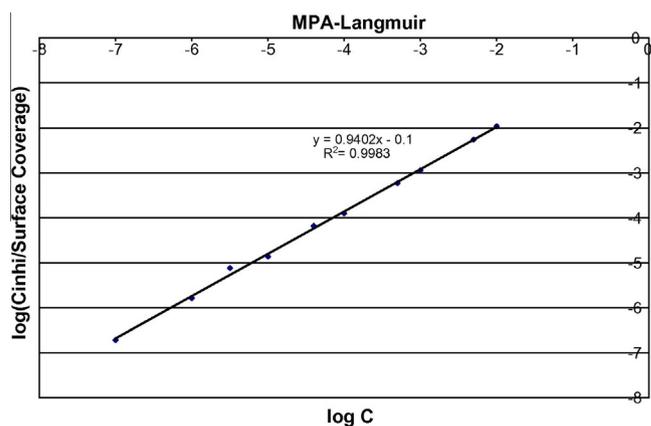


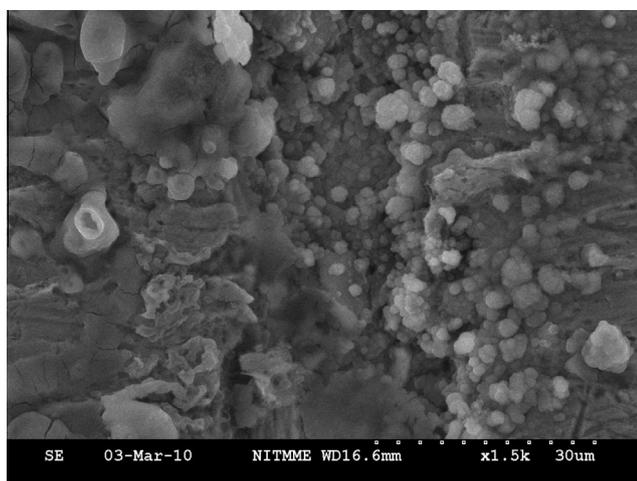
Figure 6 Langmuir's adsorption isotherm plot for the adsorption of MPA on mild steel in 1.0 M HCl solution.

**Table 6** Thermodynamic parameters for adsorption of 0.01 M concentration of MPA in 1.0 M HCl on mild steel at different temperatures.

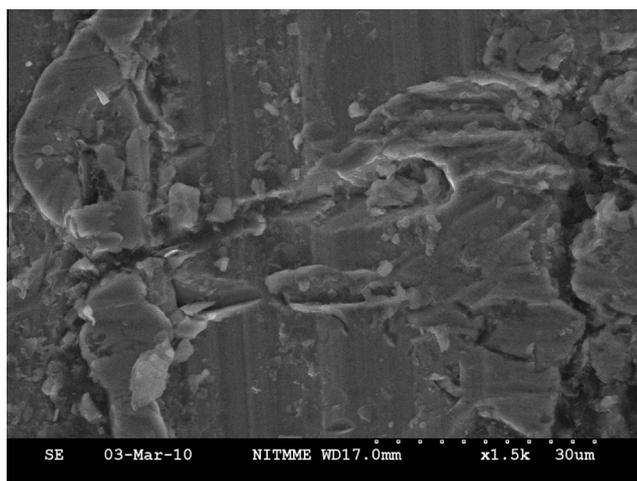
| S. no | Temperature (K) | $\Delta G_{\text{ads}}^0$ (kJ mol <sup>-1</sup> ) | $K_{\text{ads}}$ (M <sup>-1</sup> ) |
|-------|-----------------|---|-------------------------------------|
| 1     | 303             | -27.82  | 1125.49                             |
| 2     | 308             | -28.30  | 1137.62                             |
| 3     | 313             | -28.77  | 1140.69                             |
| 4     | 318             | -28.25  | 788.89                              |
| 5     | 323             | -27.99  | 607.21                              |
| 6     | 328             | -26.72  | 324.27                              |
| 7     | 333             | -26.11  | 224.99                              |

### 3.7. SEM analysis

SEM photograph of the metal sample in the presence and absence of inhibitor are shown in Figs. 7 and 8. The inhibited me-



**Figure 7** SEM image of surface of mild steel after immersion for 2 h in 1.0 M HCl.



**Figure 8** SEM image of surface of mild steel after immersion for 2 h in 1.0 M HCl in presence of 0.01 M MPA.

tal surface is smoother than the uninhibited surface indicating a protective layer of adsorbed inhibitor preventing acid attack.

### 3.8. Mechanism of corrosion inhibition

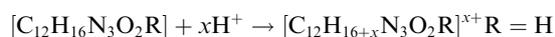
It is well recognized that organic inhibitor molecules set up their inhibition action via the adsorption of the inhibitor molecules onto the metal/solution interface. The adsorption process is affected by the chemical structures of the inhibitors, the nature and charged surface of the metal and the distribution of charge over the whole inhibitor molecule. In general, owing to the complex nature of adsorption and inhibition of a given inhibitor, it is impossible for single adsorption mode between inhibitor and metal surface.

Organic inhibitor molecules may be adsorbed on the metal surface in one or more of the following ways:

- Electrostatic interaction between the charged molecules and the charged metal;
- interaction of unshared electron pairs in the molecule with the metal;
- interaction of *p*-electrons with the metal; and/or
- a combination of types (a–c) (Schweinsberg et al., 1988; Shorky et al., 1998).

The inhibition efficiency afforded by MPA may be attributed to the presence of electron rich *N*, *O* and aromatic rings. One phenyl ring, one amide linkage and one morpholine ring in the structure of the MPA. Therefore, the possible reaction centers are unshared electron pair of hetero atoms and *p*-electrons of aromatic ring.

The adsorption and inhibition effect of MPA in 1 M HCl solution can be explained as follows. Mannich bases might be protonated in the acid solution as:



Thus, in aqueous acidic solutions, MPA exists either as neutral molecules or in the form of protonated MPA (cations). MPA may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated MPA with already adsorbed chloride ions, (ii) donor–acceptor interactions between the *p*-electrons of aromatic ring and vacant *d* orbital of surface iron atoms, (iii) interaction between unshared electron pairs of heteroatoms and vacant *d* orbital of iron surface atoms.

Generally, two modes of adsorption could be considered. In one mode, the neutral MPA may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the heteroatoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between *p*-electrons of the heterocyclic ring and vacant *d* orbitals of surface iron. In another mode, since it is well known that the steel surface bears positive charge in acid solution (Mu et al., 1996), so it is difficult for the protonated MPA to approach the positively charged mild steel surface ( $\text{H}_3\text{O}^+$ /metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated MPA adsorb

through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus there is a synergism between adsorbed  $\text{Cl}^-$  ions and protonated MPA.

It should be noted that the molecular structure of protonated MPA remains unchanged with respect to their neutral form, the N-atoms on the ring remaining strongly blocked, so when protonated MPA adsorbed on metal surface, coordinate bond may be formed by partial transference of electrons from the hetero-atoms to the metal surface.

#### 4. Conclusions

1. Results obtained from the experimental data shows that MPA acts as inhibitor for the corrosion of mild steel in 1 M HCl.
2. Inhibition efficiency increases with increase in the concentration of the studied inhibitor but decreases with rise in temperature.
3. Potentiodynamic polarization studies showed that the inhibition action is concentration dependent, at low concentration anodic, higher concentration cathodic inhibition predominant.
4. EIS measurements also indicate that the inhibitors increase the charge transfer resistances and show that inhibitive performance depends on adsorption of the molecule on the metal surface.
5. The adsorption of MPA on mild steel surface from 1 M HCl obeys the Langmuir adsorption isotherm.
6. The adsorption of MPA onto mild steel surface was a spontaneous process. Further the adsorption of MPA on mild steel surface is complex in nature and predominantly physical adsorption type.

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