

**N-((4-CHLOROPHENYL)(MORPHOLIN-4-YL)METHYL)BENZAMIDE AS cc FOR  
MILD STEEL IN SULPHURIC ACID MEDIUM**

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**ABSTRACT**

The inhibiting effect and adsorption behavior of N-[(4-chlorophenyl)(morpholin-4-yl)methyl]benzamide (CPMB) on mild steel in sulphuric acid solution were studied by weight loss measurements, effect of temperature studies, potentiodynamic polarization and scanning electron microscopic 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. The adsorption process of CPMB at the mild steel/sulphuric acid solution interface is described by Temkin's adsorption isotherm model. The negative value of standard free energy of adsorption in the presence of inhibitor suggests spontaneous adsorption of CPMB molecule on the mild steel surface. The protective film formation against the acid attack is confirmed by SEM.

**KEYWORDS:** Mild steel, Temkin's adsorption isotherm, corrosion inhibitor, potentiodynamic polarization and scanning electron microscopy

**INTRODUCTION:**

Sulphuric acid is a strong inorganic acid that is used in many industrial

processes. The most important areas of applications are acid pickling, acid descaling and oil-well acidizing<sup>1,2</sup>. During these

processes, metal such as steel is subjected to serious acid corrosion and inhibitors are often needed to reduce corrosion rates in this media. Most of the efficient inhibitors used in industry are organic compounds having multiple bonds in their molecules, which mainly contain nitrogen and sulphur<sup>3,4</sup>. Many heterocyclic compounds containing heteroatom like N, O, S, have been reported to be effective inhibitors for the corrosion of steel in acid media by several authors<sup>5-7</sup>. Under certain conditions, the electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency to the metal<sup>8-9</sup>. Some Mannich bases have been reported as efficient corrosion inhibitors<sup>10-11</sup> and the literature available to date about the Mannich bases functioning as corrosion inhibitors is limited. The present work, and in continuation of our previous study<sup>12-13</sup>, is devoted to investigation of N-[(4-chlorophenyl)(morpholin-4-yl)methyl]benzamide (CPMB) as inhibitor for mild steel corrosion in 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions. Thus, the present study aims at determining the effectiveness of CPMB as the corrosion inhibitor by weight loss method as well as by electrochemical studies.

## 2.0. MATERIALS AND METHODS:

### 2.1 Materials :

Mild steel strips with the composition Carbon = 0.07%; Sulphur = 0% ; Phosphorus = 0.008% ; Silicon = 0% ; Manganese = 0.34% and Iron = Reminder and size of 4 × 1 × 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 cm<sup>2</sup> were used for potentiodynamic polarization measurements. The electrode was polished using a sequence of emery papers of different grades and then degreased with acetone. N-[(4-chlorophenyl)(morpholin-4-yl)methyl]benzamide (CPMB) was synthesized, 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 studied compound was given as Figure 1.

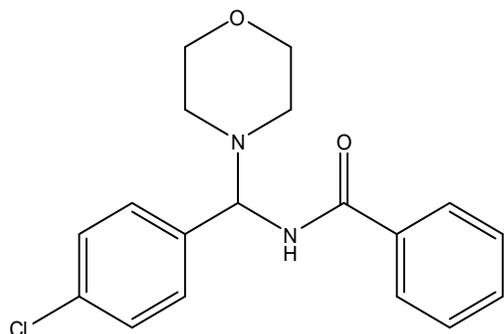


Figure 1 Molecular Structure of CPMB

The acid solution (1M H<sub>2</sub>SO<sub>4</sub>) was prepared by dilution of an analytical grade H<sub>2</sub>SO<sub>4</sub> 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<sup>3</sup>. Weight loss measurements were performed at 303±1 K for 2h by immersing the mild steel coupons into acid solution (100 mL) without and with various amounts of inhibitor. After the elapsed time, the specimen were taken out, washed, dried, and weighed accurately. All the tests were performed in triplicate and average values were reported. All the concentrations of an inhibitor for weight loss and electrochemical study were taken in M.

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

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

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

Where, W<sub>1</sub> and W<sub>o</sub> are the weight loss value in presence and absence of inhibitors, respectively.

## 2.3. Effect of Temperature:

The loss in weights was calculated at different temperatures from 303 K to 333 K. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in 1M H<sub>2</sub>SO<sub>4</sub> 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 (mVs<sup>-1</sup>) using the corrosion measurement system BAS (Model: 100 A) computerized electrochemical analyzer and PL-10 digital Plotter. A platinum foil and Hg|Hg<sub>2</sub>Cl<sub>2</sub>|1M

H<sub>2</sub>SO<sub>4</sub> 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 mV s<sup>-1</sup>.

### 2.5. Standard free energy of adsorption:

The adsorption free energy changes in 10<sup>-2</sup>M concentration (best inhibition) of CPMA at different temperatures (313 K to 333K) were calculated<sup>14</sup> using the equation  $\Delta G^0 = -RT \ln (K 55.5)$  kJ/mole, 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.

### 2.6. SEM analysis:

The specimens used for surface morphological examination were immersed in acid containing various concentrations of inhibitor and blank for 2 hours. Then they were removed, rinsed quickly with rectified spirit, and dried. The analysis was

performed on HITACHI-model S-3000 H SEM.

## 3.0. RESULTS AND DISCUSSION:

### 3.1.Weight loss measurements:

The effect of concentration of CPMA on the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> is given in Table 1. It has been observed from the results that IE of CPMB 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 formation mechanism, which decreases the effective area of corrosion attack. The results confirm that CPMB is an excellent corrosion inhibitor, which gives efficiency values as high as 90 % in the room temperature. The excellent 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 adsorbed 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 CPMB may be due to the presence of an amide moiety and two phenyl rings. The co-ordination bonding between the inhibitor molecule and

the mild steel surface probably occurs through both nitrogen and oxygen atoms.

**Table 1: Corrosion rate, inhibition efficiency and surface coverage of mild steel immersed in 1M H<sub>2</sub>SO<sub>4</sub> for various concentrations of CPMB obtained by weight loss method at 303 ± 1K.**

S. No.	Concentration of inhibitor (M)	Corrosion Rate (mpy)	Inhibition Efficiency (%)	Surface coverage (θ)
1.	Blank	2.5496	-	-
2.	0.0000001	1.9388	23.96	0.2396
3.	0.000001	1.4784	42.01	0.4201
4.	0.00001	0.8764	65.63	0.6563
5.	0.0001	0.6463	74.65	0.7465
6.	0.001	0.3895	84.72	0.8472
7.	0.01	0.2390	90.63	0.9063

### 3.2. Effect of Temperature:

The temperature increases the rate of all electrochemical processes and influences adsorption equilibrium and kinetics as well<sup>15</sup>. 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<sup>16</sup>.

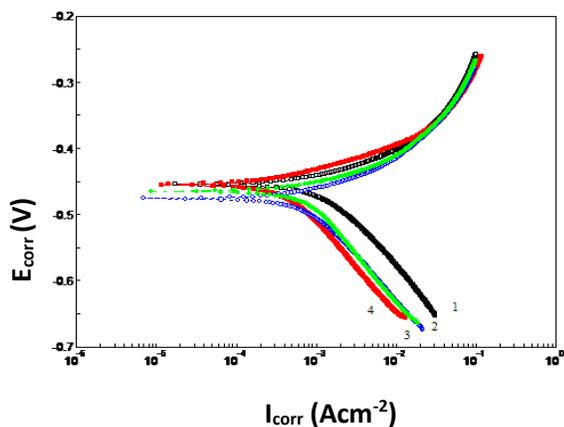
**Table II: Values of corrosion rate, inhibition efficiency and surface coverage for different temperatures in the presence of 0.01M concentration of CPMB in 1M H<sub>2</sub>SO<sub>4</sub>.**

S. No.	Temperature (K)	Corrosion Rate (mpy)	Inhibition Efficiency (%)	Surface coverage (θ)
1.	303	0.2390	90.63	0.9063
2.	308	0.2656	89.76	0.8976
3.	313	0.3098	88.49	0.8849
4.	318	0.3807	86.31	0.8631
5.	323	0.5754	80.36	0.8036
6.	328	0.9030	71.35	0.7135
7.	333	1.4164	65.72	0.6572

### 3.3 Potentiodynamic Polarization Studies:

The inhibition effects of CPMB on the corrosion of mild steel in 1 M sulphuric acid solutions, studied by potentiodynamic polarization technique at different concentrations are shown in Table 3. It can be seen from the polarization curves (Figure 2) 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 CPMB is a cathodic inhibitor.



**Figure 2** Potentiodynamic polarization curve for mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of various concentration of CPMB

- 1) 1M H<sub>2</sub>SO<sub>4</sub>
- 2) 1M H<sub>2</sub>SO<sub>4</sub> + 0.000001 M CPMB
- 3) 1M H<sub>2</sub>SO<sub>4</sub> + 0.0001 M CPMB
- 4) 1M H<sub>2</sub>SO<sub>4</sub> + 0.01 M CPMB

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 absence and in presence of inhibitor, respectively.

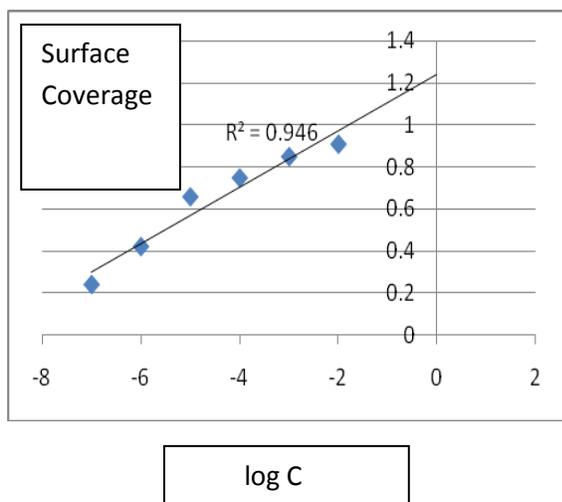
**Table III:** Potentiodynamic polarization parameters for mild steel without and with different concentrations of CPMB in 1M H<sub>2</sub>SO<sub>4</sub>

S. No.	Concentration of inhibitor (M)	$E_{CORR}$ (V)	Tafel slope		$I_{CORR}$ (A/cm <sup>2</sup> )	Inhibition Efficiency (%)
			$b_a$ (V/dec)	$b_c$ (V/dec)		
1.	Blank	-0.4559	0.1251	0.1311	$2.74 \times 10^{-3}$	-
2.	0.000001	-0.4562	0.1342	0.1542	$1.61 \times 10^{-3}$	41.24
3.	0.0001	-0.4612	0.1438	0.1671	$7.20 \times 10^{-4}$	73.72
4.	0.01	-0.4775	0.1586	0.1762	$2.71 \times 10^{-4}$	90.10

### 3.5. Temkin's 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 thermodynamic way using the appropriate adsorption isotherm.

The degree of surface coverage ( $\theta$ ) for different concentrations of CPMB in 1M H<sub>2</sub>SO<sub>4</sub> have evaluated from weight loss values. The data were graphically by fitting it to Temkin's isotherms. Figure 3 shows the plots of Surface coverage ( $\theta$ ) versus log C and the expected linear relationship is obtained for CPMB in 1M H<sub>2</sub>SO<sub>4</sub>. The strong correlation ( $R^2 = 0.946$  for CPMB) confirm the validity approach<sup>12</sup>.



**Figure 3 Temkin's adsorption isotherm plot for the adsorption of CPMB on mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solution**

It is well recognized that the first step in 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<sub>2</sub>O 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<sub>(sol)</sub>] and water molecules at the metal surface [H<sub>2</sub>O<sub>(ads)</sub>].



Where x is the size ratio, which is the number of water molecules replaced by one organic inhibitor. Basic information on the

interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm<sup>14</sup>.

### 3.6. Free Energy of Adsorption:

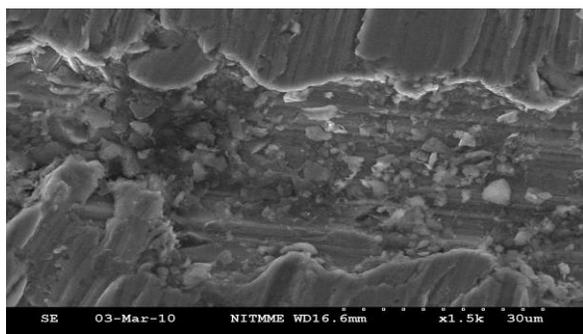
The negative values of  $\Delta G^{\circ}_{\text{ads}}$  ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface<sup>10</sup>. It is usually accepted that the value of  $\Delta G^{\circ}_{\text{ads}}$  around -20 kJmol<sup>-1</sup> or lower indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution while those around -40 kJmol<sup>-1</sup> or higher involve charge sharing or charge transfer between the metal surface and organic molecules. In the present study, the  $\Delta G^{\circ}_{\text{ads}}$  values obtained for the CPMB on mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> solution are ranging between -25 and -27 kJmol<sup>-1</sup>, which are higher than -20 kJmol<sup>-1</sup> and lower than -40 kJmol<sup>-1</sup> (Table 4); 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 predominant mode of adsorption.

**Table IV: Free energy for adsorption of 0.01 M concentration of CPMB in 1M H<sub>2</sub>SO<sub>4</sub> on mild steel at different temperatures**

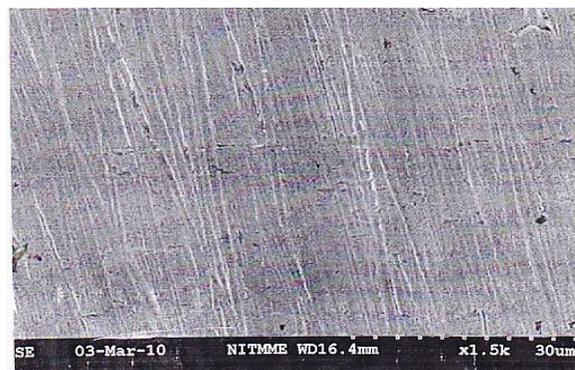
S. No.	Temperature (K)	$\Delta G^{\circ}_{ads}$ (kJ mol <sup>-1</sup> )
1.	303	-27.44
2.	308	-27.64
3.	313	-27.74
4.	318	-27.66
5.	323	-26.94
6.	328	-25.99
7.	333	-25.67

### 3.7 SEM analysis :

SEM photograph of the metal sample in the presence and absence of inhibitor are shown in Figure 4 and 5. The inhibited metal surface is smoother than the uninhibited surface indicating a protective layer of adsorbed inhibitor preventing acid attack.



**Figure 4 SEM image of surface of mild steel after immersion for 2 hours in 1 M H<sub>2</sub>SO<sub>4</sub>**



**Figure 5 SEM image of surface of mild steel after immersion for 2h in 1M H<sub>2</sub>SO<sub>4</sub> in presence of 0.01M CPMB**

### 4. Conclusions:

Results obtained from the experimental data show that CPMB acts as inhibitor for the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub>.

- ❖ Inhibition efficiency increases with increase in the concentration of the studied inhibitor but decreases with rise in temperature.

- ❖ Potentiodynamic polarization measurements show that the CPMB acts as cathodic type inhibitor.

- ❖ The adsorption of CPMB on mild steel surface from 1 M H<sub>2</sub>SO<sub>4</sub> obeys the Temkin's adsorption isotherm.

- ❖ The adsorption of CPMB onto mild steel surface was a spontaneous process. Further the adsorption of CPMB on mild steel surface is complex in nature and predominantly chemisorption type.

❖ The formation of protective layer against the attack is confirmed by SEM.

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