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## N-((4-Chlorophenyl)(morpholin-4-yl)methyl)acetamide as corrosion inhibitor for mild steel in hydrochloric acid medium

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#### ABSTRACT

The inhibiting effect and adsorption behavior of N-[(4-chlorophenyl)(morpholin-4-yl)methyl]acetamide (CPMA) on mild steel in hydrochloric acid solution were studied by weight loss measurements, effect of temperature studies, potentiodynamic polarization and scanning electron microscopic techniques. The inhibitor showed greater than 89 % 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 CPMA at the mild steel/hydrochloric 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 CPMA 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, Scanning electron microscopy and Hydrochloric acid

#### INTRODUCTION

Mild steel finds a variety of applications industrially, in mechanical and structural purposes, like bridge work, building, boiler plates, steam engine parts and automobiles. It finds various uses in most of the chemical industries due to its low cost and easy availability for fabrication of various reaction vessels, tanks, pipes, etc. Since it suffers from severe corrosion in aggressive environment, it has to be protected. Acids like HCl and  $H_2SO_4$  have been used for drilling operations, pickling baths and in descaling processes [1-3].

In such aggressive medium, the use of corrosion inhibitors is one of the most common, effective and economic methods to protect metals in acid medium [4]. 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 [5-7]. Under certain conditions, the electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency to the metal. Some Mannich bases have been reported as efficient corrosion inhibitors [8-10] 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 [11-12], is devoted to investigation of N-[(4-chlorophenyl)(morpholin-4-yl)methyl]acetamide (CPMA) as inhibitor for mild steel corrosion in 1.0 M HCl solutions. Thus, the present study aims at determining the effectiveness of CPMA as the corrosion inhibitor by weight loss method as well as by electrochemical studies.

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#### MATERIALS AND METHODS

#### 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  $4 \times 1 \times 0.025$  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 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]acetamide (CPMA) was synthesized, and purified by recrystalization 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.



The acid solution (1M HCl) was prepared by dilution of an analytical grade HCl with double distilled water. All tests were conducted at different temperatures in magnetically stirred solutions.

#### Weight loss measurements:

Weight loss measurements were done according to the method described previously [13]. Weight loss measurements were performed at  $303\pm1$  K for 2h by immersing the mild steel cupons 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:

$$\theta = \frac{W_o - W_1}{W_o} \tag{1}$$

$$I.E.(\%) = \frac{W_o - W_1}{W_o} X100$$
<sup>(2)</sup>

Where, W1 and Wo are the weight loss value in presence and absence of inhibitors, respectively.

#### **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 HCl with and without the addition of the inhibitor at their best inhibiting concentrations. Percentage inhibitions of the inhibitor at various temperatures were calculated.

#### **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 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 mV s<sup>-1</sup>.

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#### Standard free energy of adsorption:

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

#### 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.

#### **RESULTS AND DISCUSSION**

#### Weight loss measurements:

The effect of concentration of CPMA 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 CPMA 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 CPMA is an excellent corrosion inhibitor, which gives efficiency values as high as 89% 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 CPMA may be due to the presence of an amide moiety and one phenyl ring. 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 HCl for various concentrations of CPMA obtained by weight loss method at 303 ± 1K

S No	Concentration of inhibitor	Corrosion Rate	Inhibition Efficiency	Surface coverage
5.INO.	(M)	(mpy)	(%)	(θ)
1	Blank	0.8676	-	-
2	0.0000001	0.4603	46.94	0.4694
3	0.000001	0.3895	55.10	0.5510
4	0.000005	0.3453	60.20	0.6020
5	0.00001	0.3098	64.29	0.6429
6	0.00005	0.2659	69.39	0.6939
7	0.0001	0.2213	74.49	0.7449
8	0.0005	0.1859	78.57	0.7857
9	0.001	0.1505	82.65	0.8265
10	0.005	0.1151	86.73	0.8673
11	0.01	0.0885	89.80	0.8980

# Table 2 Values of corrosion rate, inhibition efficiencies and surface coverage for different temperatures in the presence of 0.01M concentration of CPMA in 1M HCl

S.No.	Temperature	Corrosion Rate	Inhibition Efficiency	Surface coverage
	(K)	(mpy)	(%)	(θ)
1	303	0.0885	89.80	0.8980
2	308	0.0974	89.42	0.8942
3	313	0.1062	89.08	0.8908
4	318	0.1416	87.02	0.8702
5	323	0.1948	84.29	0.8429
6	328	0.3453	74.34	0.7434
7	333	0.4781	66.67	0.6667

#### **Effect of Temperature:**

The temperature increases the rate of all electrochemical processes and influences adsorption equilibrium and kinetics as well [15]. 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.

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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 [16].

#### **Potentiodynamic Polarization Studies:**

The inhibition effects of CPMA on the corrosion of mild steel in 1 M hydrochloric acid solutions, studied by potentiodynamic polarization technique at different concentrations are shown in Table 3. It can 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 CPMA is a cathodic inhibitor.



Figure 2 Potentiodynamic polarization curve for mild steel in 1 M HCl in the absence and presence of various concentration of CPMA

1) 1M HCl	2) 1M HCl + 0.000001 M CPMA
3) 1M HCl+0.0001 M CPMA	4) 1M HCl + 0.01 M CPMA

The inhibition efficiency was evaluated from the measured I<sub>corr</sub> values using the relationship.

Inhibition efficiency =  $i^{o}_{corr} - i^{i}_{corr} / i^{o}_{corr} \times 100$ 

Where, i<sup>o</sup><sub>corr</sub> and i<sup>i</sup><sub>corr</sub> are values of corrosion current density in absence and in presence of inhibitor, respectively.

S.No.	Concentration of inhibitor (M)	E <sub>corr</sub> (V)	Tafel b <sub>a</sub> (V/dec)	slope b <sub>c</sub> (V/dec)	I <sub>corr</sub> (A/cm <sup>2</sup> )	Inhibition Efficiency (%)
1	Blank	-0.4759	0.0451	0.1204	5.10 x10 <sup>-4</sup>	-
2	0.000001	-0.4702	0.0483	0.1312	2.39 x10 <sup>-4</sup>	53.14
3	0.0001	-0.4814	0.0567	0.1394	1.33 x10 <sup>-4</sup>	73.92
4	0.01	-0.4878	0.0642	0.1574	5.40 x10 <sup>-5</sup>	89.41

Table 3 Potentiodynamic polarization parameters for mild steel without and with different concentrations of MCPA in 1M HCl

#### **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 CPMA in 1M HCl 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 CPMA in 1M HCl. The strong correlation ( $R^2 = 0.9712$  for CPMA) confirm the validity approach [12].



Figure 3 Temkin's Adsorption Isotherm Plot for the adsorption of CPMA on mild steel in 1 M HCl 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  $H_2O$  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)] [5].

 $Org_{(sol)} + x H_2O_{(ads)} \leftrightarrow Org_{(ads)} + x H_2O_{(sol)}$ 

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 [11].

#### **Free Energy of Adsorption:**

The negative values of  $\Delta G^{\circ}_{ads}$  ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface [17]. It is usually accepted that the value of  $\Delta G^{\circ}_{ads}$  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 [5]. In the present study, the  $\Delta G^{\circ}_{ads}$  values obtained for the CPMA on mild steel in 1 M HCl 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 4 Free energy for adsorption of 0.01 M concentration of CPMA in 1 M HCl on mild steel at different temperatures

S. No.	Temperature (K)	$\Delta G^{o}_{ads}$ (kJ mol <sup>-1</sup> )
1	303	-27.05
2	308	-27.28
3	313	-27.35
4	318	-27.39
5	323	-26.59
6	328	-25.46.
7	333	-25.13

#### 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 HCl



Figure 5 SEM image of surface of mild steel after immersion for 2 h in 1M HCl in presence of 0.01M CPMA

#### CONCLUSION

1. Results obtained from the experimental data show that CPMA 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 measurements show that the CPMA acts as cathodic type inhibitor.

4. The adsorption of CPMA on mild steel surface from 1 M HCl obeys the Temkin adsorption isotherm.

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

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

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