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Inhibitive Effect of N’-(7-chloroquinolin-4-yl)-N,N-diethyl-pentane-1,4-diamine Towards Mild Steel / Sulphuric Acid Solution Interface

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Corrosion inhibition of mild steel by N’-(7-chloroquinolin-4-yl)-N,N-diethyl-pentane-1,4-diamine (CDPD) towards mild steel / sulphuric acid solution interface using weight loss, electrochemical impedance spectroscopy (EIS) and polarization studies. The inhibitor showed 98.9 % inhibition efficiency at 4×10^{-4} M CDPD concentration. Polarization studies showed that CDPD is a mixed type inhibitor. Adsorption of CDPD molecules follows Langmuir adsorption isotherm on mild steel surface in sulphuric acid medium. SEM studies supported the data evaluated by different techniques by showing the less rough surface in presence of inhibitor than the in absence of inhibitor. Contact angle experiments shows the hydrophobic nature of mild steel surface with the CDPD molecules,

Keywords: Corrosion inhibition; Weight loss; EIS; Polarization; Langmuir adsorption isotherm, Contact angle measurements

1. INTRODUCTION

Organic compounds are widely used to protect metals against corrosion in acidic media [1-4]. These acidic solutions were used in various industrial applications e.g. acid pickling, cleaning of metal articles etc. Sulphuric acid is an important mineral acid as industrial point of view. This leads the researchers to develop the corrosion inhibitors for the sulphuric acid medium [5-9]. Most of the inhibitors functional in industries are the organic compounds which contain hetero atoms such as oxygen, sulphur, nitrogen etc. These hetero atoms play an important role in inhibition due to the availability of free electron pairs. Compounds that contain π- bonds generally exhibit good inhibitive effects via supplying the electrons through π-orbital. When both the effects combine, enhances the inhibition significantly by increasing the adsorption behavior [10-12]. Most of the commercially available inhibitors are toxic in nature; therefore their replacement by environmentally benign inhibitor is required. Recently some of the non-toxic inhibitors are reported in literature [8-16].

The inhibition effect of CDPD on the corrosion of mild steel in 1M sulphuric acid solution was studied using weight loss, potentiodynamic polarization and electrochemical methods. These studies also included the contact angle measurements by static sessile drop method and the surface characterization done by SEM studies.

N'-(7-chloroquinolin-4-yl)-N,N-diethyl-pentane-1,4-diamine (CDPD) is an antimalarial drug. It is marketed as various trade names and commonly known as chloroquine. The structure of CDPD is shown in figure 1.

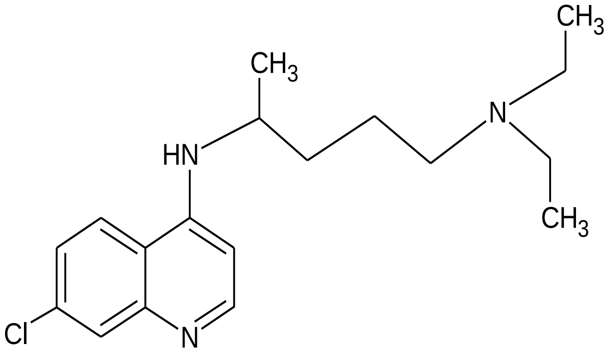


Figure1. Structure of N'-(7-chloroquinolin-4-yl)-N,N-diethyl-pentane-1,4-diamine (CDPD)

2. EXPERIMENTAL

2.1. Inhibitor:

A stock solution of CDPD was made in 10:1 water ethanol mixture to ensure solubility. This stock solution was used for all experimental purposes.

2.2. Corrosion Study

The mild steel strips having composition (wt %): C 0.14, Mn 0.035, Si 0.17, S 0.025, P 0.03 and balance Fe were used for weight loss as well as electrochemical studies. The test solution of sulphuric acid (AR grade) is used for all the studies.

2.2.1. Weight loss Studies

Weight loss experiments were conducted on the mild steel strips having dimension 5.0 ×2.0 ×0.025 cm^3. The study was carried out at 308°K temperatures for 3h time duration in 1M H_2SO_4 solution in Stoppard conical flasks to know the optimum concentration of CDPD used in the study. The inhibition efficiency (%) and surface coverage (θ) was determined by following equation:

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

$$\theta = \frac{W_o - W_i}{W_o}$$

where, W_o and W_i is the weight loss value in absence and in presence of inhibitor respectively.

The weight loss study was also conducted at temperature range, different immersion time and different concentration of H_2SO_4 solution at optimum concentration of PDA.

2.2.2. Electrochemical Studies

The electrochemical studies were carried out in a three electrode cell assembly [17, 18] at 35°C. The working electrode was a mild steel of above composition of 1 cm^2 area and the rest being covered by commercially available lacquer. A large rectangular platinum foil was used as counter electrode and saturated calomel electrode as reference electrode. The working electrode was polished with different grades of emery papers (600-1200), washed with water and degreased with acetone. The polarization and impedance studies were carried out using Gamry potentiostat / galvanostat (model G-300) with Gamry EIS software, Gamry Instruments Inc., USA. All the experiments were carried out without purging nitrogen. All the experiments were carried out after stabilizing the OCP.

The tafel polarization studies were carried out from cathodic potential of -0.25V *vs.* SCE to an anodic potential of + 0.25V *vs.* SCE with respect to the open circuit potential at a sweep rate of 0.5 mVs^{-1} without de-aerated to study the effect of inhibitor on mild steel corrosion. The linear tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}). The corrosion inhibition efficiency (% IE) was evaluated from the measured I_{corr} values using the relationship:

$$I.E.(\%) = \frac{I^{o}_{corr} - I^{'}_{corr}}{I^{o}_{corr}} \times 100$$

where, I^{o}_{corr} and I^{i}_{corr} are the corrosion current densities in absence and in presence of various concentrations of the inhibitor.

Linear polarization resistance studies were carried out form cathodic potential of -0.02 V *vs* SCE to an anodic potential of +0.02 V *vs* SCE with respect to open circuit potential at a sweep rate 0.125 mVs^{-1} to study the effect of inhibitor on polarization resistance on mild steel. The inhibition efficiency was measured by following relationship:

$$IE\% = \frac{(1/R_{P_o}) - (1/R_{P_i})}{(1/R_{P_o})} \times 100$$

The impedance studies were carried out using ac signals of 10 mV amplitude for the frequency range from 100 kHz to 0.01 Hz. All the studies were performed after immersion of 30 minutes. The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation

$$IE\% = \frac{(1/R_{t0}) - (1/R_{ti})}{(1/R_{t0})} \times 100$$

where, R_{ct}^{o} and $R_{ct}^{'}$ are the charge transfer resistance in absence and in presence of inhibitor.

2.2.3. Contact angle measurements (Static sessile drop method)

Mild steel sample were carefully cleaned to avoid the surface contaminations, which influence the contact angle measurements through surface pining of the liquid drop and or contamination of the liquid when the latter is put in to contact with the sample surface. Aquous acid solutions with different concentrations of the CPDP were prepared and the samples were then immersed into these solutions for 3 h. Upon removal from the solutions the sample were dried by gentle nitrogen flow. Contact angle measurements were performed using the static drop method with the Reme-Hart goniometer (Netcong, USA).

2.3.4. Scanning electron microscopy

The morphology of the corrosion products formed on the surface of the mild steel in 0.5 M H_2SO_4 solution in the absence and presence of 4×10^{-4} M of CDPD were examined by SEM using a Traktor TN-2000 energy dispersive spectrometer and a Joel-Jem-1200 EX II electron microscope.

3. RESULTS AND DISCUSSIONS

3.1. Weight loss method

3.1.1. Effect of inhibitor concentration

Weight loss measurements were carried out for the different concentration of CDPD. The weight loss, inhibition efficiency and corrosion rate were reported in table 1. The trend of the inhibition efficiency with respect to CDPD concentration is plotted in figure 2(A). Figure 2(A) shows the tendency of increment of inhibitor efficiency with the increase in CDPD concentration in 1 M sulphuric acid solution. It is clearly visible from the Table 1 that the corrosion rate decreases and inhibition efficiency increases with increase in CDPD concentration.

Table 1. Corrosion parameters for mild steel in aqueous solution of 1 M suphuric acid in presence and absence of different concentrations of CDPD from weight loss measurements at 308 K for 3 h

Inhibitor Concentration (M)	Weight loss (mg cm^{-2})	Inhibition efficiency (%)	Corrosion rate (mm/y)
Blank	46.0	-	165.0
0.5×10-4 M	7.1	84.6	25.5
1×10-4 M	4.9	89.3	17.6
2×10-4 M	2.8	93.9	10.0
3×10-4 M	1.5	96.7	5.4
4×10-4 M	0.5	98.9	1.8

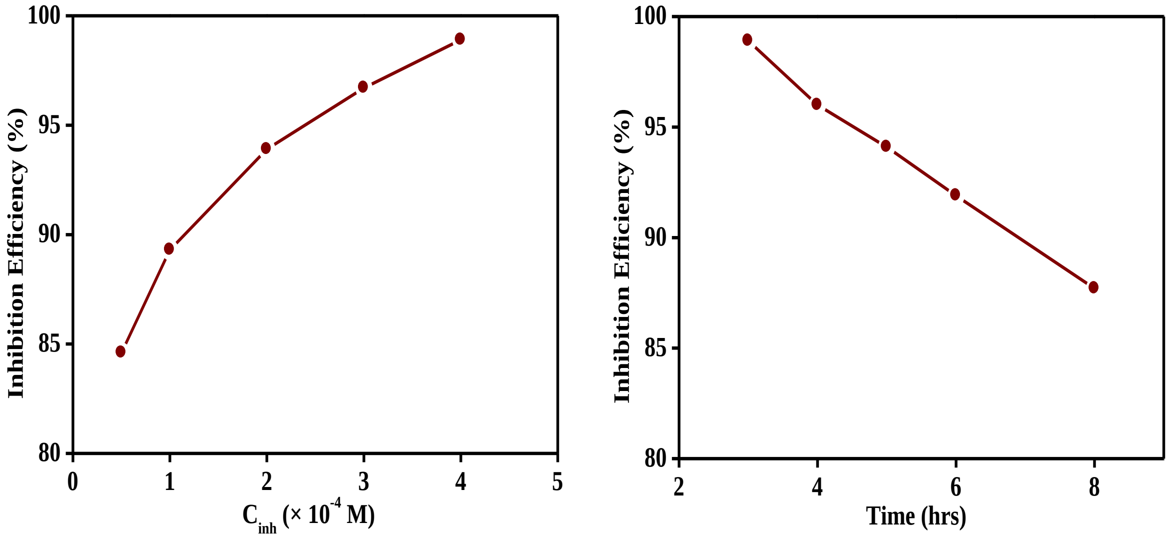
3.1.2. Effect of Immersion time

Effect of immersion time against inhibition efficiency graph was plotted in figure 2(B). It is evident from the figure that the increase in the immersion time inhibition efficiency decreases slowly. This slow decrease in inhibition efficiency suggesting that the compound is firmly adsorbed on mild steel surface and desorption rate is slow.

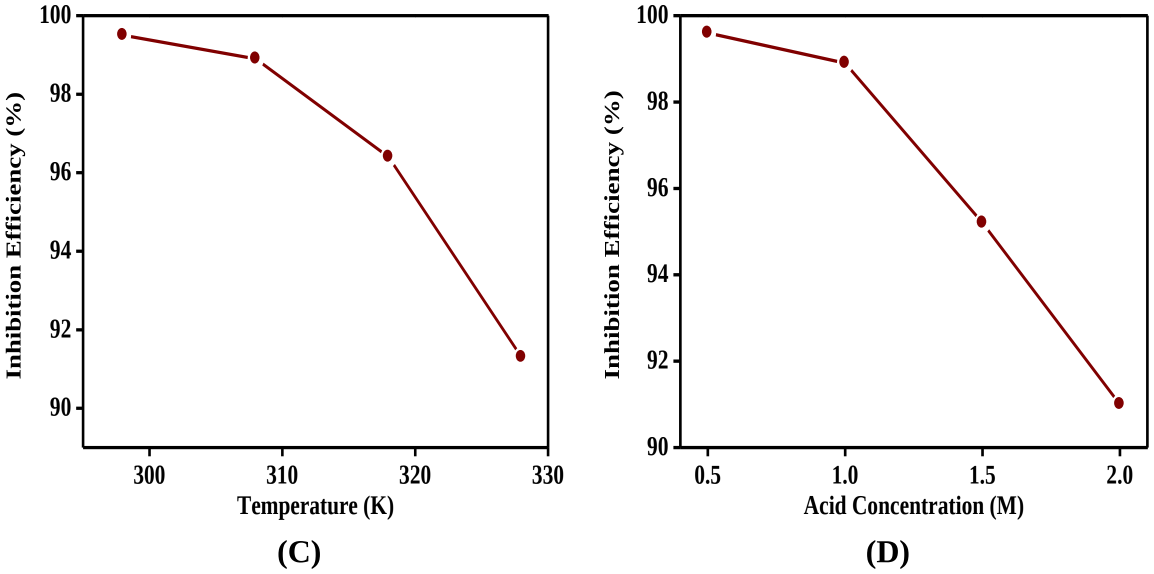
3.1.3. Effect of solution temperature

Effect of temperature was studied at optimum concentration of the condensation product used in corrosion inhibition at temperature range of 298-328K. Effect of temperature on inhibition efficiency shown in figure 2(C). It is clear from figure that temperature is decreasing with increase in solution temperature. This change in inhibition efficiency with temperature may attribute to desorption of the inhibitor molecule from mild steel surface with increase in temperature.

3.1.4. Effect of acid concentration



(A) **(B)**



(C) (D)

Figure 2. Variation in inhibition efficiency in 1 M sulphuric acid on mild steel of surface area 20 cm^2 with (A) different concentration of CDPD (B) different immersion time (C) different temperature and (D) different acid concentration range; using weight loss data.

Effect of acid concentration with inhibition efficiency was reported in figure 2 (D). The inhibition efficiency decreases with increase in the acid concentration. This reveals that the inhibitor is good for the lower concentration of the sulphuric acid solution.

3.1.5. Adsorption isotherm

Adsorption isotherm study describes the adsorptive behaviour of organic inhibitors to know the adsorption mechanism. The most usually used adsorption isotherms are Langmuir, Temkin, Frumkin and other various isotherms. The surface coverage (θ) values were calculated using weight loss data.

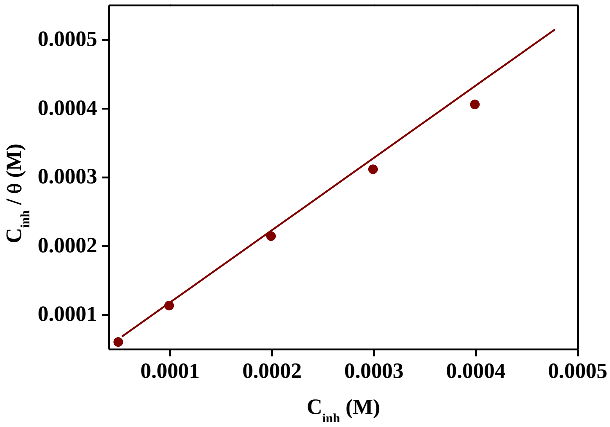


Figure 3. Langmuir's Adsorption isotherm plot for the adsorption of CDPD in 1 M sulphuric acid on the surface of mild steel.

Langmuir adsorption isotherm were tested and found most appropriate isotherm to explain the experimental data. Langmuir adsorption isotherm is represented by following equations:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

where, K_{ads} is the adsorption equilibrium constant and C_{inh} is the concentration of inhibitor used in the corrosive medium. A straight line was obtained by plotting the graph of C_{inh} vs C_{inh}/θ with the R value almost unity (Figure 3). The slope is reported almost unity suggesting that the Langmuir adsorption isotherm model provides the best description of the adsorption behaviour (19, 20).

3.2. Tafel polarization study:

The potentiodynamic polarization measurements were carried out to study the kinetics of the cathodic and anodic reactions. Figure 4 shows the results of the effect of CDPD inhibitor on the cathodic as well as anodic polarization curves of mild steel in 1M H_2SO_4 respectively. It is observed from the figure that both cathodic and anodic reactions were suppressed with the addition of the CDPD. This suggests that inhibitor reduced the anodic dissolution reactions as well as retarded the hydrogen evolution reactions on the cathodic sites.

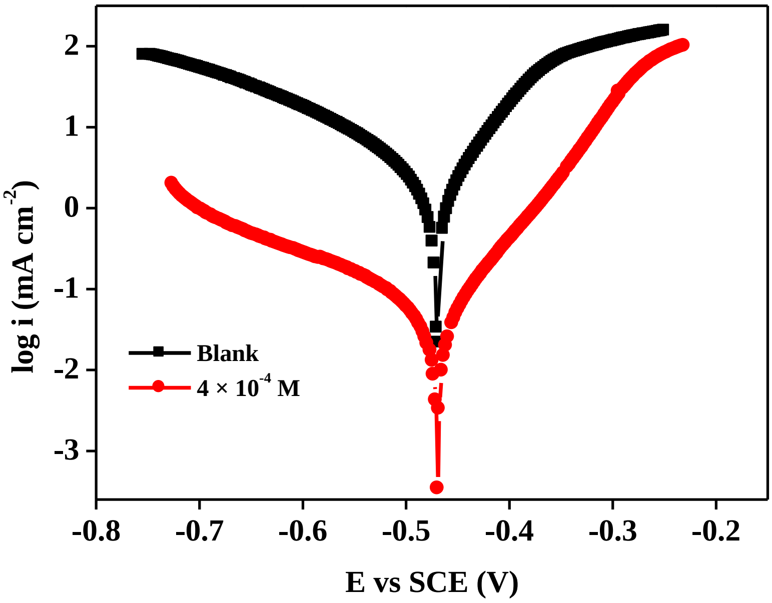


Figure 4. Tafel polarization curve in absence and presence of CDPD on mild steel surface in 1M sulphuric acid

Electrochemical corrosion kinetic parameters namely corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained from the extrapolation of the polarization curves are listed in Table 2. The corrosion current density (I_{corr}) decreased by the increase in the adsorption of the inhibitor with increasing inhibitor concentration. The inhibition efficiency increases with increase in the inhibitor concentration was calculated by the I_{corr} values and listed in Table 2. According to Ferreira et.al [21] and Li et. al. [22], if the displacement in corrosion potential is more than 85 mV with respect to the corrosion potential of blank solution, the inhibitor can be consider as a cathodic or anodic type. In present study, displacement was 01 mV with respect to the corrosion potential of the uninhibited sample which indicates that the studied inhibitor is a mixed type of inhibitor. The results obtained from Tafel polarization showed good agreement with the results obtained from the weight loss data.

3.3. Linear polarization measurements:

Polarization resistance values were determined from the slope of the potential current lines

$$R_P = A\frac{dE}{di}$$

where, A is the surface area of the electrode, dE is change in potential, and di is change in current. The inhibition efficiencies and polarization resistance parameters are reported in table 2. The results obtained from the tafel polarization studies were in good agreement with results obtained from linear polarization studies.

Table 2. Potentiodynamic polarization parameters for mild steel without and with CPDP in 1 M sulphuric acid

Inhibitor Conc.	Tafel data					Linear Polarization data	
	$-E_{corr}$ (mV vs SCE)	b_a (mV dec^{-1})	b_c (mV dec^{-1})	I_{corr} (μA cm^{-2})	IE (%)	R_p (Ω cm^2)	IE (%)
Blank	470	77	154	2240	-	11.1	-
4×10-4 M	469	71	169	57	97.5	409.5	97.3

3.4. Electrochemical impedance spectroscopy:

Corrosion behaviour of mild steel in 1.0 M sulphuric acid solution was investigated with and without CDPD by electrochemical impedance spectroscopic measurements. Figure 5 shows the impedance spectra of mild steel corrosion in the form of Nyquist plots. A single semicircle has been clearly shown at high frequency which can be ascribed to charge transfer of the corrosion process and the diameter of the semicircle was increased with increase in the increasing inhibitor concentration. Figure 5 clearly shown that the impedance spectra is depressed semicircle with centre under real axis and resembles as depressed capacitive loops. Such phenomenon often corresponds to surface heterogeneity which may be the result of surface roughness, dislocations, distribution of the active sites or adsorption of the inhibitor molecules [23-25]. An equivalent circuit was introduced to explain the EIS data shown in figure 6. This circuit is generally used to describe the iron / acid interface model [26]. In this circuit R_s is solution resistance, R_t is charge transfer resistance and CPE is a constant phase element. The impedance function of the CPE is as follows:

$$Z_{CPE} = Y^{-1}(j\omega)^{-n}$$

where, Y is the magnitude of the CPE, ω is the angular frequency and the deviation parameter n is a valuable criterion of the nature of the metal surface and reflects microscopic fluctuations of the surface. For n=0 Z_{CPE} represents a resistance with $R=Y^{-1}$; n=-1 an inductance with $L=Y^{-1}$ and n=1 an ideal capacitor with $C=Y$ [27]. In iron/acid interface systems, ideal capacitor behaviour is not observed due to the roughness or uneven current distributions on the electrode surface which results in frequency dispersion [24, 28, 29].

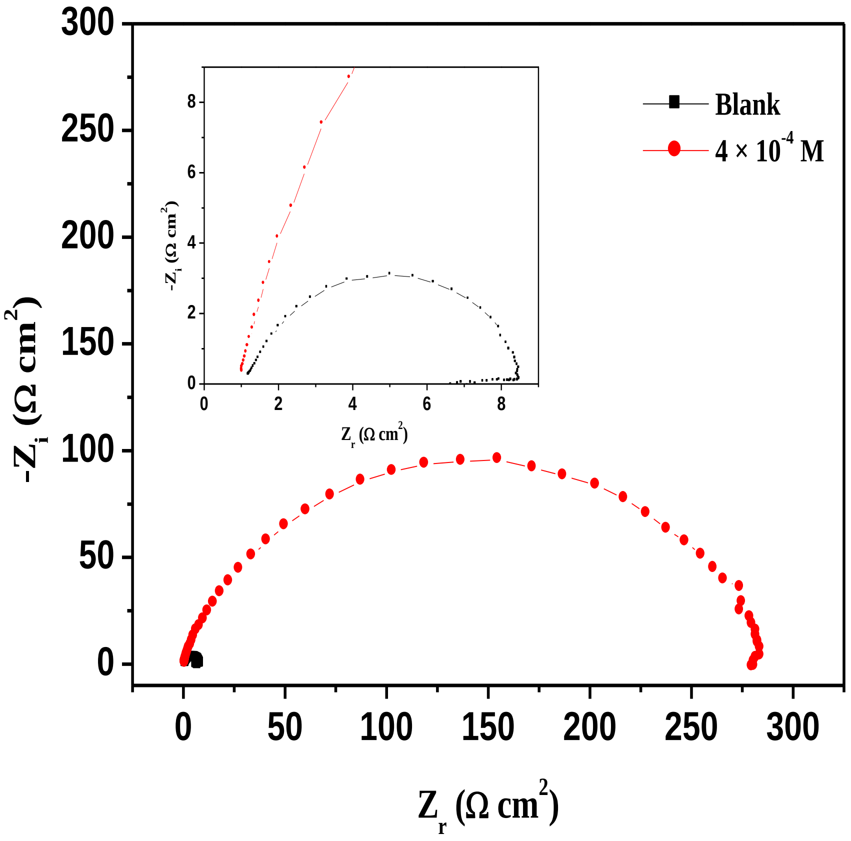


Figure 5. Nyquist plot of mild steel in the absence and presence of CDPD in 1M sulphuric acid solution.

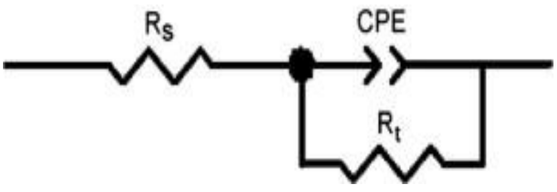


Figure 6. The electrochemical equivalent circuit used to fit the impedance spectra

The electrochemical parameters (R_s, R_t Y_o and n) obtained from the fitting the recorded data using the equivalent circuit of Figure 6 are listed in Table 3. C_{dl} values listed in Table 3 were derived from CPE parameters calculated by use of following equation [30]:

$$C_{dl} = (Y_{o} . R_t^{1-n})^{1/n}$$

From the Table 3 it is evident that the R_t values increases with the increase in CDPD concentration. The increase in R_t value is attributed to the formation of protective film on metal/solution interface. The increase in the values of n of the inhibited samples in comparison with uninhibited samples can be explained by decrease of the surface heterogeneity, due to the adsorption of the inhibitor on the most active adsorption sites [31]. The values of double layer capacitance (C_{dl}) decreased with increasing CDPD concentration. The thickness of the protective layer (d) is related to C_{dl} according to the following equation [32]:

$$C_{dl} = \frac{\varepsilon \varepsilon_o}{d}$$

where, ε is the dielectric constant of the protective layer and ε_o is the permittivity of the free space.

Table 3. Electrochemical impedance parameters values of without and with CDPD for mild steel corrosion in 1M sulphuric acid solution

Inhibitor concentration (M)	R_s (Ω cm^2)	R_p (Ω cm^2)	Y_o (μF cm^{-2})	n	C_{dl} (μF cm^{-2})	IE (%)
Blank	1.13	8.2	121.5	0.868	58	-
4×10-4 M	1.09	283.1	73.3	0.822	31	97.1

It is obvious from the results that the CDPD inhibited the corrosion of mild steel in 1M H_2SO_4 solution at all the concentrations used in the study and IE % was increase continuously with increasing in the inhibitor concentration (Table 3). The inhibition efficiencies calculated from EIS show the same trend as those obtained from weight loss and tafel polarization data.

3.5. Contact angle of acid solution on mild steel:

Figure 7 displays the contact angle as a function of CDPD concentration for acid solutions on mild steel. For acid solution without inhibitor, contact angle is lowest (10.5) thus metal showed most hydrophilic behaviour to the solution. Whereas contact angle increases regularly with increase in CDPD and therefore showing the increasing hydrophobic behaviour to the inhibited solutions.

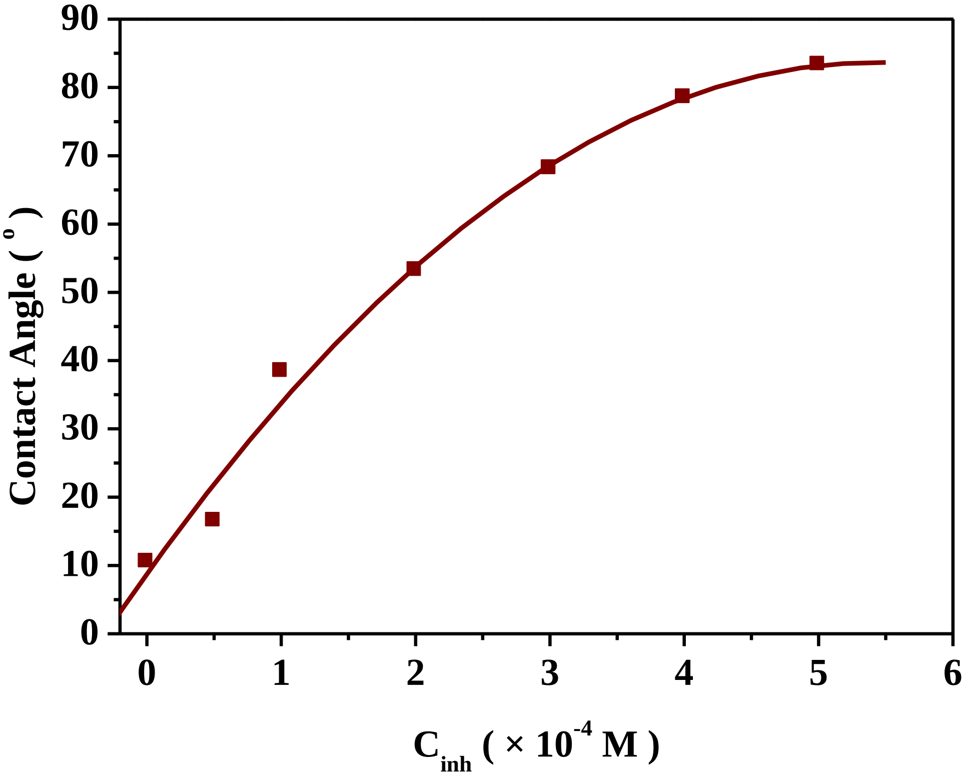
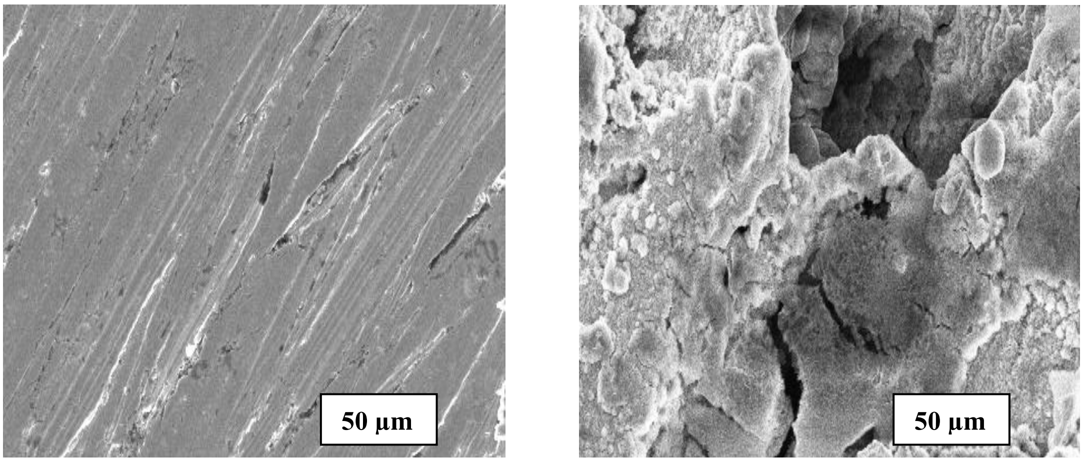


Figure 7. Variation of contact angle of mild steel surface to the acid solution with inhibitor concentration

3.6. Scanning Electron Microscopy:

The SEM images of mild steel surfaces are given figure 8(a-c). Figure 8a presented bare mild steel surface whereas figure 8b presented mild steel surface in 1 M H_2SO_4 solution. Figure 8c shows the mild steel surface in 1M sulphuric acid in presence of 4×10^{-4}M CDPD. It is clear from the figures that the surface of mild steel with inhibitor is more intact and smooth than the without inhibitor system.



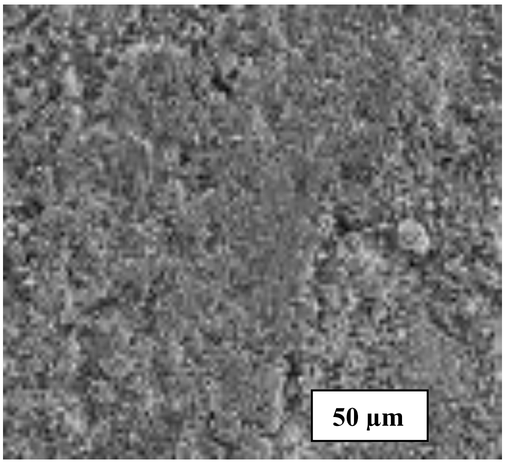


Figure 8. Scanning electron micrographs of mild steel surface of (a) polished mild steel (b) mild steel in 1M H_2SO_4 (c) inhibited mild steel in 1M H_2SO_4 + 4×10^{-4}M CDPD.

4. CONCLUSION

- CDPD was found to be a good inhibitor for mild steel corrosion in sulphuric acid medium.
- Potentiodynamic polarization study revealed that CDPD is a mixed-type inhibitor.
- The inhibition efficiency of CDPD increases with an increase in concentration of inhibitor.
- CDPD was found to be good corrosion inhibitor for mild steel in sulphuric acid medium.
- Contact angle of acid solution increased with inhibitor concentration and thereby confirming the hydrophobic nature of metal to the acid solution containing inhibitor.
- SEM surface characterization also supported that the compound is very good corrosion inhibitor.

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