Int. J. Electrochem. Sci., 7 **(2012)** 12134 - 12145

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Condensation Product of Thiosemicarbazide and Phenyl Isothiocynate on Corrosion of Mild Steel in Sulphuric Acid Medium

Sudhish Kumar Shukla[*], *Eno E. Ebenso*

Department of Chemistry, School of Mathematical and Physical Sciences, North-West University
(Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[*]E-mail: sudhish.shukla@gmail.com

Received: 5 October 2012 / *Accepted:* 17 November 2012 / *Published:* 1 December 2012

Condensation reaction of thiosemicarbazide and phenyl isothiocynate resulting the N-phenylhydrazine-1,2-dicarbothioamide (PDA). Corrosion inhibition properties of this condensation product (PDA) for mild steel in sulphuric acid were analyzed by electrochemical impedance spectroscopy, potentiodynamic polarization and weight loss techniques. Increase in the inhibitor concentration showed positive effects on the inhibition efficiency. Potentiodynamic polarization show that PDA acts as mixed type of inhibitor. The adsorption of mild steel in sulphuric acid solutions obeys Langmuir's adsorption isotherm model. The results obtained from the different methods used are in good agreement. AFM and SEM studies also supported the results obtained.

Keywords: Condensation product; Corrosion inhibition; Weight loss; EIS; Polarization; Langmuir adsorption isotherm

1. INTRODUCTION

Serious corrosion damage arises in the industries due to wide use of different acids in various processes on metal surfaces [1-7]. This leads researchers to develop the corrosion inhibitors in acidic medium [8-12]. Most of the inhibitors 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. A combination of both effects enhances the inhibition significantly by increasing the adsorption behavior [13-14].

In present study, we use the condensation product of thiosemicarbazide and phenyl isothiocynate to investigate the inhibitive tendency of the mild steel corrosion in 1M H_2SO_4 using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. Surface characterizations were also done to support the results.

2. EXPERIMENTAL

2.1. Inhibitor

n-Phenylhydrazine-1,2-dithiocarboamide (PDA) was synthesized by method reported in literature [15,16]. The structural formula of the PDA is given in Figure 1.

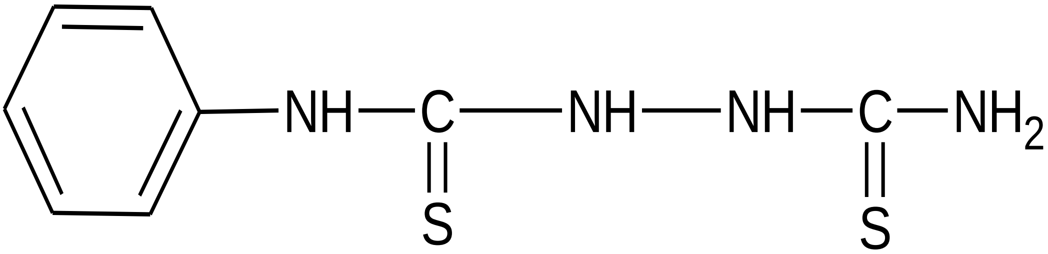


Figure 1. Structure of PDA

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.

2.3. 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 35°C temperatures for 3h time duration in 1M H_2SO_4 solution in Stoppard conical flasks to know the optimum concentration of PDA used in the study. The inhibition efficiency (%) and surface coverage (θ) was determined by following equation:

$$I.E.(\%) = \frac{W_o - W_i}{W_o} \times 100 \qquad (1)$$

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

where, W_o and W_i are the weight loss values 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.

2.4. Electrochemical Studies

The electrochemical studies were carried out in a three electrode cell assembly [17] 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:

$$I.E.(\%) = \frac{I^{o}_{corr} - I^{'}_{corr}}{I^{o}_{corr}} \times 100 \qquad (2)$$

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

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

$$IE\% = \frac{(1/\boldsymbol{R}_{t0}) - (1/\boldsymbol{R}_{ti})}{(1/\boldsymbol{R}_{t0})} \times 100 \qquad (3)$$

where, R^{o}_{ct} and $R^{'}_{ct}$ are the charge transfer resistance in absence and in presence of inhibitor. The interfacial double layer capacitance (C_{dl}) values have been estimated from the impedance value using bode plot by the formula

$$|Z| = \frac{1}{2\pi f_{\max} C_{dl}} \qquad (4)$$

2.5. Atomic force microscopy

The surface morphology of mild steel specimen was investigated by using atomic force microscope (AFM). Atomic force microscopy was performed using a NT-MDT multimode AFM, Russia, controlled by Solver scanning probe microscope controller. Semi-contact mode was used with the tip mounted on 100 µm long, single beam cantilever with resonant frequency in the range of 240000-255000 Hz, and the corresponding spring constant of 11.5 N m^{-1} with NOVA programme used for image rendering. The mild steel strips of 1.0 × 1.0 × 0.025 cm sizes were prepared as described in section 2.2. After immersion in 1 M H_2SO_4 with and without addition of 100 ppm of PDA at 308 K for 3 h, the specimens were cleaned with distilled water, dried and then used for AFM.

2.6. Scanning electron microscopy

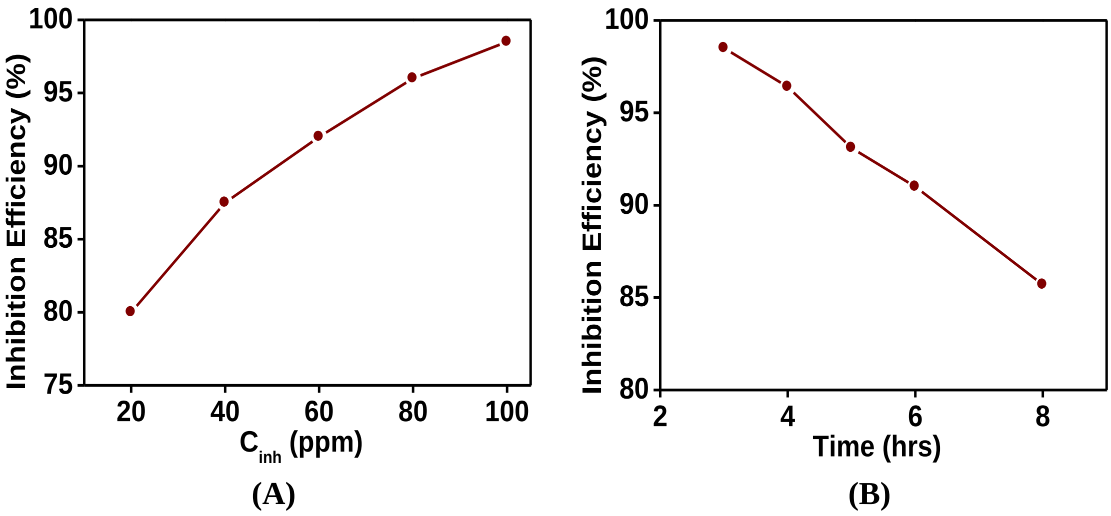
The morphology of the corrosion products formed on the surface of the mild steel in 1M H_2SO_4 solution in the absence and presence of 100 ppm of PDA were examined by SEM using a Traktor TN-2000 energy dispersive spectrometer and a Joel-Jem-1200 EX II electron microscope.

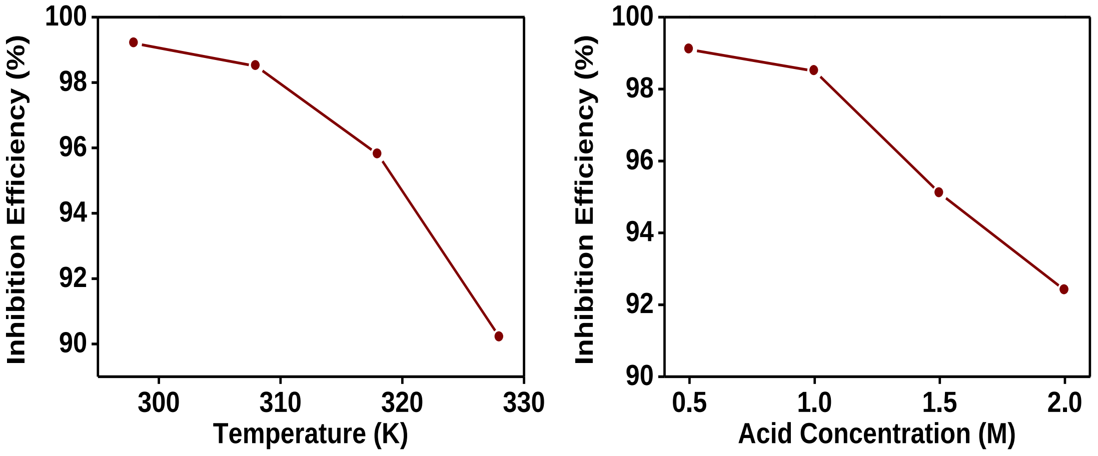
3. RESULTS AND DISCUSSIONS

3.1. Weight loss method:

3.1.1. Effect of inhibitor concentration:

Weight loss measurements were carried out for the different concentrations of PDA. The weight loss, inhibition efficiency and corrosion rate are reported in table 1. The trend of the inhibition efficiency with respect to PDA concentration is plotted in figure 2(A). Figure 2(A) shows the tendency of increment of inhibitor efficiency with the increase in PDA 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 PDA concentration [17].





(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 inhibitor (B) different immersion time (C) different temperature and (D) different acid concentration range; using weight loss data.

3.1.2. Effect of Immersion time:

Effect of immersion time against inhibition efficiency is shown in figure 2(B). It is evident from the figure that the increase in the immersion time slows down the inhibition efficiency. This decrease in inhibition efficiency suggest that the compound is firmly adsorbed on mild steel surface and desorption rate is slow [14].

Table 1. Weight loss parameters calculated in 1M sulphuric acid on mild steel.

Inhibitor Concentration (ppm)	Weight loss (mg cm^{-2})	Inhibition efficiency (%)	Corrosion rate (mm/y)
Blank	46.0	-	165.0
20	9.2	80.0	33.0
40	5.8	87.5	20.8
60	3.7	92.0	13.3
80	1.9	96.0	6.8
100	0.7	98.5	2.5

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 presented in figure 2(C) shows that inhibition efficiency decreases with increase in solution temperature. This change in inhibition efficiency with temperature may be attributed to desorption of the inhibitor molecule from mild steel surface with increase in temperature [12].

3.1.4 Effect of acid concentration:

Effect of acid concentration with inhibition efficiency is reported in figure 2 (D). The inhibition efficiency decreases with increase in the acid concentration. This reveals that the inhibitor is good at lower concentrations of the sulphuric acid solution [4].

3.2 Adsorption isotherm

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

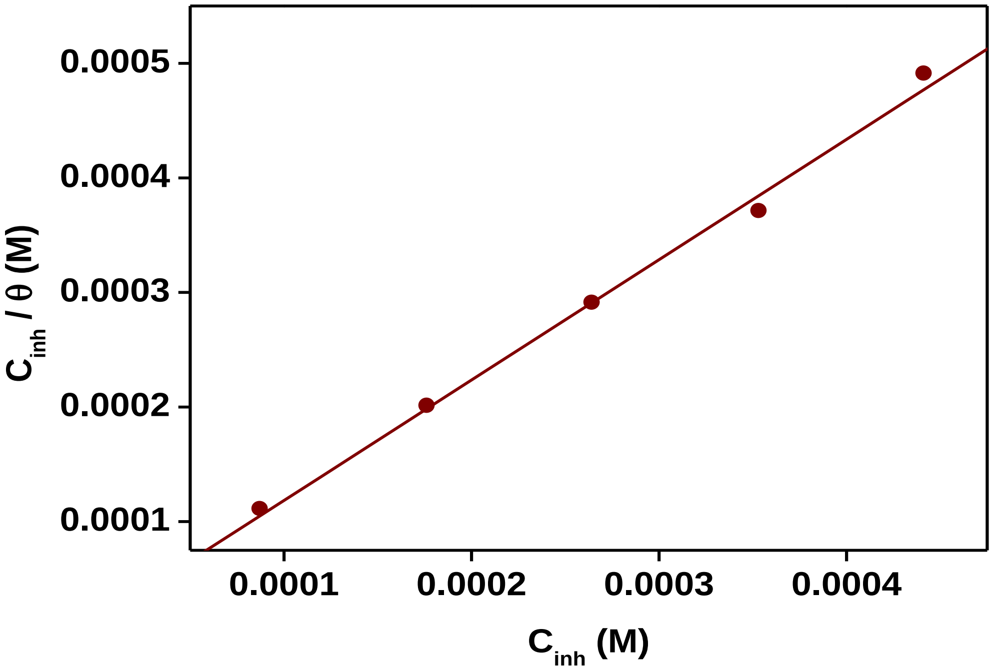


Figure 3. Langmuir's Adsorption isotherm plot for the adsorption of PDA in 1 M sulphuric acid on the surface of mild steel.

Langmuir adsorption isotherm was tested and found to be the most appropriate isotherm to explain the experimental data. Langmuir adsorption isotherm is represented by following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{5}$$

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}/θ vs C_{inh} 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 [18, 19].

3.3 Potentiodynamic 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 PDA inhibitor on the cathodic as well as anodic polarization curves of mild steel in 1M H_2SO_4 respectively. It is evident from the figure that both reactions were suppressed with the addition of the inhibitor. This suggests that PDA reduced the anodic dissolution reactions as well as retarded the hydrogen evolution reactions on the cathodic sites.

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 [20] and Li et. al. [21], 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 14 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.

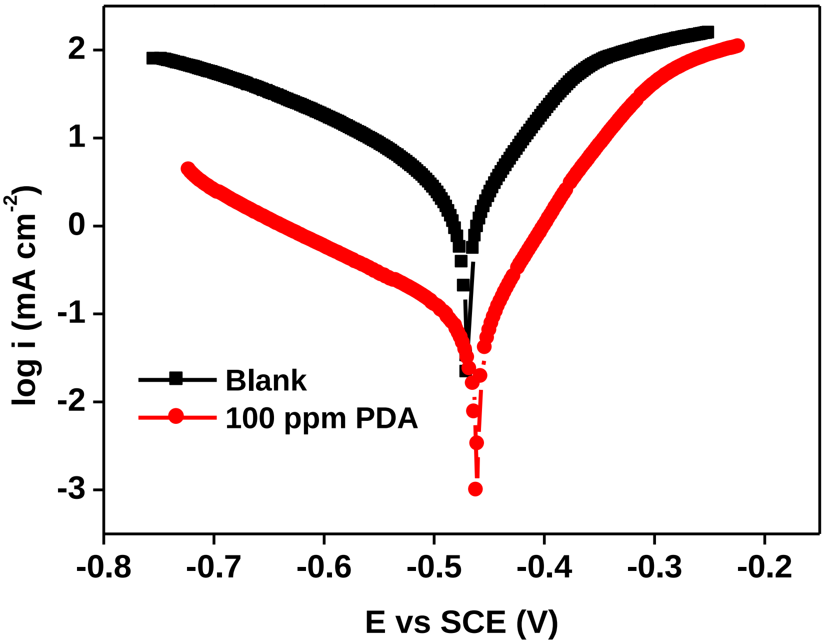


Figure 4. Tafel polarization graph of without and with 100 ppm PDA in 1M H_2SO_4 on mild steel

Table 2. Tafel polarization parameters calculated without and with 100 ppm PDA in 1M H_2SO_4 on mild steel

Concentration of Inhibitor	$-E_{corr}$ (mV vs SCE)	b_a (mV dec^{-1})	b_c (mV dec^{-1})	I_{corr} (µA cm^{-2})	IE (%)
Blank	470	77	154	2240	-
100 ppm	461	56	160	79	96.5

3.4 Electrochemical Impedance Spectroscopy:

Nyquist representation of the EIS study of mild steel in 1M H_2SO_4 in absence and presence of 300 ppm PDA were presented in figure 5. The large capacitive loop attributed to the adsorption of the inhibitor molecule [22]. The simple equivalent Randle circuit for studies is shown in Fig. 6, where R_s represents the solution and corrosion product film; the parallel combination of resister, R_t and capacitor C_{dl} represents the corroding interface. The existence of single semi circle showed the single charge transfer process.

Table 3. Electrochemical impedance parameters calculated without and with 100 ppm PDA in 1M H_2SO_4 on mild steel

Concentration of inhibitor (ppm)	R_s (Ω cm^2)	R_t (Ω cm^2)	C_{dl} (µF cm^{-2})	IE (%)
Blank	0.856	8.2	65.7	-
100 ppm	0.801	275.1	15.3	97.0

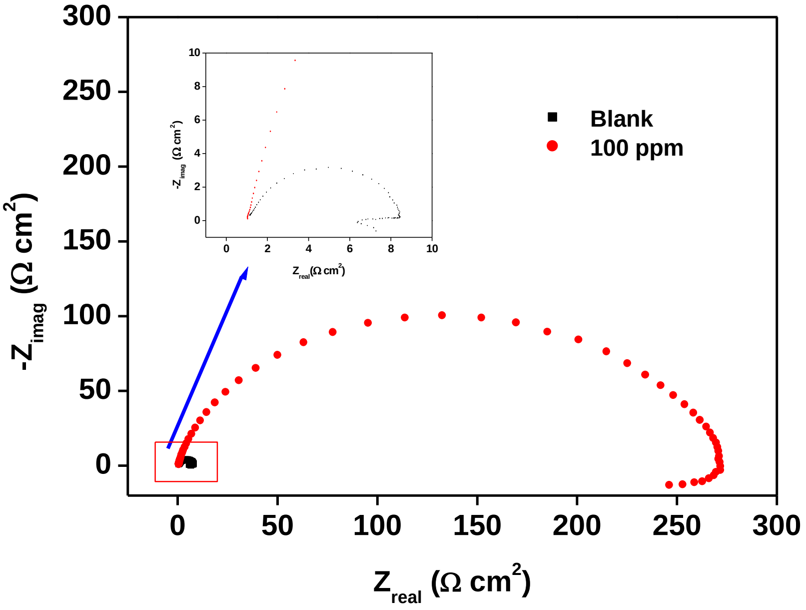


Figure 5. Nyquest plot for mild steel corrosion in absence and presence of 100 ppm PDA

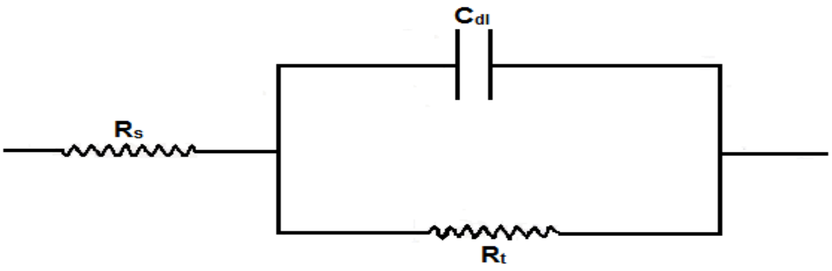
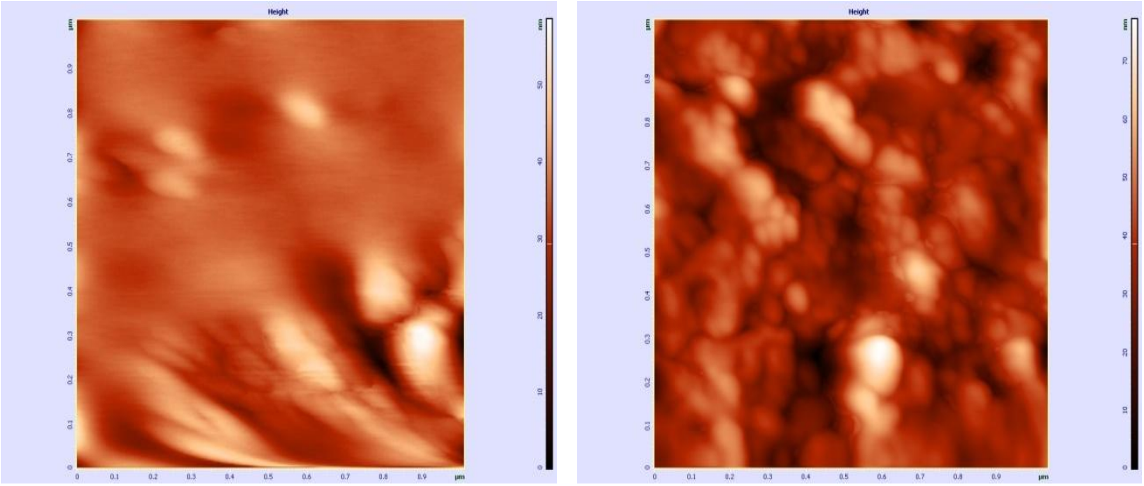


Figure 6. The electrochemical equivalent circuit used to fit the impedance measurements.

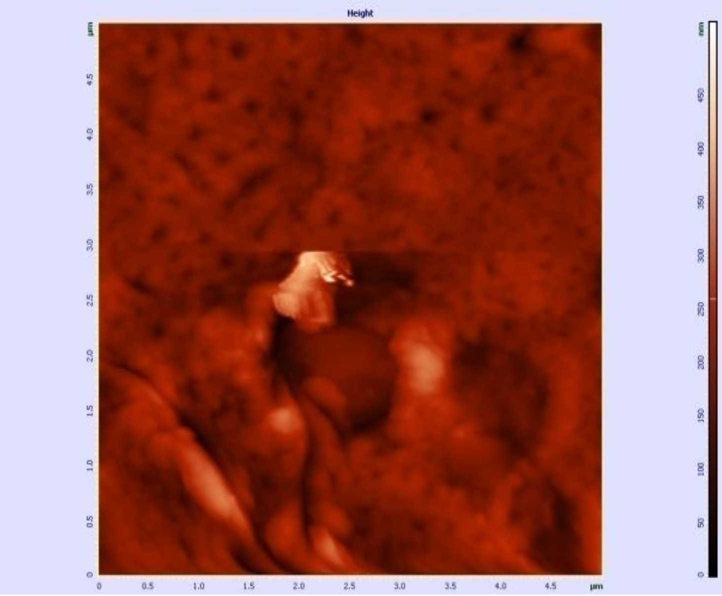
Depression from the perfect semi circle is due to the inhomogeneous nature of the metal surface arising from the surface roughness or the interfacial phenomenon [23]. The increase in R_t value due to the addition of inhibitor in comparison to the absence of inhibitor is attributed to the formation of protective film on the metal / solution interface. These observations suggest that PDA molecules function by adsorption at metal surface thereby causing the decrease in C_{dl} values and increase in R_t values [22-24]. The charge transfer resistance (R_t) and the interfacial double layer capacitance (C_{dl}) derived from these curves are given in Table 3. Inhibition efficiency was calculated by the using the charge transfer resistance values. The results obtained from the EIS studies showed good agreement with the results obtained from the Tafel polarization and weight loss study.

3.5 Atomic force microscopy:

AFM is a powerful technique to investigate the surface morphology at nano to micro scale and has become a new choice to study the influence of inhibitor on the generation and progress of the corrosion at metal solution interface [25, 26]. Surface images taken by AFM techniques are reported in figure 7a-c. The surface roughness of untreated mild steel shows average of 50 nm. When this mild steel was immersed in 1M sulphuric acid solution the surface roughness increases up to 450 nm.



(A) **(B)**



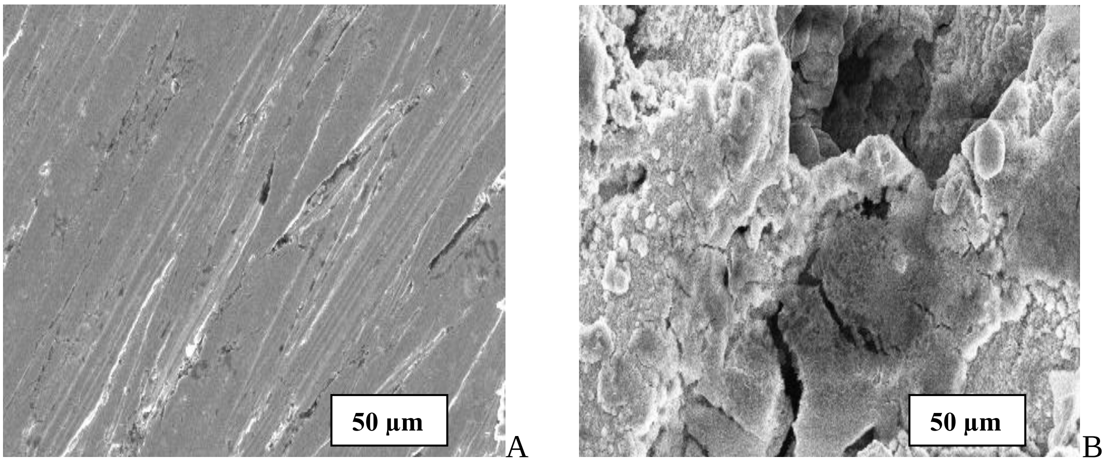
(C)

Figure 7. AFM micrograph of polished Mild Steel (b) mild steel after immersion in 1 M H_2SO_4 (c) Mild steel after immersion in 100 ppm PDA + 1 M H_2SO_4

Meanwhile, when same mild steel was immersed in 1M sulphuric acid solution with 100 ppm of PDA inhibitor it decreases appreciably to 70 nm in roughness in comparison with the one in the uninhibited solution. This study suggests that the mild steel surface in presence of inhibitor is less affected by the acid attack.

3.6 Scanning Electron Microscopy:

The SEM images of mild steel surfaces are given figure 8(a-c). Figure 8a shows the bare mild steel surface whereas figure 8b shows the mild steel surface in 1 M H_2SO_4 solution. Figure 8c shows the mild steel surface in 1M sulphuric acid in the presence of 100 ppm PDA. It is clear from the figures that the surface of mild steel with inhibitor is more intact and smooth than without inhibitor system.



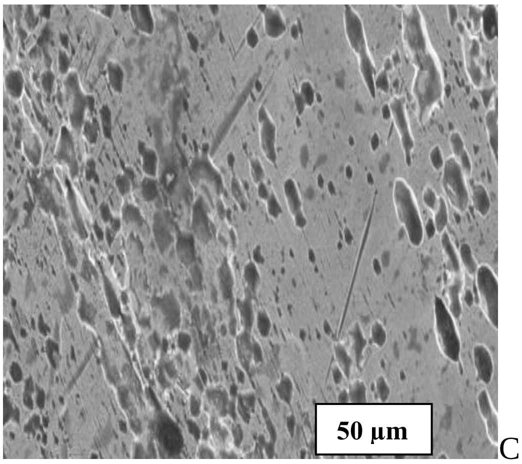


Figure 8. Scanning electron micrographs of mild steel surface of (a) polished mild steel (b) mild steel in 1M H_2SO_4 (c) inhibited mild steel in 1M H_2SO_4 + 100 ppm PDA.

4. CONCLUSION

1. PDA was found to be a good inhibitor for mild steel corrosion in sulphuric acid medium.
2. Potentiodynamic polarization study revealed that PDA is a mixed-type inhibitor.
3. The inhibition efficiency of PDA increases with an increase in concentration of inhibitor.
4. PDA shows Langmuir's adsorption isotherm.
5. AFM and SEM surface characterization also supported that the compound is very good corrosion inhibitor.

ACKNOWLEDGEMENT
SKS is thankful to North-West University, Republic of South Africa for Post-doctoral fellowship.

References

1. G. Ji, S.K. Shukla, P. Dwivedi, S. Sundaram, R. Prakash, *Ind. Engg. Chem Res.* 50 (2011) 11954.
2. S.K. Shukla, M.A. Quraishi, E.E. Ebenso, *Int. J. Electrochem. Sci*, 6 (2011) 2912.
3. S.K. Shukla, A.K. Singh, M.A. Quraishi, *Int. J. Electrochem. Sci.,* 7 (2012) 3371.
4. S.K. Shukla, M.A. Quraishi, *J. Appl. Poly. Sci.* 124 (2012) 5130.
5. S.K. Shukla, L.C. Murulana, E.E. Ebenso, *Int. J. Electrochem. Sci* 6 (2011) 4286.
6. Y.C. Pan, Y. Wen, L.Y. Xue, X.Y. Guo, H.F. Yang, *J. Phys. Chem. C,* 116 (2012) 3532.
7. H.D. Johansen, C.M.A. Brett, A.J. Motheo, *Corros. Sci.* 63 (2012) 342.
8. M. Benabdellah, A. Ousslim, B. Hammouti, A. Elidrissi, A. Aouniti, A. Dafali, K. Bekkouch, M. Benkaddour, *J. Appl. Electrochem.* 37 (2007) 819.
9. P.C. Okafor, M.E. Ikpi, I.E. Uwaha, E.E. Ebenso, U.J. Ekpe, S.A. Umoren *Corros. Sci.* 50 (2008) 2310.
10. F. Bentiss, M. Labrini, M. Traisnel, M. Lagrenee, *J. Appl. Electrochem.* 39 (2009) 1399.
11. A.K. Singh, S.K. Shukla, M.A. Quraishi, *Int. J. Electrochem. Sci* 6, (2011) 5802.
12. A.K. Singh, S.K. Shukla, M.A. Quraishi, E.E. Ebenso, *J. Taiwan Inst. Chem. Eng.* 43 (2012) 463

13. S.K. Shukla, A.K. Singh, I. Ahmad, M.A. Quraishi, *Matter. Lett.* 63 (2009) 819.
14. S.K. Shukla, M.A. Quraishi, *Corros. Sci.* 51 (2009) 1007.
15. M.M. Singh, R.B. Rastogi, B.N. Upadhyay, M. Yadav, *Mater. Chem. Phys.* 80 (2003) 283.
16. S.K. Shukla, A.K. Singh, M.A. Quraishi, *Int. J. Electrochem. Sci.* 6 (2011) 5779.
17. S.K. Shukla, M.A. Quraishi, R. Prakash, *Corros. Sci.* 50 (2008) 2867.
18. S.K. Shukla, E.E. Ebenso, *Int. J. Electrochem. Sci.*, 6 (2011) 3277.
19. S.K. Shukla, M.A. Quraishi, *Mater. Chem. Phys.* 120 (2010) 142.
20. E.S. Ferreira, C. Giancomelli, F.C. Giacomelli, A. Spinelli, *Mater. Chem. Phys.* 83 (2004) 129.
21. W.H. Li, Q. He, C.L. Pei, B.R. Hou, *J. Appl. Electrochem*. 38 (2008) 289.
22. S.K. Shukla, M.A. Quraishi, *Corros. Sci.* 52 (2010) 314.
23. S.K. Shukla, M.A. Quraishi, *Corros. Sci* 51 (2009) 1990.
24. F. Bentiss, M. Traisnel, M. Lagrenee, *Corros. Sci.* 42 (2000) 127.
25. M.A. Quraishi, S.K. Shukla, *Mater. Chem. Phys.* 113 (2009) 685.
26. A.K. Singh, S.K. Shukla, M. Singh, M.A. Quraishi, *Mater. Chem. Phys.* 129 (2011) 68.