Role of 2-Chlorobenzimidazole to Control Corrosion of Mild Steel in 1M Sulfuric Acid Solution

Dr. Balkrishna D. Ambhore

Chemistry Research Laboratory, Bhavan's H. Somani College of Arts & Science, Chowpatty, Mumbai-400007.

E-mail: balkrishna67ambhore@gmail.com

Abstract: Corrosion control of mild steel has been investigated by newly synthesized 2-Chlorobenzimidazole as an inhibitor with different concentrations, 10 ppm - 500 ppm in 1M sulfuric acid solution. Various techniques such as Weight Loss, Open Circuit Potential and Potentiodynamic Polarization have been used to study the mechanism and kinetics of corrosion and its mitigation. The inhibition begins just from 10 ppm solution and optimized at 300 ppm solution by about 49%; but thereafter, at further higher concentrations, the rate of corrosion inhibition decreases. The surface analysis performed by Scanning Electron Microscope. The adsorption obeys the Langmuir's adsorption isotherm phenomenon of a straight-line graph with slope nearly one. From the polarization of both the electrodes it is revealed that the inhibitor is of a mixed type.

Keywords: Mild steel, Sulfuric acid, Inhibitor, Polarization, Adsorption.

Introduction:

The Phenomenon of corrosion mainly of Fe, Al, Cu, Zn, Mg and their alloys remain a measure concern to industries around the world. In spite of much more advancement in this field, there are serious consequences due to the corrosion mainly the economics losses [1]. Since corrosion is an electrochemical process, it can be controlled to a great extent by selection of a proper corrosion inhibitor [2]. Corrosion inhibitors have wide commercial applications in industries such as in water cooling, oil, gas fields, acid cleaning, descaling, acid pickling, in petrochemical, oil wells, refineries, containers, in building and bridges construction etc. In spite of highly efficient and durable inhibitors that can be protect iron and low carbon steel, in aggressive environments such as sulfuric acid it yet to be realize completely [3].

In present investigation, 2-chlorobenzimidazole is synthesized in laboratory by procedure given in literature and used as a corrosion inhibitor on mild steel with different concentrations range of 10 ppm to 500 ppm in 1M sulfuric acid solution. The inhibition increases with increase in concentration of inhibitor solution; but 300 ppm solution exhibits its best performance and thereafter the inhibition efficiency decreases. This decrease in corrosion inhibition efficiency most probably may be due the aggressive nature of chloride in the structure of an inhibitor molecule [4-7]. In present research work, it is observed that after 300 ppm of inhibitor solution, chloride ions of inhibitor molecules penetrate aggressively through the pores and some defects of the protective film on the surface of mild steel than does sulfate ions.

Fig.1: Molecular Structure of 2-Chlorobenzimidazole

Material and Solution Preparation:

Mild steel was used as a corrosion testing substrate material. It refers to a low carbon steel which have composition- C= 0.16%, Si= 0.10%, Mn= 0.40%, P= 0.013%, S= 0.02% and remainder iron. For weight loss and polarization analysis, the commercial grade mild steel sheets were sheared in to coupons of size, 1 cm x 3 cm. The aggressive solution made of AR grade sulfuric acid obtained from Merck Chemicals. 2-Chlorobenzimidazole was synthesized in laboratory and used as a corrosion inhibitor. The experimental measurements were carried out at room temperature, $26^0C \pm 1^0C$ with 10 ppm - 500 ppm inhibitor solution in 1M sulfuric acid.

Method:

1) **Weight Loss Measurement:** Weight loss measurements readings were carried out in triplicates in test tubes containing 10 ml. test solutions, with and without inhibitor at the range, 10 ppm - 500 ppm. The immersion time was 24 h. at $26^0C \pm 1^0C$ after immersion time, the coupons were withdrawn from test tubes, rinsed with double distilled water, washed with acetone, dried and weighed. The average value of weight loss was noted, as shown in Table 1.
2) **Electrochemical Measurement System (EMS):** Electrochemical Measurement System, DC-105, software of DC corrosion techniques from M/S Gamry Instruments Inc., USA was used for Corrosion potential and Potentiodynamic polarization study.

The experiments were performed in a three electrodes Pyrex glass vessel with mild steel coupon (working electrode). The surface of mild steel coupons was abraded successively by silicon carbide emery papers from 300 to 2000 grades, obtained from Sianor, Switzerland so as to get the surface free from scratches and other apparent defects. These polished coupons were washed with soap solution, rinsed with double distilled water, degreased with acetone, by leaving 1 cm^2 on one side and small portion at the tip to provide the electrical contact, rest of the surface was coated with enamel lacquer including side all edges and finally the coupon dried in desiccators. In addition, two other electrodes were used- one is a saturated calomel electrode (reference electrode) and other is graphite rod (counter electrode). An about 50 ml. of corrosive medium solution was taken in a mini corrosion testing electrochemical cell to permit desired immersion of electrodes and all three electrodes were immersed into it and connected to the EMS, DC-105, Gamry Instrument through a connecting wire. The potential was swept between -0.5 V and 0.5 V at the scan rate of 5 mV/s.

The Open Circuit Potential (OCP) was carried out for 2 hours exposure time so that to obtained a steady horizontal curve and then Potentiodynamic polarization was run. Variation in potential of mild steel in 1 M sulfuric acid solution was measured against saturated Calomel electrode in absence and presence of various concentrations, 10 ppm - 500 ppm of inhibitor solutions. Different Potentiodynamic polarization results obtained are reported in Table 3.

Inhibitor	Conc. (ppm)	Weight Loss (mg)	Surface coverage (θ)	Inhibition Efficiency (IE%)
Blank	-	278	-	-
2-Chlorobenzi-midazole	10	204	0.2662	26.62
	100	163	0.4136	41.36
	200	152	0.4532	45.32
	300	141	0.4928	49.28
	400	175	0.3705	37.05
	500	192	0.3093	30.93

Table 1: Weight loss data for corrosion inhibition of mild steel with different concentrations of 2-Chlorobenzimidazole in 1M sulfuric acid.

Conc. (ppm)	Log C	Θ	(1-θ)	θ/(1-θ)	Log θ/(1-θ)
0.000010	-5.0000	0.2662	0.7338	0.3628	-0.4403
0.000100	-4.0000	0.4136	0.5864	0.7053	-0.1516

0.000200	-3.6989	0.4532	0.5468	0.8289	-0.0815
0.000300	-3.5228	0.4928	0.5072	0.9716	-0.0125
0.000400	-3.3979	0.3705	0.6295	0.5886	-0.2301
0.000500	-3.3010	0.3093	0.6907	0.4478	-0.3489

Table 2: Adsorption isotherm parameters for 2-Chlorobenzimidazole

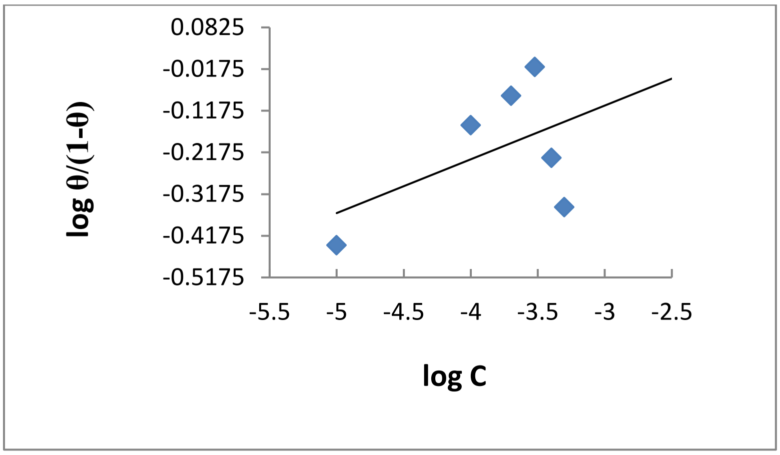

Fig. 2: Langmuir adsorption isotherm of mild steel

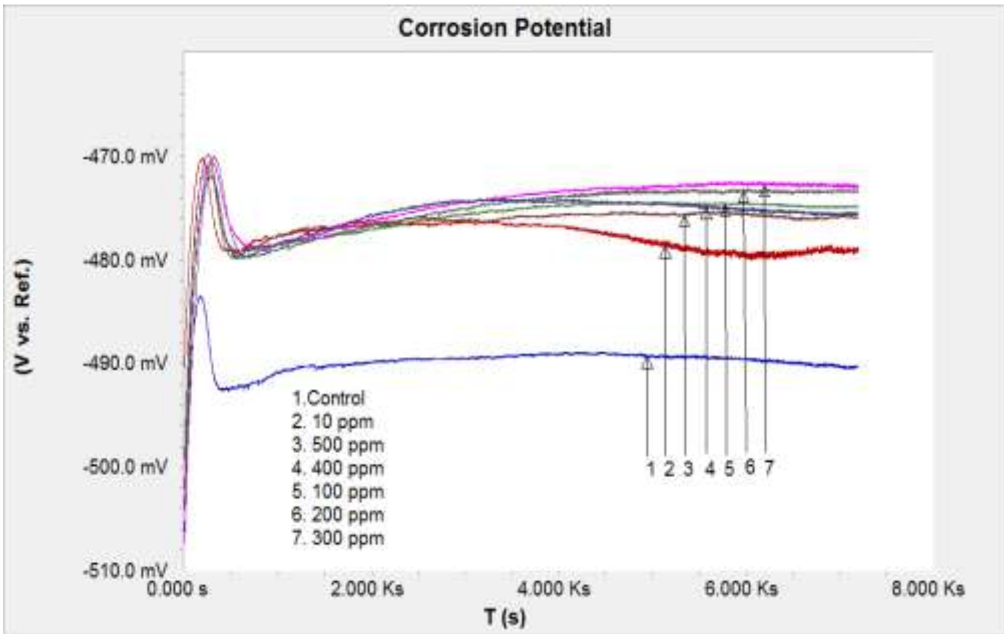

Fig. 3: OCP of mild steel with different concentrations of inhibitor in 1 M sulfuric acid

Conc. (ppm)	βa (V/dec.) e-3	βc (V/dec.) e-3	I_{corr} (mA)	E_{corr} (mV)	Corros. Rate (mpy)	IE %
Control	150.2	308.8	9.290	-446.0	4.245	
2-Chloro-benzimidazole						
10	87.10	220.3	6.750	-431	3.083	27.34
100	79.20	215.4	5.350	-432	62.07	42.41

200	74.20	201.5	4.950	-433	2.261	46.71
300	80.70	218.4	4.810	-432	2.197	48.22
400	82.50	234.6	5.730	-435	2.617	38.22
500	88.40	212.2	6.320	-436	2.890	31.96

Table 3: Electrochemical parameters of mild steel in 1M sulfuric acid with and without different concentration of inhibitor.

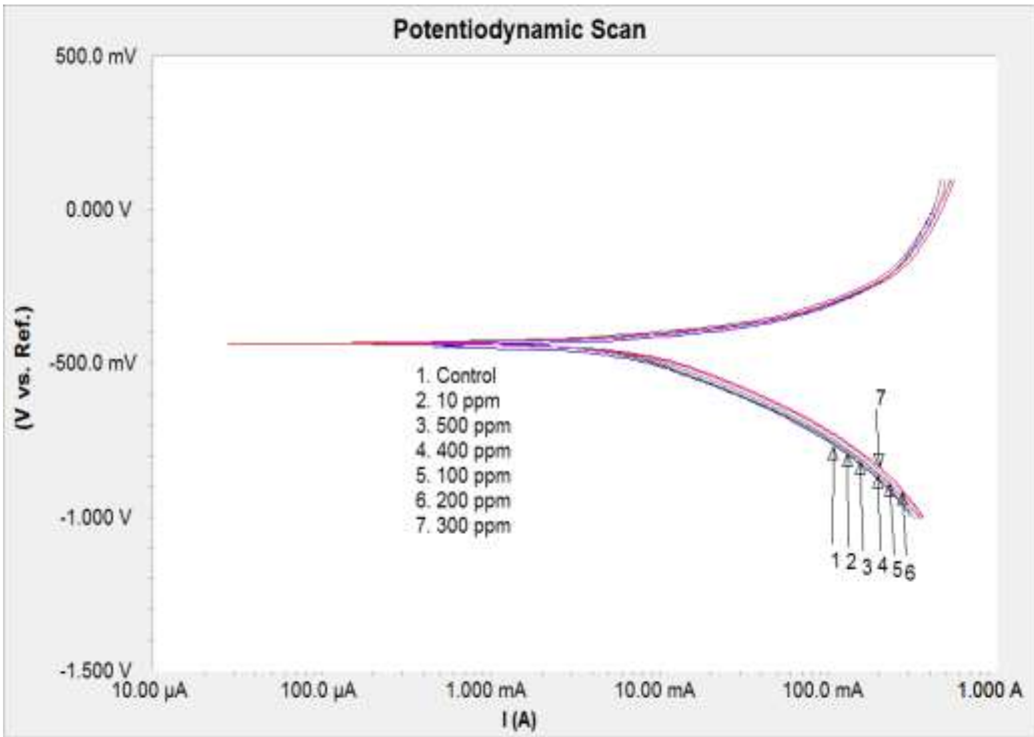

Fig. 4: Potentiodynamic polarization of mild steel with different concentrations of inhibitor in 1 M sulfuric acid

3) Scanning Electron Microscopic Analysis (SEM): The surface morphology of mild steel after 24 h immersion in 1M sulfuric acid in the absence and presence of 300 ppm of 2-Chlorobenzimidazole, was studied by a scanning electron microscope, Hitachi S-3400 N . The accelerating voltage for SEM was 10.0 KV.

(a) (b) (c)

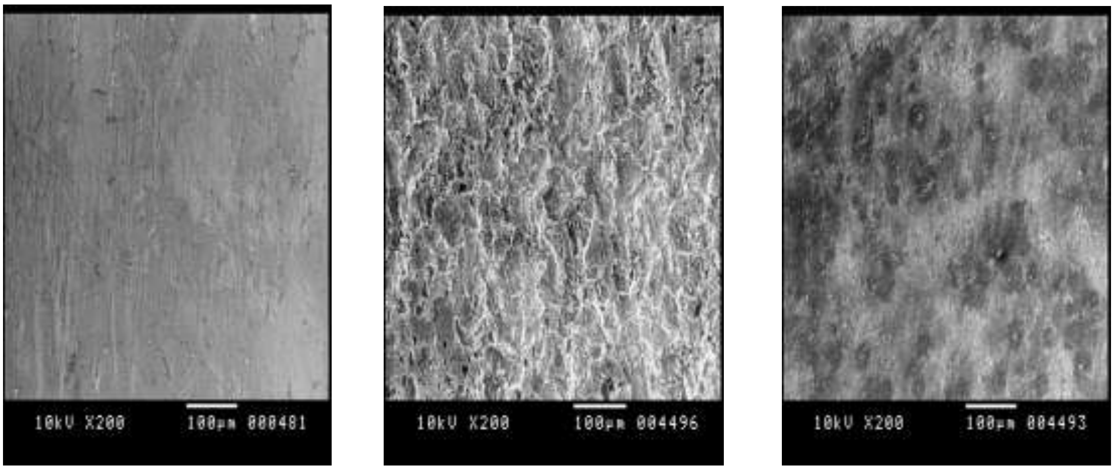

Fig. 5: SEM of mild steel: a) Polished and without inhibitor. b) After immersion 1M sulfuric acid without inhibitor. c) After immersion in 1M sulfuric acid with 300 ppm of inhibitor.

Result and discussion:

Weight loss measurements: The data obtained in Table 1, revealed that the rate of corrosion decreases as per the concentration of inhibitor solution increases from 10 ppm to 300 ppm. Nevertheless, by further increasing inhibitor concentration, the rate of corrosion again increases. Corrosion Inhibition Efficiency (IE) calculated by following formula.

$$IE\ \% = [W_o - W]/W_o \times 100$$

Where, W and W_o are the weight loss of mild steel in the presence and absence of inhibitor, respectively.

Adsorption isotherm: Adsorption isotherms are often used to demonstrate the adsorbent performance inhibitor molecules on the substrate which describes the relation between surface coverage, θ and bulk concentration, C [8,9]. The surface coverage values, θ (defined as $\theta = IE\%/100$), increases with increasing inhibitor concentration from 10 ppm to 300 ppm as a result of more adsorption of inhibitor molecules on the surface of mild steel (Table-1) takes placed. It is observed that the adsorption behavior of 2-Chlorobenzimidazole obeys the Langmuir's adsorption isotherm as it gives straight line when a graph of $\log(\theta/1-\theta)$ is plotted against log C as shown in Fig. 2. It was proposed that adsorption occurs by- physisorption and chemisorption processes [16-19]. Thus, the layer of inhibitor formed on the mild steel surface is the combination of physisorption and chemisorption both [10-14]

Open circuit potential measurement: It is observed that as mild steel (working electrode) immersed in to the studied solution, the potential immediately increases for few seconds then decreases and again increases and gradually attained a steady state up to the end of the experiment, as shown in Fig. 3. This sudden increase in potential may be due to the oxygen present on the surface of mild steel which in few seconds comes out in the form of baubles and then the exposed surface of the substrate starts corroding faster [20] consequently the potential decreases. After few seconds as the molecules of inhibitor start adsorption on the surface of mild steel, potential will again start increasing due to the protective film and within 30 minutes the potential achieved equilibrium and obtained a steady curve, as shown in Fig. 3. This shows that OCP of sulfuric acid in presence of inhibitor has more positive value than in absence of inhibitor which indicate the decrease in the rate of corrosion of mild steel in presence of inhibitor.

Potentiodynamic polarization measurement: Potentiodynamic polarization curves are depicted in Fig. 4, shows the polarization of anodic and cathodic curves. However, the cathodic curves comparatively are more polarized than anodic curves. This is evidenced that 2-Chlorobenzimidazole is a mixed type of inhibitor, but more cathodic. Corrosion Inhibition Efficiency (IE) calculated by the following equation:

$$(IE\ \%) = 100(i_0 - i) / i_0$$

Where, i_0 and I are the corrosion current densities in the absence and presence of inhibitor respectively. From the Table 3, it is revealed that the current density decreases as the inhibition concentration increases up to 300 ppm solution, but there after the current density increases with the higher concentrations, 400 ppm and 500 ppm respectively. This increase in current density may be due to the aggressive nature of chloride ions during the dissolution of 2-Chlorobenzimidazole. After 300 ppm, chloride ions penetrate more through the pores and some defects of the protective film on the surface of mild steel easier than does sulfate ions.

Mild steel surface in acidic media appeared negatively charged due to the adsorption of sulfate ions [15]. Now the 2-Chlorobenzimidazole molecules in protonated forms adsorbed (Physisorption) on the mild steel surface [16]. 2-Chlorobenzene being heterocyclic aromatic compound (Fig.1) containing electrons donor nitrogen atoms donates lone pair electrons to the empty d-orbitals of iron forming strong coordinate-covalent bonds (Chemisorption) [17,18]. The delocalized π-electrons of unsaturated aromatic rings of 2-Chlorobenzimidazole molecules also covalently bonded with vacant d-orbitals of iron. Thus, a thin protective layer of inhibitor molecules formed on the surface of mild steel which mitigates the corrosion [19,20].

Scanning Electron Microscopic (SEM) Analysis: SEM micrographs of mild steel in 1M sulfuric acid for 24 h in absence and presence of 300 ppm of 2-Chlorobenzimidazole are shown in Fig. 5. It is visualized that the substrate in absence of inhibitor is rough (Fig. 5 b), covered with corrosion products and strongly damaged with appearance of pits and cavities; whereas the substrate in 300 ppm is comparatively smooth (Fig. 5 c). It revealed that inhibitor adsorbed with the formation of protective film on the surface of mild steel which is responsible for the inhibition of corrosion [21].

Conclusion:

The result obtained by gravimetric analysis, hold good in agreement with the result obtained by electrochemical studies. It is revealed that the 2-Chlorobenzimidazole is acting as a good corrosion inhibitor on mild steel with 300 ppm inhibitor solution in 1M sulfuric acid, which gives about 49 % corrosion efficiency. Nevertheless, at higher inhibition concentration solution, the rate of corrosion inhibition decreases due to the aggressive nature of chloride ions of 2-Chlorobenzimidazole molecules [22]. This result is mutually in good agreement with all the techniques used in this study. 2-Chlorobenzimidazole is a mixed type of inhibitor, however more cathodic, since the cathodic polarization is more. The SEM examination shows the formation of protective surface film of inhibitor molecules on the surface of mild steel and obeys the Langmuir's adsorption isotherm.

Acknowledgements: Author thanks to Dr. R. S. Dubey, H.O.D., Department of Chemistry, R. J. College, Ghatkopar, Mumbai. Also, thanks to the Department of Science and Technology (DST), UGC and IIT, Mumbai is highly acknowledged for SEM analysis.

References:

1) Xianofan Zhai et al, Microbial corr. Resistance by 4,5-dichloro-2-n-octyl-4-isothiozolin-3-one, Elseviercorr.sci.72 (2013) 99-107.
2) Dake xu,et al,Lab. Investigation of microbiologically influence corr of C1018 carbon steel by bacillus licheniformis, Elsexier, corr. Sci. 77 (2013), 385-390.
3) Ivana Jevremovic et al, Inhibition property of talloil diethylenetriamine imidazolin for MS corr. In NaCl withCO2, Elsevier, corr. Sci. 77 (2013) , 265-273.
4) Yongming Tang, et al, Novel benzimidazole deri. Of corr. Inhibitors of MS in acidic media, Elsevier, corr.sci. 74(2013)271-282.
5) Walter W.Facke, Thermal analysis &FTIR studies of volatile corr. inhibitor model system, Elsevier, corr. Sci. 77(2013)88-96.
6) E. Alibakhshir, E. Ghasemi, et al, corr.inhibition by lithium zinc phosphate pigment, Elsevier, corr sci. 77 (2013) 222-229.
7) Matjaz Finsgar, Analysis of 1,2,4-triazole & 3-amino-1,2,4-triazole as corr. Inhibitors, Elsevier corr. Sci. 77, 2013 (350-359).
8) H. Y. Tsai, S. C. Sun, S. J. Wang, J Electrochem Soc., 147 (2000) 2766.
9) A. Krishnamoorthy, K. Chanda, S. P. Murarka, G. Ramanath, J. G. Ryan, Appl Phys Lett., 78 (2001) 2467-2469.
10) C. E. Ho, W. T. Chen, C. R. Kao, J Electron Mater, 30 (2001) 379.
11) U. R. Evans, Trans Farad Soc., 40 (1944)120.
12) A. I. Krosilshchikov, I. V. Dedova, J Gen Chem U.S.S.R., 16 (1946) 537.
13) Y. Komuro, J Chem Soc Jpn., 75 (1954) 255.A. Travincek, J. H. Weber, J Phys Chem., 65 (1961) 23
14) I. S. Smol'yaninov, I. Voronezhsk, Gos Ped Inst., 47 (1964) 34.

15) A. Rasheed Arain A. M. Shams El Din, Thermochim Acta, 89 (1985) 171.
16) A. Zarrouk, A. Dafali, B. Hammouti, H. Zarrok, S. Boukhris, M. Zertoubi, Int. J. Electrochem. Sci., 5 (2010) 46
17) A.Zarrouk, T. Chelfi, A. Dafali, B. Hammouti, S.S. Al-Deyab, I. Warad, N. Benchat, M. Zertoubi, Int. J. Electrochem. Sci., 5 (2010) 696.

18) A. Zarrouk, I. Warad, B. Hammouti, A Dafali, S.S. Al-Deyab, N. Benchat, Int. J. Electrochem. Sci., 5 (2010) 1516.
19) A. Zarrouk, B. Hammouti, A. Dafali, H. Zarrok, Der Pharma Chemica., 3 (2011) 266.
20) A.S. Fouda, H. A. Wahed, Arab. J. Chem., (2011) Article in press.
21) A.S. Fouda, M. M. Gouda and S. I. Abd El-Rahman, Bull. Korean Chem. Soc., 21 (2000) 1085.
22) K. F. Khaled, Mohammed A. Amin, Corros. Sci., 51 (2009) 2098.