

Inhibition of Mild Steel Corrosion Caused by Sulphate Reducing Bacteria by Using 2-Methylimidazole

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ABSTRACT

In this study, the inhibitive performance of 2-methylimidazole derivative as a corrosion inhibitor of mild steel was examined in Barr's medium inoculated with sulphate reducing bacteria (*Desulfovibrio desulfuricans*). The coupons were exposed with different concentrations of 2-methylimidazole in Barr's medium inoculated with sulphate reducing bacteria. The corrosion behaviour of mild steel was measured by weight loss, corrosion potential and polarization techniques. The surface analysis has been performed by scanning electron microscopy (SEM). The inhibitor exhibits their best performance at 500 ppm solution. The inhibitor obeys the Langmuir adsorption isotherm phenomenon since it obtained a straight line graph.

Keywords : SRB, Mild Steel, SEM.

I. INTRODUCTION

Though the serious consequence of corrosion can be controlled to a great extent by selection of highly corrosion resistant materials, the phenomenon of corrosion remains a major concern to industries around the world. Microbiologically Influenced Corrosion (MIC) is a major problem in many industries such as oil and gas, as well as water utilities. Sulphate Reducing Bacteria (SRB) is often found to be the cause of MIC [1-8].

Microbiologically influenced corrosion (MIC) has been estimated to account for 20% of annual corrosion damage of metallic materials, of which sulphate-reducing bacteria (SRB) are commonly considered to be the principal culprits among the causative organisms of corrosion [9-11]. SRB are strict anaerobes that gain their biochemical energy for growth by oxidizing certain organic

compounds or hydrogen (H_2) with sulphate or other sulphur compounds such as sulphite, thiosulphate or sulphur as terminal electron acceptors and reducing these compounds to sulphides (H_2S and HS^-) [12-15].

The purpose of this paper is to study inhibition performance of 2-methylimidazole as corrosion inhibitor for mild steel in Barr's medium inoculated with sulphate reducing bacteria. It has been studied through different corrosion monitoring methods and surface analytic techniques. In addition, adsorption performance and mechanism at mild steel surfaces are also discussed. The study confirms that the imidazole derivative protect mild steel from microbiological influenced corrosion due to its antimicrobial properties and by adsorption on metal surface.

II. EXPERIMENTAL DETAILS

2.1. Metals and Alloys

Mild Steel coupons having composition (C – 0.16%, Si – 0.10%, Mn – 0.40%, P - 0.013%, S - 0.02% and remaining as iron) have been used as working electrode in the present study.

2.2. Chemicals

Chemicals used in corrosion test solutions and corrosion inhibitors were obtained from Merck (India), Loba chemie (India). All these chemicals were of AR grade and were used without any further purification.

2.3. Bacteria

The bacteria used in the present study were obtained from National collection of Industrial Micro-organisms (NCIM), Biochemical Science Division, National Chemical Laboratory, Pune-411088, Maharashtra.

The bacteria used in the present study were *Desulfovibrio desulfuricans*. Composition of the culture medium is given below,

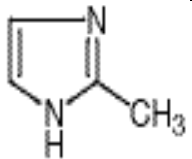
Table 1

Name of the Organism	NCI M No.	Medium used
<i>Desulfovibrio desulfuricans</i> .	2047	Barr's medium (sulfur bacteria) K ₂ HPO ₄ 0.05g, NH ₄ Cl 0.19, CaSO ₄ 0.29, Sodium Lactate 0.79, MgSO ₄ .7H ₂ O 0.29, Ferrous Ammonium Sulfate 0.05g, Distilled Water 100 cm ³ (medium is sterilized for three consecutive days at 121°C for 20 min and the final pH is adjusted to 7.0-7.5).

2.4. Biocide:-

The biocide 2-methylimidazole is added in to the test solution. The chemical structure of 2-methylimidazole is as follows,

Table 2

Inhibitor	Molecular Structure.
2-methylimidazole	

2.5. Sample Preparation:

For weight loss experiments, rectangular shaped coupons (1 cm X 3 cm) were sheared from sheets of mild steel and flag shaped specimens with 1 cm² working area were used for electrochemical experiments. The surface of specimens was prepared by sequential polishing with 1/0, 2/0, 3/0, 4/0 grade emery papers, it was polished with the next higher grade in a right angle to the first. During the polishing of mild steel surface, the emery paper was impregnated with a dilute solution of paraffin wax in kerosene oil. All specimens were washed with triple distilled water and degreased with 95% ethyl alcohol. Specimens were dried and stored over silica gel in vacuum desiccators.

2.6. Immersion Test

Specimens were weighed on an electronic balance (Shimadzu Type BL220H, least count 0.001g) before and after immersion tests. After removing the specimens from the test solution the corrosion products were removed from the surface with the help of brush. Generally duplicate experiments were performed in each case and the mean value of the weight loss was recorded.

2.7. Electrochemical Measurements

The variation of corrosion potential of mild steel was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of OCP for different experiments was recorded for one hour

exposure period. Then same sample was used for potentiodynamic polarization (PD) experiments. Different electrochemical results obtained from potentiodynamic polarization are reported. The polarization studies were carried out in unstirred solutions. For electrochemical polarization studies (corrosion potential and potentiodynamic polarization) flag shaped specimens with sufficiently long tail were cut from the mild steel sheet. These samples were polished as described earlier leaving a working area of 1 cm² on one side of the flag and a small portion at the tip for providing electrical contact. Rest of the surface was coated with enamel lacquer including side edges. The test specimen was connected to the working electrode holder through the tip of the tail. About 50 ml of the corrosive medium was taken in a mini corrosion testing electrochemical cell.

Electrochemical measurement system, DC 105, containing software of DC corrosion techniques from M/S Gamry Instruments Inc., (No. 23-25), Louis Drive, Warminster, PA- 18974, USA has been used for performing corrosion potential and polarization experiments. The electrochemical studies were performed in a three electrodes Pyrex glass vessel with mild steel coupons as working electrode, saturated calomel electrode as reference electrode and spectroscopic grade graphite rod as counter electrode.

2.8. Scanning Electron Microscopic Analysis

The composition and surface morphology of corrosion product on mild steel sample after 240 hours (10 days) immersion in the Barr's medium in the absence and presence of 2-methylimidazole was studied by a scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

3.1. Weight Loss Measurement-

Weight loss data of mild steel in Barr's medium inoculated with *Desulfovibrio desulfuricans* in

the absence and presence of various concentrations of inhibitor were obtained and are given in Table-1. Inhibition efficiencies (IE %) were calculated by formula as:

$$(IE \%) = [W_0 - W] / W_0 \times 100$$

Where W and W₀ are the weight loss of mild steel in the presence and absence of inhibitor, respectively. The results show that the inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

Table 3. Weight loss data for inhibition of corrosion of mild steel exposed to Barr's medium inoculated with *Desulfovibrio Desulfuricans* with different concentration of 2-methylimidazole.

Inhibitor	Conc. (ppm)	Weight Loss (mg)	Surface Coverage (θ)	Inhibition Efficiency (IE %)
Blank (Barr's medium inoculated with <i>Desulfovibrio Desulfuricans</i>)	-----	210	----- -	-----
2-methylimidazole	100	138	0.34	34%
	300	96	0.54	54%
	500	42	0.80	80%

3.2. Open Circuit Potential Measurement (OCP)

The electrochemical behavior of mild steel in 1M HCl was studied by monitoring change in corrosion potential (E_{corr}) with time. The change in open circuit potential of mild steel in absence and presence of various concentrations of inhibitor 2-methylimidazole in Barr's medium is shown in figure 3.

The change in open circuit potential of mild steel in absence and presence of inhibitors were measured after 10 days exposure in Barr's medium inoculated with *Desulfovibrio Desulfuricans* for period of 1h with sample period of one data per second. The potential attains steady state after exposure of 0.5h. The steady state potential is an equilibrium state at which I_{ox} is equal to I_{red} . In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more towards positive value. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal.

The influence of various concentration (100, 300, and 500 ppm) of 2-methylimidazole on open circuit potential of mild steel in Barr's medium is given in fig .3 . It is obvious from figure that, it exhibit good inhibition performance at 100 ppm and above. Inhibition efficiency increases with increase in concentration of 2-methylimidazole.

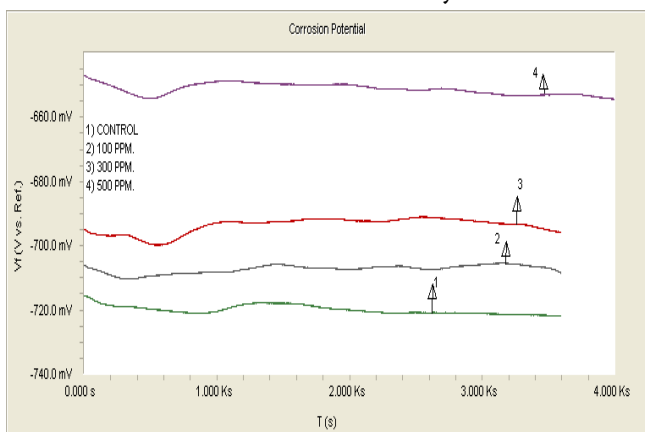


Figure 1. Corrosion potential of mild steel exposed to the solution of Barr's medium with different concentrations of 2-methylimidazole.

3.3. Potentiodynamic Polarization Measurement

Figure 4 depicts typical potentiodynamic polarization curves for mild steel in Barr's medium solution in the absence and presence of different concentrations of 2-methylimidazole at 30°C.

It could be observed that extent of damage to mild steel surface is very less, the rate of corrosion was reduced considerably in the presence of inhibitors, it revealed that there was a good protective film adsorbed on metal surface, which acted as a barrier and was responsible for the inhibition of corrosion.

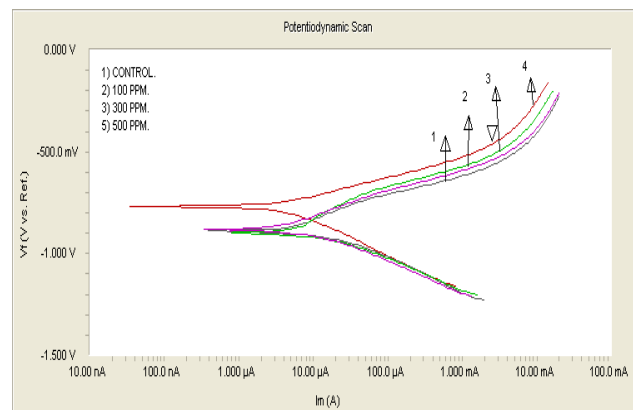


Figure 2. Potentiodynamic polarization curve of mild steel exposed to Barr's medium inoculated with *Desulfovibrio Desulfuricans* with different concentrations of 2-methylimidazole.

Table 4. Electrochemical Parameters for Inhibition of corrosion of mild steel exposed to 1M HCl with different concentration of 2-methylimidazole.

Conc. (ppm)	β_a (V/dec.) e^{-3}	β_c (V/dec.) e^{-3}	I_{corr} ($\mu A.cm^2$)	E_{corr} (mV)	%IE
Contro	231.4	113.0	15.10	-897.0	-
2-methylimidazole.					
100	160.7	128.7	8.52	-881.0	43.57
300	106.0	176.6	5.45	-768.0	63.90
500	104.3	175.2	3.12	-765.0	79.33

3.4. Adsorption Isotherm

The surface coverage values, θ , (defined as $\theta = \text{IE} \% / 100$), increases with increasing inhibitor concentration as a result of adsorption of more inhibitor. The corrosion inhibition efficiency was calculated by using the following equation: Inhibition efficiency (IE %) = $\frac{100(i_0 - i)}{i_0}$, Where i_0 and i are the corrosion current densities in the absence and presence of inhibitor in the solution, respectively.

Table 5. Adsorption parameters of 2-methylimidazole.

C (PPM)	θ	IE%
100	0.4357	43.57
300	0.6390	63.90
500	0.7933	79.33

It is observed that the adsorption behavior of 2-methylimidazole obeys the Langmuir's adsorption isotherm as it gives straight line when graph of $C \text{ (ppm)} / \theta$ is plotted against $C \text{ (ppm)}$ as shown in Fig 1. It was proposed that adsorption of 2-methylimidazole occurs by physisorption and chemisorptions. Thus the surface of inhibitor layer formation on the mild steel is the combination of both, physisorption and chemisorptions.

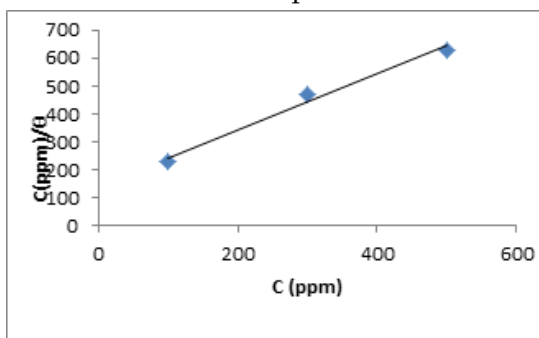


Figure 3. Adsorption Isotherm of 2-methylimidazole.

3.5. Scanning Electron Microscopic (SEM) Analysis

SEM micrographs obtained from unexposed and exposed specimen coupons in Barr's medium inoculated with *Desulfovibrio Desulfuricans* for 240 hours in the absence and presence of 500 ppm 2-methylimidazole which are shown in Fig. 2, respectively. The accelerating voltage for SEM scanning was 10KV. The results obtained from weight loss and electrochemical measurements were further supported by SEM analysis.

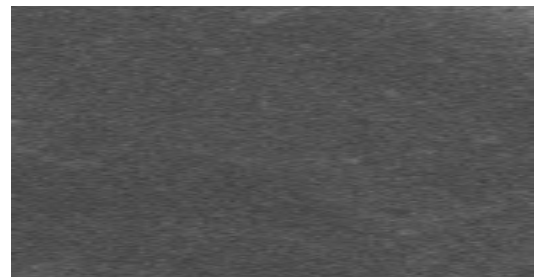


Figure 4. SEM of mild steel: a) Polished and without inhibitor.

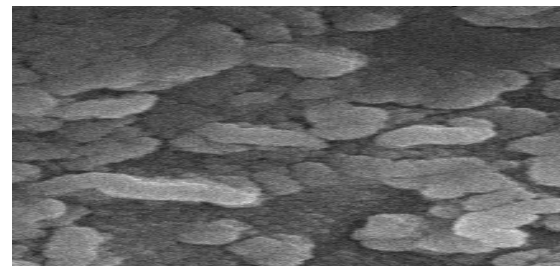


Figure 4.b) After immersion in Barr's medium inoculated with *Desulfovibrio desulfuricans* without inhibitor.

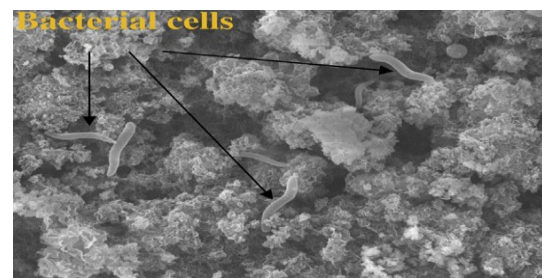


Figure 4. c). After immersion in Barr's medium inoculated with *Desulfovibrio desulfuricans* with 500 ppm of inhibitor.

IV. CONCLUSION

On the basis of above results following conclusions are obtained:

- 1] The result obtained by gravimetric analysis, hold good agreement with the result obtained by electrochemical studies; revealed that 2-methylimidazole is acting as a very good corrosion inhibitor of mild steel in Barr's medium.
- 2] The inhibition efficiency increases with the increasing concentration of inhibitor.
- 3] In the present investigation, 500 ppm solution of 2-methylimidazole shows nearly 80% inhibition.
- 4] 2-methylimidazole is mixed type of inhibitor.
- 5] The SEM examination shows the formation of protective surface film of inhibitor molecules on the surface of mild steel and obeys the Langmuir adsorption isotherm.

V. REFERENCES

- [1] Hamilton WA. Sulfate-reducing bacteria and anaerobic corrosion. *Annu Rev Microbiol* 1985;39:195–217.
- [2] Rueter P, Rabus R, Wilkest H, Aeckersberg F, Rainey FA, Jannasch HW, et al. Anaerobic oxidation of hydrocarbons in crude oil by new types of sulphate reducing bacteria. *Nature* 1994;372:455–8.
- [3] Miranda E, Bethencourt M, Botana F, Cano M. Biocorrosion of carbon steel alloys by an hydrogenotrophic sulfate-reducing bacterium *Desulfovibrio Capillatus* isolated from a Mexican oil field separator. *Corros Sci* 2006;48:2417–31.
- [4] AlAbbas FM, Williamson C, Bhola SM, Spear JR, Olson DL, Mishra B, et al. Influence of sulfate reducing bacterial biofilm on corrosion behavior of lowalloy,high-strength steel (API-5L X80). *Int Biodeter Biodegr* 2013;78:34–42.
- [5] Guamet PS, Gomez de Saravia SG. Laboratory studies of biocorrosion control using traditional and environmentally friendly biocides: an overview. *Latin Am Appl Res* 2005;35(4):295–300.
- [6]. Antony P.J., Chongdar S., Kumar P., Ramana R., *Electrochim. Acta.* 52 (2007) 3985.
- [7]. Beech I.B., Gaylarde C.C., *Rev. Microbiol.* 30 (1999) 177.
- [8] Beech I.B., *Int. Biodeterior. Biodegrad.* 53 (2004) 177.
- [9] Castaneda H., Benetton X.D., *Corros. Sci.* 50 (2008) 1169.
- [10]Wagner P ; Little B. *Materials Performance*,1993,9:65-68.
- [11] Ehrlich H.I. In: *Geo-microbiology*, M.Dekker, New York, 1996, 338.
- [12] Reza Javaherdashtia, R.K. Singh Ramanb, C. Panterc, E.V. Perelomad, *Microbiologically assisted stress corrosion cracking of carbon steel in mixed and pure cultures of sulfate reducing bacteria*, *Int. Biodeter. Biodegr.* 58 (2006) 27–35.
- [13] Reza Javaherdashti, *Impact of sulphate-reducing bacteria on the performance of engineering materials*, *Appl Microbiol Biotechnol*, 91 (2011)1507–1517.
- [14] W. Sand, T. Gehrke, *Microbially Influenced Corrosion of Steel in Aqueous Environments*, *Reviews in Environmental Science and Biotechnology*, Volume 2, Issue 2-4, (2003) 169–176.
- [15] Michael J. Franklin, David C. White, Hugh S. Isaacs, *Pitting corrosion by bacteria on carbon steel, determined by the scanning vibrating electrode technique*, *Corrosion Science*, 32 (1991) 945–952.