Corrosion Inhibition Studies of Mild Steel by New Inhibitor in Different Corrosive Medium

Shylesha B.S.[1], Venkatesha T.V.[1*] and Praveen B.M.[2]
[1]Dept. of PG Studies and Research in Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta 577451, INDIA
[2]Dept. of Chemistry, Srinivas School of Engineering, Mukka, 575021, Mangalore, INDIA

Abstract

2 – methyl -3- (trifluromethyl) aniline was tested as a corrosion inhibitor for mild steel in 1 M HCl and 0.5 M H_2SO_4 separately using mass loss and electrochemical studies. The inhibition efficiencies were evaluated at different concentrations of the inhibitor. The inhibition efficiency increased with increase in inhibitor concentration. Electrochemical studies showed that the inhibitor is of mixed type with a slight predominance of anodic character. The inhibitor was more active in HCl than in H_2SO_4. The maximum inhibition efficiency approached at 0.20 m M in both the acid medium. The surface morphology of mild steel in the presence and absence of inhibitor was studied by using SEM images.

Key words: Inhibitor, mass loss; impedance, polarization, SEM.

Introduction

Most of the metals tend to corrode easily due to their thermodynamic instability. Mild steel is very prone to corrosion particularly in acidic medium. As mild steel is prominently used as structural, instrumental and industrial material, the prevention of its corrosion is very essential. Many experimental methods are employed to control the corrosion of mild steel. The use of inhibitors is one of the practical methods for preventing corrosion of mild steel especially in acidic media[1]. Organic compounds containing electron donor atoms like nitrogen, oxygen and sulphur have been found to be effective corrosion inhibitors for steel [2-4].

The existing data showing that the inhibition action of most of the organic compounds is due to the adsorption of their molecules on metal surface. The most favorable qualities possessed by compounds to act as efficient inhibitors are; the compounds should form a compact barrier films on the surface of the metal by adsorption and they should have high adsorption energy[5]. Though the use of aniline derivative as inhibitors for mild steel has been reported[6], their use as effective inhibitors for mild steel in acidic media has been rarely cited.

The present paper deals with the corrosion inhibition action of the 2 – methyl -3- (trifluromethyl) aniline on mild steel in HCl and H_2SO_4 solutions. The effect of inhibitor in different concentrations on corrosion rate is investigated by using weight loss and electrochemical measurements.

Material and Methods

The inhibitor used in this experiment was 2 – methyl -3- (trifluromethyl)aniline. The structure was shown in figure 1.

The treatment solution is different concentration of inhibitor in 1 M HCl and 0.5 M H_2SO_4. All the chemicals used were of AR grade (sd. fine chemicals Ltd., Mumbai) and doubly distilled water was used for the preparation of solutions. All the tests have been conducted in an aerated and unstirred solution. Mild steel strips having chemical composition (C-0.14%, Si-0.17%, Mn-0.35%, P-0.03%,S-0.025% the remainder being Fe.) were used. Samples were abraded with 600 grit SiC paper and degreased with acetone and then used for mass loss and electrochemical measurements.
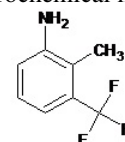

Figure-1
Structure of the inhibitor

The mass loss measurements were carried out as described elsewhere[7]. The mild steel specimens of dimension 3cm X 3cm X 0.1cm were used. The steel specimens were immersed in 400 cm^3 of solution containing different concentration of inhibitor, according to ASTM standards for 2 hour. The corrosive mediums were 1M HCl and 0.5 M H_2SO_4.

The polarization studies were carried out for steel strips having an exposed area of 1 cm^2. The specimens were mechanically polished using different grades of emery paper and washed thoroughly with distilled water and degreased with acetone. Polarization experiments were performed using different concentration of inhibitor in different corrosive medium. A conventional three-electrode compartment consisting of steel specimen, saturated calomel and platinum as the working, reference and counter electrodes respectively

were selected. Electrochemical measurements were carried out using CHI 660C electrochemical analyzer (USA make). The polarization curves were potentiodynamically obtained at open circuit potential (OCP) with a scan rate of 1mVs⁻¹. Initially the potentials were scanned in the cathodic direction from the corrosion potential and consequently in the anodic direction.

The impedance measurements were carried at OCP in the frequency range 1 mHz to 100 kHz with 5 mV sine wave as the excitation signal. The interfacial double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) values were calculated from Nyquist plots. In order to study the surface nature of the steel specimens, SEM images of steel specimens were taken after polarization studies in absence and presence of inhibitor in corrosive medium using JOEL-JEM-1200, EX II electron microscope.

Results and Discussion

Mass loss studies: The values of inhibition efficiency (η_w) obtained from mass loss experiment for the corrosion of steel in 1.0 M HCl and 0.5 M H_2SO_4 in presence of different concentration of inhibitor at 30 °C are given in table 1. The η_w was calculated from following relationship

$$\eta_w = \frac{W^{\circ} - W}{W^{\circ}} \times 100$$

Where, W° and W are weight loss of steel in absence and presence of inhibitor. The variation of η_w with different concentration of inhibitor at 30 ºC is shown in table 1. It is evident from the data that, inhibitor has remarkable protection ability, both in HCl and H_2SO_4 media, but slightly better in HCl. It showed marginal raise in η_w with concentration up to 0.15 mM for both HCl and H_2SO_4, thereafter, a appreciable rise was observed. In the given temperature, η_w increased with inhibitor concentration in both HCl and H_2SO_4 medium. This suggests magnitude of adsorption and surface coverage by inhibitor, on steel surface increases with concentration of inhibitor[8-9].

Table-1
Corrosion rate measurements by using mass loss measurements

	mM	% IE
H_2SO_4	Blank	-
	0.01	47.4
	0.05	74.0
	0.10	79.5
	0.15	80.5
	0.20	81.7
HCl	Blank	-
	0.01	53.5
	0.05	74.8
	0.10	78.1
	0.15	80.9
	0.20	84.2

Polarization studies: The polarization behavior of steel immersed in 1.0 M HCl and 0.5 M H_2SO_4 at 30 ºC in absence and presence of different concentration of inhibitor is shown figure 2.
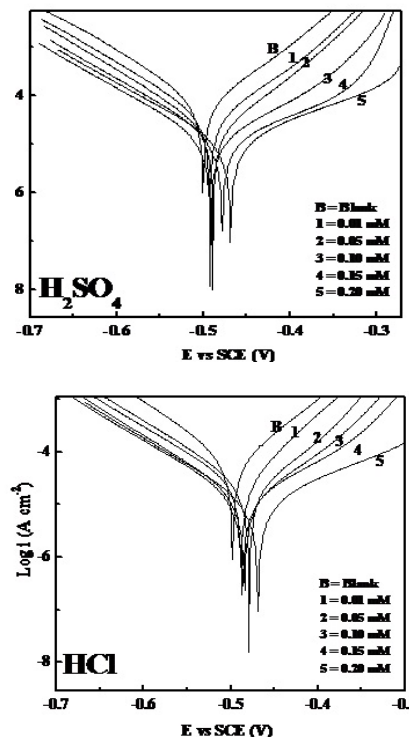

Figure-2
Polarisation profiles in different corrosive medium

Electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and percentage inhibition efficiency according to polarization studies (η_p) are listed in table 2. The η_p was calculated from following relation

$$\eta_P = \frac{I^{\circ}_{corr} - I_{corr}}{I^{\circ}_{corr}} \times 100$$

where, I°_{corr} and I_{corr} are corrosion current densities in absence and presence of inhibitor, respectively. Results mainly point out the following: (a) I_{corr} decreased with increase in concentration of inhibitor in the order HCl < H_2SO_4 which reiterates inhibitor is more effectual in HCl. (b) E_{corr} value was shifted towards less negative (noble) potential. It has been reported that[10]; a compound can be classified as an anodic or a cathodic-type inhibitor on the basis of shift in E_{corr} value. If displacement in E_{corr} is greater than 85 mV, towards anode or cathode with reference to blank, then an inhibitor is categorized as either anodic or cathodic type inhibitor. Otherwise inhibitor is treated as mixed type. In our study, maximum displacement in E_{corr} value was around 32 mV indicating inhibitor is a mixed type inhibitor. (c) β_c and β_a values have changed with respect to

inhibitor free solution, for both acids which reiterate that inhibitor is mixed type inhibitor. It can also be seen from figure 2 that shape of anodic and cathodic polarisation curve of steel in HCl looks almost similar to that in H_2SO_4. This indicates that not much difference in inhibitive mechanism of the inhibitor in HCl and H_2SO_4[11]. Obtained η_p values are in agreement with η_w values.

EIS studies: Electrochemical impedance spectra for steel in 1.0 M HCl and 0.5 M H_2SO_4 with and without different concentration of inhibitor at 30°C are presented as Nyquist plot in figure 3. The diameter of semicircle increased with inhibitor concentration and is significant in HCl, reflects the effectiveness of inhibitor[12]. An equivalent circuit model was proposed to fit and analyze EIS data is given in figure 4 [13] . EIS parameters calculated in accordance with equivalent circuit are listed in table 2. Popova et al.[14] said that sum of charge transfer resistance (R_{ct}) and adsorption resistance

(R_{ad}) is equivalent to polarisation resistance (R_p). Inhibition efficiency (η_z) was calculated using following equation.

$$\eta_Z = \frac{R_p - R_p^o}{R_p} \times 100 \qquad (4)$$

where, R_p and R_p^o are polarisation resistance values in presence and absence of inhibitor. Table 2 revealed that R_p values increased and capacitance values decreased with inhibitor concentration for both the acids. Decrease in capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer, suggests that the inhibitor molecules act by adsorption at metal/solution interface. This indicated the formation of a surface film on steel. Obtained η_z are in good agreement with η_p and η_w.

Table-2
Corrosion rate measurements by using electrochemical measurements

| Inhibitor	Inhibitor con^n (mM)	Tafel					EIS		
		E_{corr} vs SCE (mV)	I_{corr} x10^{-5}A cm^{-2}	βa mV/decade	βc mV/decade	(%) IE	R_{ct} Ωcm^2	C_{dl} (μF cm^{-2})	(%) IE
H2SO4	Blank	501	6.3	13.3	11.1	-	261	0.39	-
	0.01	493	3.2	12.9	10.8	48.1	519	0.30	49.7
	0.05	489	1.8	14.2	11.2	71.2	828	0.17	68.4
	0.1	478	1.2	07.2	10.6	79.7	1202	0.16	78.2
	0.15	492	1.2	09.8	10.0	80.5	1387	0.15	81.1
	0.2	469	1.1	06.6	09.8	81.9	1493	0.14	82.5
HCl	0.01	488	2.5	14.4	09.9	59.7	712	0.20	63.3
	0.05	479	1.8	15.5	10.4	71.8	1202	0.16	78.2
	0.1	487	1.3	09.3	09.7	78.4	1495	0.14	82.5
	0.15	484	1.2	12.6	10.4	80.7	1664	0.11	84.3
	0.2	469	1.1	06.8	09.8	82.1	2196	0.12	88.1
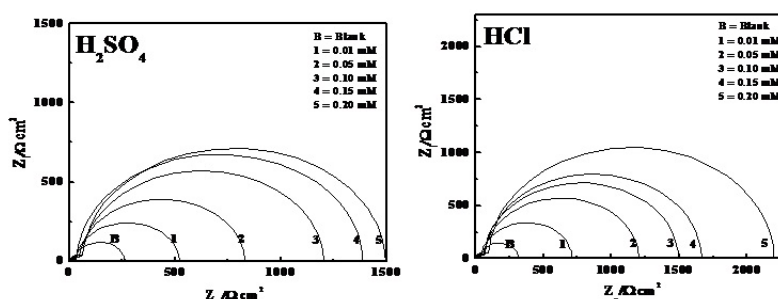
Figure- 3
Nyquist plots in HCl and H_2SO_4 containing different concentrations of inhibitor
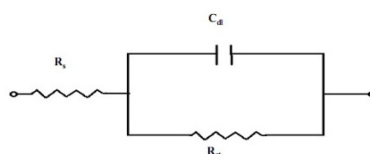

Figure-4
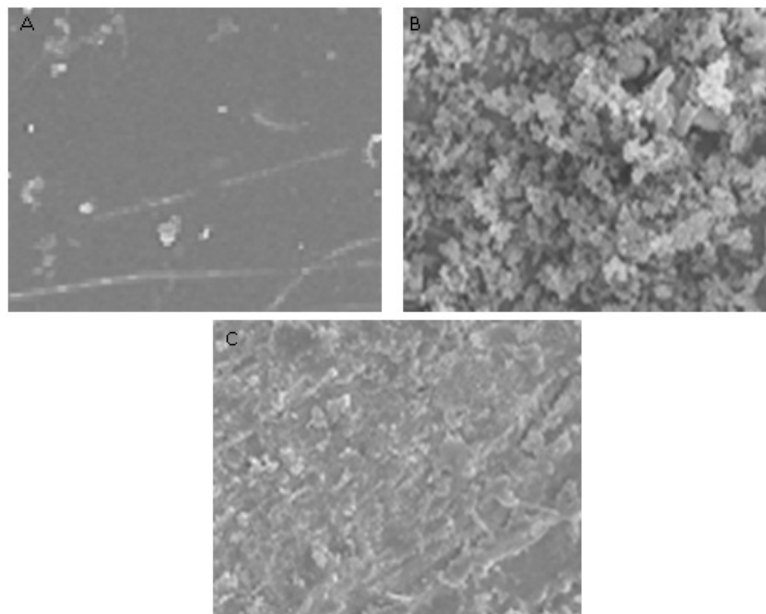**Equivalent circuit used to interpret the results of EIS**

Figure-5
SEM images of steel samples; Absence of inhibitor (a), In HCl medium at 0.20 M inhibitor (B)
In H$_2$SO$_4$ medium at 0.20 M inhibitor(C)

The surface morphology of steel surface was studied by scanning electron microscopy (SEM). Figure 5 Shows the SEM photograph of the steel surface with and without inhibitor in hydrochloric acid and sulphuric acid media. The SEM photographs showed that the surfaces of metal has pits and crevices, but in presence of inhibitor they are minimized on the metal surface . The sample in HCl medium is completely covered by the inhibitor so it gave more corrosion resistance values.

Conclusions

The Inhibitor used in this study is acts as a effective inhibitor for mild steel in both HCl and H$_2$SO$_4$, but stands slightly better in HCl. which is related to the synergistic adsorption of inhibitor molecules through acid anion Cl^{-1} on metal surface. Inhibition efficiency increased with concentration up to 0.2 Mm inhibitor concentration. Both mass loss and electrochemical studies values are agreed with each other. SEM studies supports the results obtained in both the methods.

Acknowledgements

References

1. Trabanelli G., Inhibitors-An Old Remedy for a New Challenge*, Corrosion.,* **47,** 410 -419 **(1991)**

2. Abd S.S., El-Rehim, Ibrahim M.A.M. and Khalid K.F., 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution, *J Appl. Electrochem*, **29(5),** 593-599 **(1999)**

3. Abd S.S., El-Rehim, Relay S.A.M., Taha F., Saleh M.B. and Ahmed R.A., Corrosion Inhibition of Mild Steel in Acidic Medium using 2-amino Thiophenoland 2-Cyanomethyl Benzothiazole, *J Appl. Electrochem.,* **31 (4)**, 429 – 435 **(2001)**

4. Quraishi M.A., Sardar R. and Jamal., corrosion inhibition of mold steel in hydrochloric acid by some aromatic hydrzides, *Mater. Chem. Phys*., **71 (3)** 30 -313 **(2001)**

5. Rajappa S.K. and Venkatesha T.V., New condensation products as corrosion inhibitors for mild steel in an hydrochloric acid medium, *Indian J Eng. Mater Sci,.* **(9),** 213 -217 **(2002)**

6. Quraishi M.A. and Danish Jamal., Dianils as new and effective corrosion inhibitors for mild steel in acidic solutions, *Mater. Chem. Phys*., **78(3)**, 608– 613 **(2003)**

7. Prabhu R.A., Shanbhag A.V. and Venkatesha T.V., Influence of tramadol [2-[(dimethylamino) methyl]-1-(3-methoxyphenylcyclohexanolhydrate] on corrosion inhibition of mild steel in acidic media, *J.App. Electrochem,* **37(4),** 491-497 **(2007)**

8. Singh Ashish Kumar and Quraishi M.A., Effect of Cefazolin on the corrosion of mild steel in HCl solution, Corros. Sci., **52(1)**, 152–160 **(2010)**

9. Ahamad I., Gupta C., Prasad R. and Quraishi M.A., An experimental and theoretical investigation of adsorption characteristics of a Schiff base compound as corrosion inhibitor at mild steel/hydrochloric acid interface, *J Appl Electrochem*, **40(12)**, 2171–2183 **(2010)**

10. Ahamad Ishtiaque, Prasad Rajendra and Quraishi M.A., Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steel in acidic media, *Corros. Sci.,* **52 (4),** 1472–1481 **(2010)**

11. Aljourani J., Golozar M.A., and Raeissi K., The inhibition of carbon steel corrosion in hydrochloric and sulfuric acid media using some benzimidazole derivatives, *Mater. Chem. Phys*., **121(12),** 320–325 **(2010)**

12. Shanbhag A.V., Venkatesha T.V., Prabhu R.A., Kalkhambkar R.G. and Kulkarni G.M., Corrosion inhibition of mild steel in acidic medium using hydrazide derivatives, *J Appl. Electrochem,* **38 (3)**, 279–287 **(2008)**

13. Ying Yan., Weihua Li., Lankun Cai. and Baorong Hou., Electrochemical and quantum chemical study of purines as corrosion inhibitors for mild steel in 1 M HCl solution, *Electrochim. Acta,* **53 (20),** 5953–5960 **(2008)**

14. Popova A., Raicheva S., Sokolova E. and Christov M., Frequency Dispersion of the Interfacial Impedance at Mild Steel Corrosion in Acid Media in the Presence of Benzimidazole Derivatives, Langmuir, **12 (8),** 2083-2089 **(1996)**