



ELECTROCHEMICAL AND SURFACE ANALYSIS STUDIES ON CORROSION INHIBITION OF MILD STEEL BY 1-(8-HYDROXY QUINOLIN-2-YLMETHYL)THIOUREA

S. S. Syed Abuthahir,^[a,b] A. Jamal Abdul Nasser,^[a] S. Rajendran^{[b]*}

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1-(8-Hydroxyquinolin-2-yl-methyl)thiourea (HTF) has been used as a corrosion inhibitor in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm of Cl⁻. Weight loss method reveals that 250 ppm of HTF + 25 ppm of Zn²⁺ provide 95% of inhibition efficiency. Polarization study indicates that the system controls anodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. The protective film has been analyzed using Fourier Transform Infrared and fluorescence spectra.

* Corresponding Authors

E-Mail: srmjoany@sify.com

[a] Post Graduate & Research Department of Chemistry, Jamal Mohamed College, Tiruchirappalli 620 020, India. Email : syedchem05@gmail.com, ajanasser@yahoo.com

[b] Department of Chemistry, RVS School of Engineering and Technology, Dindigul-624 005, India.

Introduction

Water contains many corrosive electrolytes such as NaCl, MgCl₂ etc. Hence mild steel immersed in water containing NaCl is corroded slowly because of chemical reactions between the metal and the electrolytes.¹⁻³ Corrosion is the gradual destruction of materials usually by chemical reaction with its environment. The corrosion is severe due to the presence of Cl⁻ ions and dissolved oxygen. Water has been used as cooling fluid in various industries. Mild steel is widely used in infrastructure in marine environments.⁴ It is one of the major constituents in structural steel applications including body of a ship, offshore platforms, foundation piling, sheet piling and coastal facilities. It is also used in industry where the metal is exposed to acid corrosion. So it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in water. Inhibition of corrosion and salting can be done by the applications of inhibitors which is one of the most practical and economic methods for protection against metallic corrosion.⁵⁻⁶ The use of inhibitor is one of the most practical methods to protect the metal from corrosion.⁷⁻⁸ Most of the effective inhibitors are compounds containing in their structures, nitrogen, phosphorous and sulphur. Heteroatom's such as nitrogen, phosphorous and sulphur are capable of forming coordinate covalent bond with metal owing to their free electron pairs and thus acting as inhibitor.⁷⁻⁹ This inhibitor used in protection against the corrosion of certain metals such as Ni, Co, Cu, iron and steel.¹⁰⁻¹¹ The aim of the present study was to investigate the corrosion inhibition for HTF to mild steel immersed in aqueous solution containing 60ppm Cl⁻. The corrosion inhibition efficiencies were evaluated using weight loss methods and Polarization spectra. The protective film formed on the metal surface

characterized with the help of surface analytical techniques such as fluorescence, UV-Visible and Fourier Transform Infrared Spectroscopy.

Experimental Procedure

Mild steel specimens; (0.0267% S, 0.067% P, 0.4 % Mn, 0.1 % C and the rest iron) of dimensions 1.0 cm ×4.0×0.2 cm were polished to mirrors finish and degreased with acetone and used for weight loss method.

Weight loss method

Mild steel specimens triplicate were immersed in 100 ml beaker containing 100 ml of aqueous solution containing 60 ppm of Cl⁻ containing various concentrations of the HTF-inhibitors and Zn²⁺ for one day. After one day immersion the specimens were taken out, washed in running water, dried and weighed using a Shimadzu balance, model AY62.

The corrosion inhibition efficiency (IE) was calculated using the equation:

$$IE (\%) = 100 \left(1 - \frac{W_2}{W_1} \right) \quad (1)$$

where

W_1 is the corrosion rate in the absence of inhibitor

W_2 is the corrosion rate in the presence of inhibitor.

Potentiodynamic polarization study

Polarization studies were carried out in a CHI electrochemical workstation with impedance model 643, Austin, USA. A three electrode cell assembly was used. The working electrode was mild steel. The exposed surface area was 1 cm². A saturated calomel electrode (SCE) was

Table 1. Corrosion rates (*CR*) of mild steel immersed in an aqueous solution containing 60 ppm Cl⁻ in the presence and absence of inhibitor systems at various concentrations and the inhibition efficiency (*IE*, %) obtained by weight loss method.

Cl ⁻	HTF, ppm	Zn ²⁺ , ppm	CR, mdd	IE, %
60	0	0	34.55	-
60	0	25	10.36	70
60	50	25	7.25	79
60	100	25	6.91	80
60	150	25	5.52	84
60	200	25	3.45	90
60	250	25	1.72	95

used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The results such as Tafel slopes, I_{corr} , E_{corr} and LPR values were calculated.

Surface characterization studies

The mild steel specimens were immersed in various test solution for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

FTIR studies

The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The film formed on the metal surface was carefully removed and mixed thoroughly with KBr making the pellet.

Surface analysis by fluorescence spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco-F-6300 spectra fluorometer.

Results and Discussion

The corrosion rates (*CR*) of mild steel immersed in aqueous solution containing 60 ppm Cl⁻ and also inhibition efficiencies (*IE*) in the absence and presence of inhibitor (HTF) and Zn²⁺ obtained by weight loss method are given in Table 1. It is observed from Table.1 that HTF + Zn²⁺ shows good inhibition efficiency. The formulation consisting of 250 ppm of HTF and 25 ppm of Zn²⁺ has 95% inhibition efficiency.

Analysis of polarization curves

The polarization study has been used to investigate the formation of protective film on metal surface.¹²⁻¹⁶ The polarization curves of mild steel immersed in aqueous solution containing 60 ppm of Cl⁻ are shown in Figure 1. The corrosion parameters such as Corrosion potential (E_{corr}), Corrosion Current density (I_{corr}), Tafel slopes (b_c and b_a) and linear polarization curves (LPR) are given in Table 2.

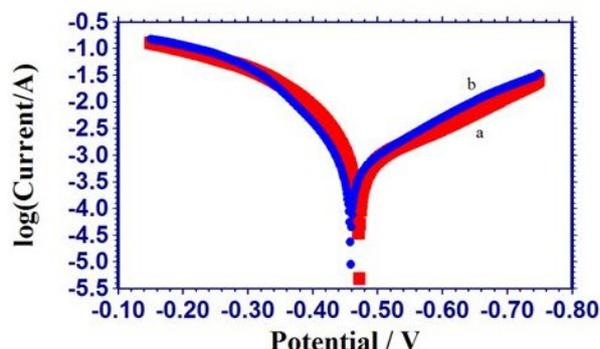


Figure 1. Polarization Curves of mild steel immersed in various test solutions: (a) Mild steel immersed in aqueous solution containing 60 ppm of Cl⁻ (b) Mild steel immersed in 250 ppm of HTF + 25 ppm of Zn²⁺.

When mild steel is immersed in aqueous solution containing 60 ppm of Cl⁻, the corrosion potential is -472 mV Vs SCE. The formulation consisting of 250 ppm of HTF + 25 ppm of Zn²⁺ shifts the corrosion potential to -459. It shows that the corrosion potential is shifted to positive side. This suggests that the anodic reaction is controlled predominantly.

The corrosion current density value and LPR value for aqueous solution containing 60 ppm of Cl⁻ are 1.261×10^{-3} A cm⁻² and 25.74 ohm cm² respectively. For the formulation of 250 ppm of HTF and 25 ppm of Zn²⁺ the corrosion density value has decreased to 8.207×10^{-4} A cm⁻² and the LPR value has increased to 30.58. The fact that the LPR value increases with decrease in corrosion current density indicates the absorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface.

Analysis of the UV-visible spectra

The UV-Visible absorption spectrum of an aqueous solution containing HTF is shown in Figure 2. A peak appears at 450 nm. When Fe²⁺ solution is added to the solution the intensity of the UV-Visible spectra increases at 600nm. This peak is due to formation of Fe²⁺-HTF complex in solution.^{17,18}

Table 2. Corrosion parameters of mild steel in aqueous solution containing 60 ppm of Cl⁻ in the absence and presence of inhibitor obtained by polarization method.

Systems	E_{corr} , mV vs SCE	I_{corr} , A cm ⁻²	b_a , mV/dec ⁻¹	b_c , mV dec ⁻¹	LPR, Ω cm ²
60 ppm Cl ⁻	-472	1.261×10^{-3}	117	140	25.74
60 ppm Cl ⁻ + 250 ppm HTF + 25 ppm Zn ²⁺	-459	8.207×10^{-4}	096	144	30.58

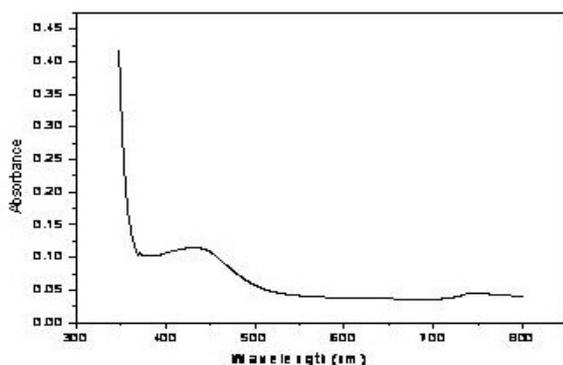


Figure 2a. UV-absorption spectrum solution containing HTF

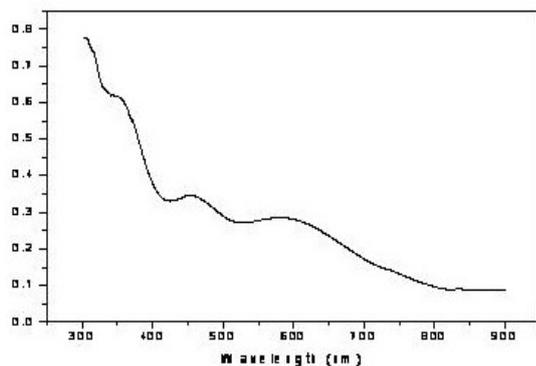


Figure 2b. UV- absorption spectra solution containing HTF-Fe²⁺

Fluorescence spectra

The emission spectrum (λ_{ex} : 460nm) of solution containing HTF-Fe²⁺ solution is shown in Figure 3a. The emission spectrum of the film formed on the metal surface after immersion in solution containing 250 ppm of HTF and 25 ppm of Zn²⁺ is shown in Figure 3b.

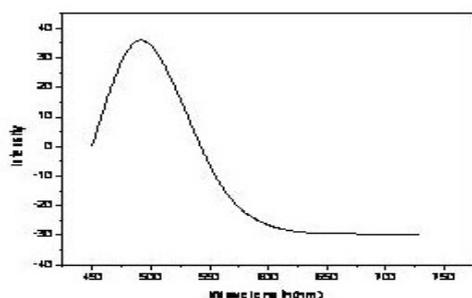


Figure 3a. Fluorescence spectrum of HTF solution

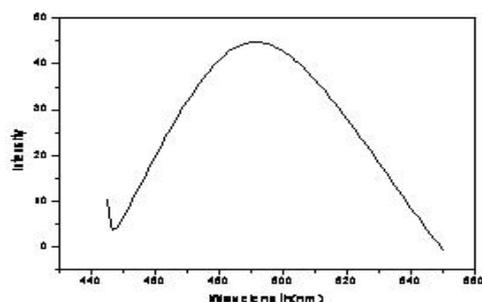


Figure 3b. Fluorescence spectra of solution containing HTF-Fe²⁺ complex.

A peak appears at 490nm. Hence it is concluded that the protective film consists of HTF-Fe²⁺ complex. The number peak obtained is only one. Hence it is confirmed that the complex of somewhat highly symmetric in solution.¹⁹

Analysis of FTIR spectrum

The FTIR spectra have been used to analyze the film formed on the metal surface.²⁰ The FTIR spectrum (KBr) of pure HTF is shown in figure 4a. The OH stretching frequency appears at 3300.34 cm⁻¹. The C=S stretching frequency appears at 1150.28 cm⁻¹. The CH stretching frequency appears at 3084.93 cm⁻¹. The peak due to secondary nitrogen (NH) appears at 3194.52cm⁻¹. The peak due to pyridine nitrogen (C=N) appears at 1490.36 cm⁻¹. The peak due to aromatic C=C appears at 1250.17 cm⁻¹.

The FTIR spectrum (KBr) of the film formed on the metal surface after immersion in the aqueous solution containing 60 ppm of Cl⁻ + 250 ppm of HTF + 25 ppm of Zn²⁺ for a period of one day is shown in Figure 4b. The phenolic OH stretching frequency has shifted from 3390.34 cm⁻¹ to 3490 cm⁻¹. The pyridine nitrogen frequency has shifted from 1490.36 cm⁻¹ to 1600 cm⁻¹. There is not much shift in other functional groups like C=S, NH and benzene ring. Thus it is concluded that oxygen atom of phenolic group and nitrogen atom of pyridine ring have coordinated with Fe²⁺ formed on the metal surface. The structure of the resulting HTF-Fe²⁺ complex is shown in Figure 5.

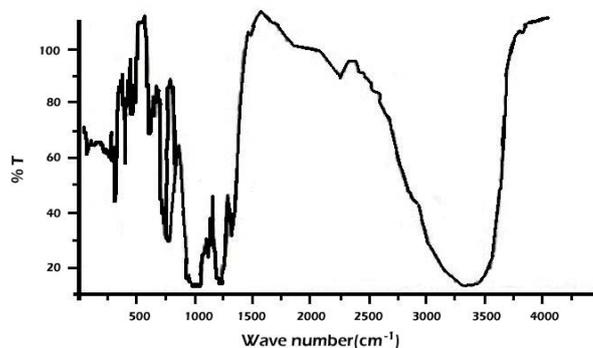


Figure 4a. FTIR spectrum of pure HTF

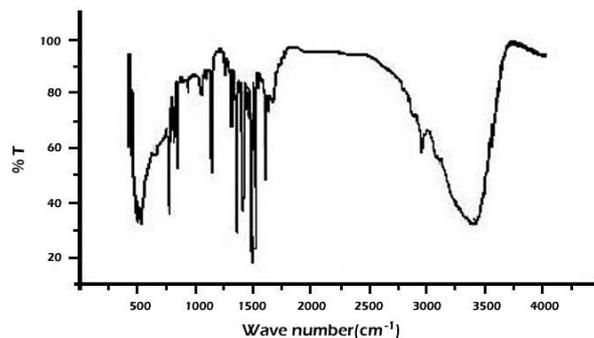


Figure 4b. FTIR spectrum of film formed on metal surface after immersion in solution containing 60 ppm Cl⁻ + 250 ppm of HTF + 25 ppm of Zn²⁺

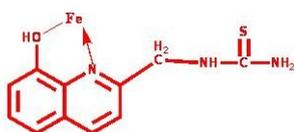


Figure 5. Structure of Fe^{2+} complex

This view is in agreement with the structure proposed by Albrecht et al. for zinc complex.²¹

Conclusion

The conclusion drawn from the results may be given as : the formulation consisting of 250 ppm of HTF and 25 ppm of Zn^{2+} has 95% inhibition efficiency. Polarization study suggests that anodic reaction is controlled predominantly. FTIR spectra show that the protective film consists of HTF- Fe^{2+} complex formed on metal surface.

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