CORROSION INHIBITION OF MILD STEEL IN SODIUM CHLORIDE SOLUTION BY NICKEL COMPLEX OF 1-(8-HYDROXY QUINOLIN-2YL-METHYL) THIOUREA

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Abstract: -
The Corrosion inhibition efficiency of an inhibitor namely Nickel complex of 1-(8-hydroxy quinolin-2ylmethyl) thiourea (Ni-HTF) in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm Cl⁻ has been investigated by polarization method. The formulation consisting of 60 ppm of Cl⁻ and 50 ppm of Ni-HTF offers good inhibition efficiency of 80 %. Polarization study reveals that this formulation functions as a cathodic inhibitor. UV-Visible spectral analysis was used to detect the presence of iron-inhibitor complex. The surface morphology has been analyzed by SEM and EDAX.

Key words: *Corrosion inhibition, Mild Steel, Polarization, UV-Visible spectroscopy, Transition metal complex, SEM, EDAX and Biocidal Efficiency.*

INTRODUCTION

Corrosion inhibitors are substances which when added in small concentrations to corrosive media decreases or prevent the reaction of the metal with the media [1]. The use of inhibitors is one of the most practical methods for protecting metals or alloys from corrosion. Compared with inorganic salt corrosion inhibitors, using organic corrosion inhibitors is an effective, inexpensive and less pollution means of reducing the degradation of metals or alloys in many fields of applications and which has been extensively investigated during the last decade [2-8]. It is generally acknowledged that the hetero atoms such as N, S and O in organic compounds show an inhibition effect toward the corrosion of iron, copper and nickel alloys. The main role of hetero atoms in the corrosion protection is the formations of insoluble deposits on inter metallic inclusions. Metal complexes are widely used as catalyst of chemical reactions, e.g. Oxidative dehydrogenation (ODH) of ethane and epoxidation of geraniol [9-11] and as stabilizer or precursor in sol-gel processes [12-14]. Very few works have been performed to study anticorrosive behavior of metal complexes. Harms et al.[15] proposed corrosion inhibition through precipitation of Fe(II) phosphate and Fe(III) phosphate in presence of Fe(III) acetylacetonate and Fe(II) acetylacetonate respectively. Palladium acetylacetonate is suggested as an effective corrosion inhibitor for water cooled nuclear reactor [16]. Interaction of transition metal complexes with mild steel is greatly affected by their standard electrode potentials, their reactivity and the nature of the ligand that could stabilize the metallic complexes. Reduction of Cu (II) and Co (II) species on mild steel surface is possible due to their noble standard electrode potential compared to Fe (II). However, it should be noted that negative charged ligands like nitro, thiocyanate, Oxalato, glucinato and acetylacetonate could stabilize the higher oxidation states [17]. The aim of the present work is to evaluate corrosion inhibitive performance of Nickel Complex of 1-(8-hydroxy quinolin-2yl-methyl) thiourea to mild steel immersed in aqueous solution containing 60 ppm Cl^-. The corrosion inhibition efficiency was evaluated using weight loss method and electrochemical impedance spectroscopy. The protective film formed on the metal surface characterized with the help of surface analytical techniques such as fluorescence and FTIR spectroscopy.

Materials and Methods

Mild steel specimens; (0.026% S, 0.068% P, 0.36 % Mn, 0.13 % C and the rest iron) of dimensions 1.0 cm $\times$4.0$\times$0.2 cm were polished to mirrors finish and degreased with acetone and used for weight loss method.

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 cm^2. A saturated calomel electrode (SCE) was 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 mid 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.

Surface analysis by UV-Visible spectroscopy

UV-Visible spectra were recorded in a Cary Eclipse Varian (Model U.3400) spectrophotometer.

SEM Analysis

SEM (Tescan, Vega 3, USA) provides a pictorial representation in the surface to understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of mild steel. The SEM micrographs of the surface are examined.

Energy Dispersive Analysis of X-rays (EDAXs)

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, dried and observed in an Energy Dispersive Analysis of X-rays (EDAXs) to examine the elements presents on the metal surface. The elements present on the metal surface were examined using Bruker computer-controlled Energy Dispersive Analysis of X-rays (Brucker, Nano, GMBH, Germany).

Bacterial Enumeration

Bacterial cell are count based on their colony forming unit (CFU) by standard plate count. The protocols are as follows. Label the plate 10^{-2}, 10^{-4}, 10^{-6} and 10^{-8} at the bottom of plate and one plate as a blank or control. Using aseptic technique transfer 1ml of four different cultures to 99ml of sterile saline blank. A test tube labelled 10^{-2} and the dilution is proceeded by taking 1ml from 10^{-2} test tube to the next 99ml sterile saline blank labeled as to the next 99ml sterile saline blank labeled as 10^{-4} and proceed until 10^{-8}. Shake all the test tubes for equal distribution of bacteria. Transfer 1ml of the sample into each of the labelled plates 10^{-2} to 10^{-8} correspondingly. Containing agar medium all the plates are immersed and incubate at 37^0C for 24 hours. After the incubation, select the plate containing 30 to 300 colonies and count the colonies. The number of CFU are calculated as

CFUs/dilution $\times$ amount plated = No.of bacterial cell / ml.

Results and Discussion

Analysis of Polarization Curves

The polarization study has been used to investigate the formation of protective film on metal surface [18-22].

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 1.
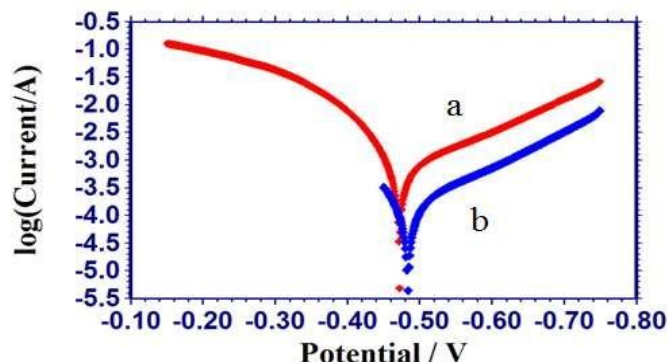

Figure 1. Polarization curves of mild steel immersed in various test solutions: a) Mild steel immersed in aqueous solution containing 60 ppm of Cl^- b) Mild steel immersed in 60ppm of Cl^- + 50ppm of Ni- HTF

Systems	E_{corr} (mV vs SCE)	Icorr (A/cm^2)	b_a (mV/dec)	bc (mV/dec)	LPR (ohm cm^2)
60 ppm Cl^-	- 472	1.261×10^{-3}	124	187	25.74
60 ppm Cl^- + 50 ppm Ni-HTF	- 483	5.486×10^{-4}	180	170	132.5

Table 1. Corrosion parameters of mild steel in aqueous solution containing 60 ppm of Cl^- in the absence and presence of Ni-HTF inhibitor obtained by polarization method.

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 50 ppm of Ni-HTF shifts the corrosion potential to -483 mV Vs SCE. It shows that the corrosion potential is shifted to negative side. This suggests that the cathodic 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 cm^2 respectively. For the formulation of 50 ppm of Ni-HTF the corrosion density value has decreased from 1.261×10^{-3}A cm^{-2} to 5.486×10^{-4}A cm^{-2} and the LPR value has increased from 25.74 ohm cm^2 to 132.5 ohm cm^2. 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 a spectrum of an aqueous solution containing Ni-HTF is shown in figure 2. A peak appears at 356nm. When Fe^{2+} solution is added to the solution the intensity of the UV-Visible spectra increases at 580nm. This peak is due to formation of Fe^{2+}-HTF complex in solution [23, 24].
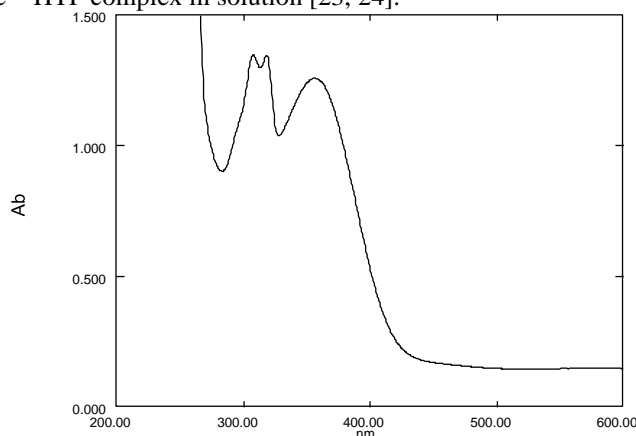

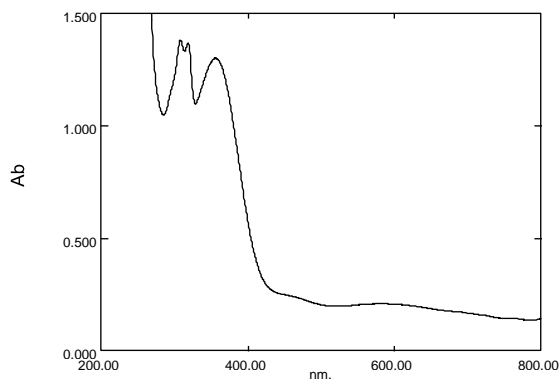**Figure 2a.UV-absorption spectrum solution containing Ni-HTF**

Figure 2b.UV- absorption spectra solution containing HTF-Fe^{2+}

It is proposed that oxygen atom of phenolic group and nitrogen atom of pyridine ring have coordinated with Fe^{2+} formed on the metal surface. The structure of the resulting HTF-Fe^{2+} complex is shown in figure 3.
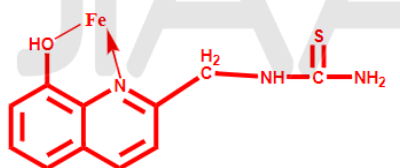

Figure 3. Structure of Fe^{2+} complex

This view is in agreement with the structure proposed by Albrecht et al. for zinc complex [25].

SEM Analysis of Metal Surface

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of mild steel, the SEM micrographs of the surface are examined [26-28]. The SEM images of different magnification (×20) of mild steel specimen immersed in aqueous containing 60ppm Cl$^-$ for one day in the absence and presence of inhibitor system are shown in figures 4(a), 4(b) and 4(c) respectively. The SEM micrographs of polished mild steel surface (control) in figure 4 (a) show the smooth surface of the metal. This shows the absence of any corrosion products (or) inhibitor complex formed on the metal surface. The SEM micrographs of mild steel immersed in aqueous containing 60ppm Cl$^-$ (Figure 4 (b)) show the roughness of the metal surface which indicates the highly corroded area of mild steel. However, Figure 4 (c) indicates that in the presence of inhibitor (60 ppm Cl$^-$ + 50 ppm Ni- HTF) the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The metal surface is almost free from corrosion due to the formation of insoluble complex on the surface of the metal [26].
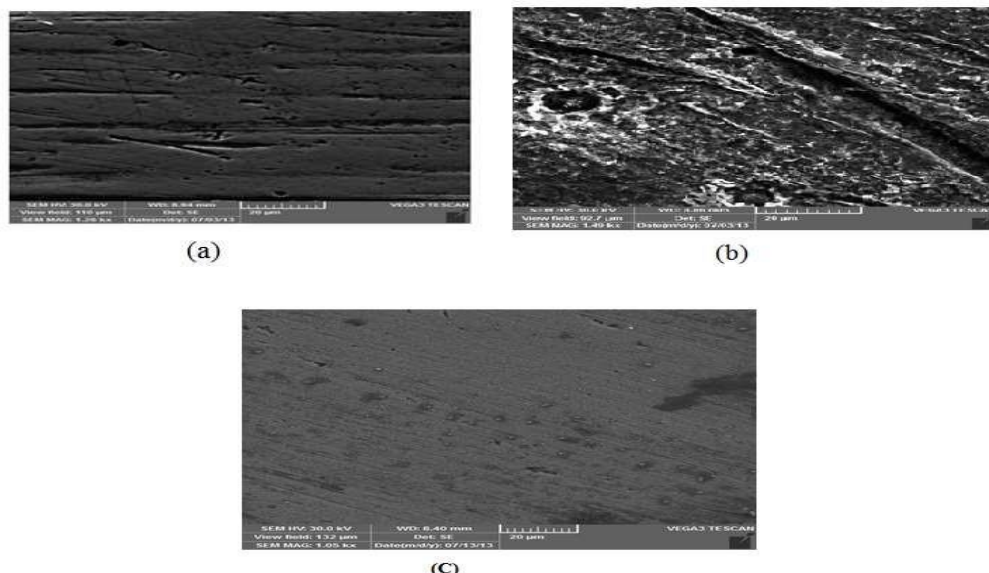

Figure 4: SEM analysis of mild steel; magnification × 20 (control). (b) Mild steel immersed in aqueous solution containing 60ppm of Cl$^-$, magnification × 20 (blank). (c) Mild steel immersed in aqueous solution containing 60ppm of Cl$^-$ + 50ppm of Ni- HTF magnification × 20

Energy Dispersive Analysis of X-Rays (EDAXs)

The EDAXs survey spectra were used to determine the elements present on the metal surface before after exposure to the inhibitor solution [27-30]. The objective of this section was to confirm the results obtained from chemical and electrochemical measurements that a protective surface film of inhibitor is formed on the metal surface. To achieve this, EDAX examinations of the metal surface were performed in the absence and presence of inhibitors system [27-30].

EDAX spectrum of mild steel immersed in aqueous solution containing 60 ppm Cl$^-$ is shown in Figure 5 (a). They show the characteristics peaks of some of the elements constituting the mild steel sample. The EDAX spectrum of mild steel immersed in aqueous solution containing 60 ppm Cl$^-$ + 50 ppm Ni- HTF is shown in figure 5 (b). It shows the additional line characteristic for the existence of Ni. In addition, the intensity of O signals is completely varnished and the intensity of Fe signal is increased. The appearance of Ni, Fe and other elements signal are due to the presence of inhibitor. These data show that metal surface covered the Fe, S, Ni, P and Mn atoms.
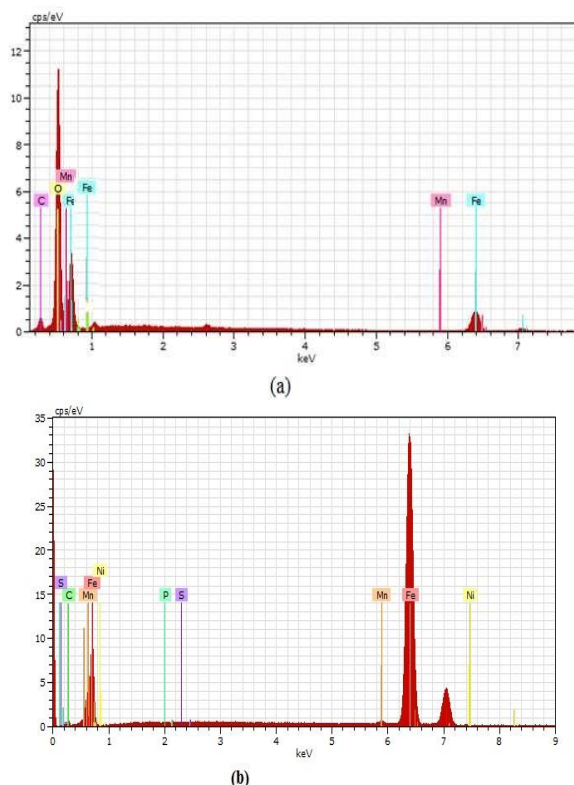

Figure 5: EDAX spectra of (a) Mild steel sample after immersion in aqueous solution containing 60 ppm of Cl$^-$. (b) Mild steel sample after immersion in aqueous solution containing 60 ppm of Cl$^-$ + 50 ppm of Cu- HTF.

Bacterial Enumeration count

The results of bacterial enumeration count [31] of the aqueous solution containing 60 ppm of Cl$^-$ and 60ppm of Cl- with Ni-HTF inhibitor are presented in Table 2. The aqueous solution containing 60 ppm of Cl$^-$ without inhibitor shows more bacterial count against the growth of pathogenic bacteria strains such as E.Coli, Streptococcus, Pseudomonas and Entrobacter. The aqueous solution containing 60 ppm of Cl$^-$ with inhibitor Ni-HTF shows less bacterial count against the growth of pathogenic bacteria strains such as E.Coli, Streptococcus, Pseudomonas and Entrobacter. A good result was obtained when addition of Ni-HTF inhibitor to the corrosive media.

Systems	Colonies Forming Unit (per ml)			
	E.Coli	Streptococcus	Pseudomonas	Entrobacter
60 ppm Cl$^-$	140×10^6	146×10^6	130×10^6	127×10^6
60 ppm Cl$^-$ + 50 ppm Ni-HTF	49×10^6	58×10^6	64×10^6	63×10^6

Table 2. Colonies forming unit (CFU) of mild steel in aqueous solution containing 60 ppm of Cl$^-$ in the absence and presence of Ni-HTF inhibitor obtained by bacterial enumeration count method.

Conclusion

The present study leads to the following conclusions. The formulation consisting of 60 ppm of Cl$^-$ and 50 ppm of Ni-HTF offers 80% inhibition efficiency in controlling corrosion of mild steel. Polarization study suggests that cathodic reaction is controlled predominantly and reveal that a protective film is formed on the metal surface. UV-Visible spectra reveals that the protective film consists of HTF-Fe^{2+} complex formed on metal surface. SEM and EDAX confirm the presence of a protective film on the metal surface. The bacterial enumeration has been reduced by the addition of Ni-HTF inhibitor to the corrosive media.

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