



# HIGHLY EFFECTIVE INORGANIC CORROSION INHIBITOR FOR MILD STEEL IN SODIUM CHLORIDE SOLUTION

S. S. Syed Abuthahir,<sup>[a]</sup> A. Jamal Abdul Nasser,<sup>[a]</sup> S. Rajendran<sup>[b]\*</sup>

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The corrosion inhibition of a inhibitor namely nickel complex of 1-(8-hydroxyquinolin-2-yl-methyl)thiourea (Ni-HTF) in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm Cl<sup>-</sup> has been investigated electrochemically and weight loss method. The formulation consisting of 60 ppm of Cl<sup>-</sup> and 50 ppm of Ni-HTF offers good inhibition efficiency of 80 %. AC impedance spectra reveal that a protective film is formed on the metal surface. Fluorescence spectral analysis was used to detect the presence of iron-inhibitor complex. The surface morphology has been analyzed by FTIR spectroscopy.

\* 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](mailto:syedchem05@gmail.com), [ajanasser@yahoo.com](mailto:ajanasser@yahoo.com)

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

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.

## Introduction

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.<sup>1-7</sup> 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 aluminium 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<sup>8-10</sup> and as stabilizer or precursor in sol-gel processes.<sup>11-13</sup> Very few works have been performed to study anticorrosive behavior of metal complexes. Harms et al.<sup>14</sup> 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.<sup>15</sup> 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 ions could stabilize the higher oxidation states.<sup>16</sup> The aim of the present work is to evaluate corrosion inhibitive performance of nickel complex of 1-(8-hydroxyquinolin-2-ylmethyl)thiourea to mild steel immersed in aqueous solution containing 60 ppm Cl<sup>-</sup>. The corrosion inhibition efficiency was evaluated using weight

## 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 ×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<sup>-</sup> containing various concentrations of the nickel complex of 1-(8-hydroxyquinolin-2-ylmethyl)thiourea inhibitors 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 and  $w_2$  is the corrosion rate in the presence of inhibitor.

### AC impedance spectra

The instrument used for polarization study was also used for AC impedance spectra. The cell set up was the same as that was used for polarization measurements. The real part ( $Z'$ ) and the imaginary part ( $Z''$ ) of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initials  $E_{(v)}=0$  V, high frequency limit was  $1 \times 10^5$  Hz, low frequency limit was 1 Hz,

amplitude = 0.005 V and quiet time  $t_q=2$  s. The values of charge transfer resistance  $R_t$  and the double layer capacitance  $C_{dl}$  were calculated.

$$C_{dl} = \frac{1}{2} \pi R_t f_{max} \quad (2)$$

where  $f_{max}$  is maximum frequency.

### 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.

### 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.

### Surface analysis by FTIR spectroscopy

The spectra were recorded in a Bruker (Model Tensor 27) spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets and the FTIR spectra were recorded.

## 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 nickel complex of 1-(8-hydroxyquinolin-2-ylmethyl)thiourea obtained by weight loss method are given in Table 1. It is observed from Table 1 that Ni-HTF shows 80 % inhibition efficiency. As the concentration of inhibitor increases, the inhibition efficiency decreases. This may be due to the fact that as the concentration of inhibitor increases, the protective film formed on the metal surface goes into solution. Similar observation has been made by A. Sahaya Raja et.al while studying the controlling corrosion of mild steel in well water by eco-friendly inhibitor glycine- $Zn^{2+}$  system.<sup>17</sup>

**Table1.** Corrosion rates ( $CR$ ) of mild steel immersed in an aqueous solution containing 60 ppm  $Cl^-$  in the presence and absence of Ni-HTF inhibitor systems at various concentrations and the inhibition efficiency ( $IE$  %) obtained by weight loss method.

$Cl^-$ , ppm	Ni-HTF, ppm	$CR$ , mdd	$IE$ , %
60	0	34.55	-
60	50	6.91	80
60	100	12.78	63
60	150	14.51	58
60	200	21.76	37
60	250	23.49	32

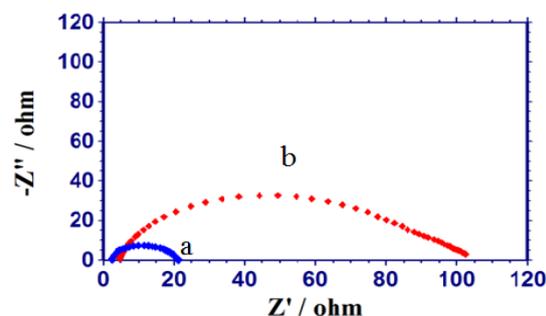
### AC impedance spectra

AC impedance spectra [electrochemical impedance spectra] have been used to confirm the formation of protective film on the metal surface.<sup>18-21</sup> The AC impedance spectra of mild steel immersed in aqueous solution containing 60ppm of  $Cl^-$  in the absence and presence of inhibitors are shown in Fig.1 (Nyquist plots) and Fig.2 (Bode plots). The impedance parameters namely charge transfer resistance ( $R_t$ ) double layer capacitance ( $C_{dl}$ ) and impedance  $\log(Z'/ohm)$  are given in Table-2. If a protective film is formed on the metal surface,  $R_t$  value increases and the  $C_{dl}$  value decreases.

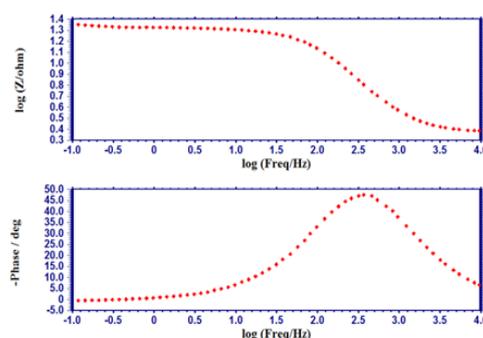
**Table 2.** The AC impedance spectra of mild steel immersed in aqueous solution containing 60ppm of  $Cl^-$  in the absence and presence of Ni-HTF inhibitor system.

Systems	$R_t$ $\Omega \text{ cm}^2$	$C_{dl}$ $F \text{ cm}^{-2}$	Impedance, $\log(Z/ohm^{-1})$
60 ppm $Cl^-$	20.19	$5.235 \times 10^{-5}$	0.973
60 ppm $Cl^-$ + 50 ppm Ni-HTF	98.47	$1.0733 \times 10^{-5}$	1.353

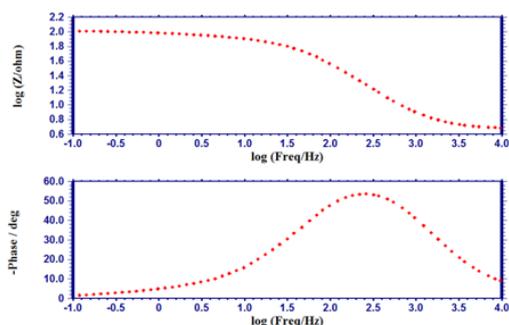
When mild steel is immersed in aqueous solution containing 60ppm of  $Cl^-$ ,  $R_t$  value is  $20.19 \Omega \text{ cm}^2$  and  $C_{dl}$  value is  $5.235 \times 10^{-5} F \text{ cm}^{-2}$ . When Ni-HTF are added to the aqueous solution containing 60ppm of  $Cl^-$   $R_t$  value increases from  $20.19 \Omega \text{ cm}^2$  to  $98.47 \Omega \text{ cm}^2$  and the  $C_{dl}$  value decreases from  $5.235 \times 10^{-5} F \text{ cm}^{-2}$  to  $1.0733 \times 10^{-5} F \text{ cm}^{-2}$ . The impedance value increases from 0.973 to 1.353. This account for the high inhibition efficiency of Ni-HTF system and a protective film is formed on the metal surface. This is also supported by the fact that for the inhibitor system the phase angle increases from  $47.88^\circ$  to  $53.66^\circ$  (Fig. 3).



**Figure 1.** AC impedance spectra (Nyquist plots) of mild steel immersed in various test solutions a) aqueous solution containing 60ppm of  $Cl^-$ . b) aqueous solution containing 60ppm  $Cl^-$  + 50 ppm Ni-HTF



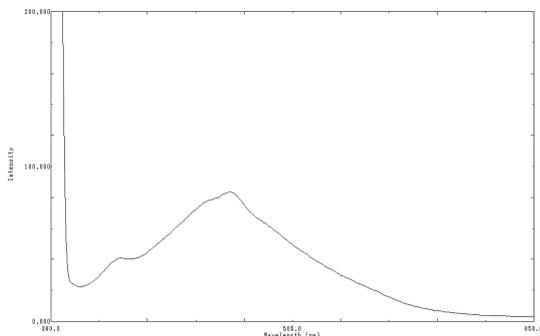
**Figure 2a.** AC impedance spectra (Bode plot) of mild steel immersed in aqueous solution containing 60 ppm of  $Cl^-$



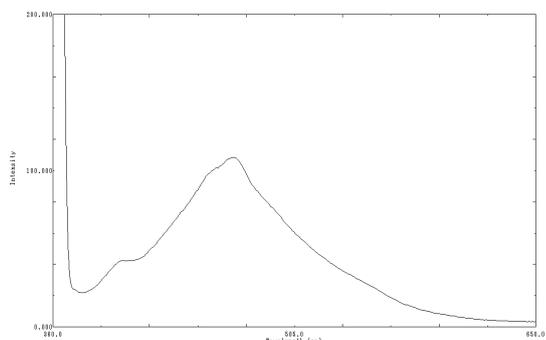
**Figure 2b.** AC impedance spectra (Bode Plot) of mild steel immersed in solution containing 60ppm of Cl<sup>-</sup> + 50ppm of Ni-HTF

### Fluorescence spectra

The emission spectrum ( $\lambda_{ex}$ : 450nm) of solution containing HTF-Fe<sup>2+</sup> solution is shown in Figure 3a. A peak appears at 460 nm. This is due to HTF-Fe<sup>2+</sup> complex formed in solution. The emission spectrum of the film formed on the metal surface after immersion in solution containing 50 ppm of Ni-HTF is shown in figure 3b. Hence it is concluded that the protective film consists of HTF-Fe<sup>2+</sup> complex. The number peak obtained is only one. Hence it is confirmed that the complex of somewhat highly symmetric in solution.



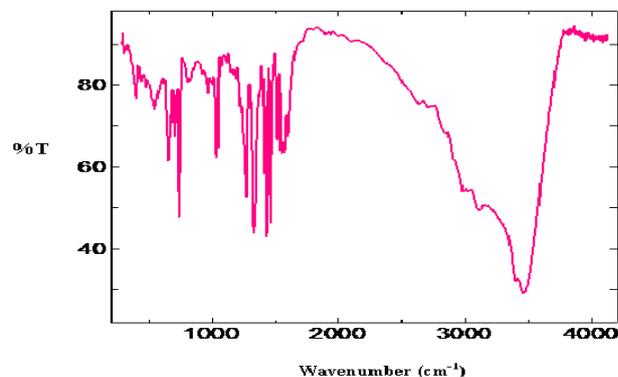
**Figure 3a.** Fluorescence spectrum of Ni-HTF solution



**Figure 3b.** Fluorescence spectra of solution containing HTF-Fe<sup>2+</sup> complex.

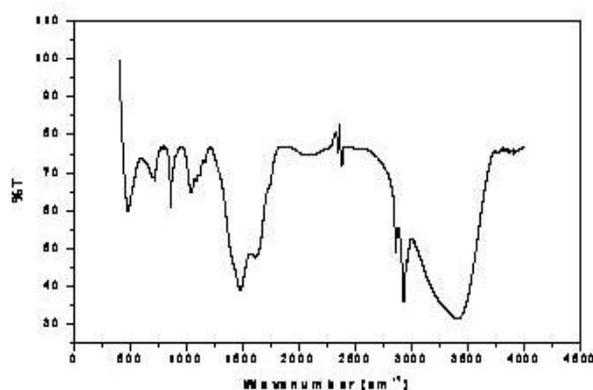
### Analysis of FTIR spectrum

The FTIR spectra have been used to analyze the film formed on the metal surface.<sup>23</sup> The FTIR spectrum (KBr) of pure Ni-HTF is shown in Figure 4a. The C=S stretching frequency appears at 1100.72 cm<sup>-1</sup>. The CH stretching frequency appears at 2940.2 cm<sup>-1</sup>. The peak due to secondary nitrogen (NH) appears at 3420.67cm<sup>-1</sup>. The peak due to pyridine nitrogen (C=N) appears at 1490.35 cm<sup>-1</sup>. The peak due to aromatic C=C appears at 1384.64 cm<sup>-1</sup>.



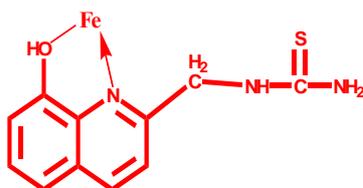
**Figure 4a.** FTIR spectrum of pure Ni-HTF

The FTIR spectrum (KBr) of the film formed on the metal surface after immersion in the aqueous solution containing 60ppm of Cl<sup>-</sup> + 50ppm of Ni-HTF for a period of one day is shown in figure 4b. The pyridine nitrogen frequency has shifted from 1490.35 cm<sup>-1</sup> to 1500 cm<sup>-1</sup>. The CH stretching frequency has shifted from 2940.2 cm<sup>-1</sup> to 2920 cm<sup>-1</sup>. The C=S stretching frequency appears at 1080 cm<sup>-1</sup>. The additional peak obtained in the region of 500 cm<sup>-1</sup> and 700 cm<sup>-1</sup> due Fe-HTF complex. Thus it is concluded that oxygen atom of phenolic group and nitrogen atom of pyridine ring have coordinated with Fe<sup>2+</sup> formed on the metal surface.



**Figure 4b.** FTIR spectrum of film formed on metal surface after immersion in solution containing 60 ppm Cl<sup>-</sup> + 50 ppm of Ni-HTF

It is proposed that oxygen atom of phenolic group and nitrogen atom of pyridine ring have coordinated with Fe<sup>2+</sup> formed on the metal surface. The structure of the resulting HTF-Fe<sup>2+</sup> complex is shown in Figure 5.



**Figure 5.** Structure of  $\text{Fe}^{2+}$  complex

This view is in agreement with the structure proposed by Albrecht et al. for zinc complex.<sup>24</sup>

## Conclusion

The results of the weight loss study shows that the formulation consisting of 60 ppm of  $\text{Cl}^-$  and 50 ppm of Ni-HTF has 80% inhibition efficiency in controlling corrosion of mild steel. AC impedance spectra reveal that a protective film is formed on the metal surface. Fluorescence spectra reveals that the protective film consists of  $\text{HTF-Fe}^{2+}$  complex formed on metal surface. The FTIR spectra shows that a protective film consists of  $\text{HTF-Fe}^{2+}$  and  $\text{Ni(OH)}_2$ .

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