



## Inhibition of Mild Steel Corrosion by Nickel Complex of 1-(8-hydroxy quinolin-2-yl-methyl) urea in Sodium Chloride solution

## KEYWORDS

Corrosion inhibition, Mild Steel, EIS, Transition metal complex

S. S. Syed Abuthahir

A. Jamal Abdul Nasser

S. Rajendran

Assistant Professor, RVS School of Engineering and Technology, Dindigul-05, Tamilnadu, India

Assistant Professor, Post Graduate & Research Department of Chemistry Jamal Mohamed College, Tiruchirappalli 620 020, Tamilnadu, India.

Professor of Chemistry, Department of Chemistry, RVS School of Engineering and Technology, Dindigul-624 005, Tamilnadu, India

## ABSTRACT

The Corrosion inhibition of a inhibitor namely Ni complex of 1-(8-hydroxy quinolin-2-yl-methyl) urea (Ni-HUF) in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm Cl<sup>-</sup> has been investigated using weight loss method. The corrosion inhibition efficiency offered by 50 ppm of Ni-HUF is 74 %. The corrosion inhibition was observed due to the formation of more stable and compact protective film on the metal surface. Fluorescence spectral analysis was used to detect the presence of iron-inhibitor complex. Polarization study and Electrochemical Impedance spectra confirm the formation of a protective film formed on the metal surface.

## Introduction

Metal complexes are widely used as catalyst of chemical reactions, e.g. Oxidative dehydrogenation (ODH) of ethane and epoxidation of geraniol [1-3] and as stabilizer or precursor in sol-gel processes [4-6]. Very few works have been performed to study anticorrosive behavior of metal complexes. Harms et al. [7] 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 [8]. 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 [9]. Hence reduction of Cu (II) and Co (II) on the steel surface could be affected by the ligands surrounded them. It is reported that sodium, zinc and calcium salts of gluconic acid could provide an effective corrosion inhibition for the mild steel immersed in near neutral media [10-13]. The effectiveness of gluconates on the anodic metal dissolution reaction and the cathodic oxygen reduction reaction in neutral solution depends on the inhibitor concentration and the nature of cations introduced in the solution as a gluconate salt [14]. The aim of the present work is to evaluate corrosion inhibitive performance of nickel complex of 1-(8-hydroxy quinolin-2-yl-methyl) urea to mild steel immersed in aqueous solution containing 60 ppm Cl<sup>-</sup>. 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 UV-Visible spectroscopy.

## Materials and Methods

Mild steel specimens; (0.026% S, 0.068% P, 0.39 % Mn, 0.11 % 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 Ni complex of 1-(8-hydroxy quinolin-2-yl-methyl) urea -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:

$$IE = 100[1 - (w_2 - w_1)] \%$$

Where  $w_1$  is the corrosion rate in the absence of inhibitor and  $w_2$  is the corrosion rate in the presence of inhibitor.

## 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<sup>2</sup>. 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.

## 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  $E_{(v)} = 0V$ , high frequency limit was  $1 \times 10^5$  Hz, low frequency limit was 1 Hz, amplitude = 0.005V and quiet time  $t_{\text{q}} = 2$  s. The values of charge transfer resistance  $R_t$  and the double layer capacitance  $C_{dl}$  were calculated.

$$C_{dl} = \frac{1}{2} \pi R_t f_{\text{max}}$$

Where  $f_{\text{max}}$  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 UV-Visible spectroscopy:**

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

**Results and Discussion**

The corrosion rates (CR) of mild steel immersed in aqueous solution containing 60 ppm Cl<sup>-</sup> and also inhibition efficiencies(IE) in the absence and presence of inhibitor Ni complex of 1-(8-hydroxy quinolin-2yl-methyl) urea obtained by weight loss method are given in Table 1. It is observed from Table-1 that Ni-HUF shows 74 % inhibition efficiency.

Cl <sup>-</sup> (ppm)	Ni-HUF (ppm)	CR (mdd)	IE (%)
60	0	34.55	-
60	50	8.98	74
60	100	11.05	68
60	150	12.78	63
60	200	16.58	52
60	250	20.03	42

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

**Analysis of Polarization Curves:**

The polarization study has been used to investigate the formation of protective film on metal surface [15-19]. The polarization curves of mild steel immersed in aqueous solution containing 60 ppm of Cl<sup>-</sup> are shown in Figure 1. The corrosion parameters such as Corrosion potential (E<sub>corr</sub>), Corrosion Current density (I<sub>corr</sub>), Tafel slopes (b<sub>c</sub> and b<sub>a</sub>) and linear polarization curves (LPR) are given in Table 2.

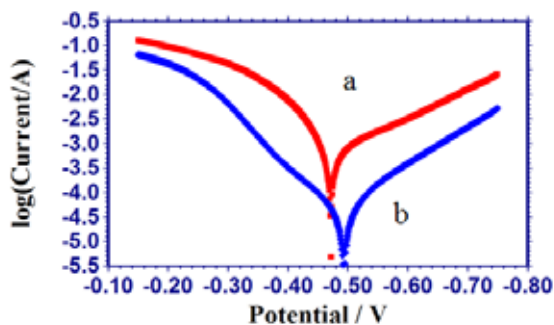


Figure 1. Polarization curves of mild steel immersed in various test solutions: a) Mild steel immersed in aqueous solution containing 60ppm of Cl<sup>-</sup> b) Mild steel immersed in 60ppm of Cl<sup>-</sup> + 50ppm of Ni- HUF

Systems	E <sub>corr</sub> (mV vsSCE)	I <sub>corr</sub> (A/cm <sup>2</sup> )	b <sub>a</sub> (mV/dec)	b <sub>c</sub> (mV/dec)	LPR (ohm cm <sup>2</sup> )
60 ppm Cl <sup>-</sup>	- 472	1.261 × 10 <sup>-3</sup>	124	187	25.74
60 ppm Cl <sup>-</sup> + 50 ppm Ni-HUF	- 494	4.857 × 10 <sup>-5</sup>	083	130	455.2

Table 2. Corrosion parameters of mild steel in aqueous solution containing 60 ppm of Cl<sup>-</sup> in the absence and presence of Ni-HUF inhibitor obtained by polarization method.

When mild steel is immersed in aqueous solution containing 60 ppm of Cl<sup>-</sup>, the corrosion potential is -472 mV Vs SCE. The

formulation consisting of 50 ppm of Ni-HUF shifts the corrosion potential to -494 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<sup>-</sup> are 1.261 × 10<sup>-3</sup> A cm<sup>-2</sup> and 25.74 ohm cm<sup>2</sup> respectively. For the formulation of 50 ppm of Ni-HUF the corrosion density value has decreased from 1.261 × 10<sup>-3</sup> A cm<sup>-2</sup> to 4.857 × 10<sup>-5</sup> A cm<sup>-2</sup> and the LPR value has increased from 25.74 ohm cm<sup>2</sup> to 455.2 ohm cm<sup>2</sup>. 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.

**AC impedance spectra**

AC impedance spectra [electrochemical impedance spectra] have been used to confirm the formation of protective film on the metal surface [20-23]. The AC impedance spectra of mild steel immersed in aqueous solution containing 60ppm of Cl<sup>-</sup> in the absence and presence of inhibitors are shown in Fig.2( Nyquist plots) and Fig.3 (Bode plots). The impedance parameters namely charge transfer resistance (R<sub>t</sub>) double layer capacitance (C<sub>dl</sub>) and impedance lg(z/ohm) are given in Table-3. If a protective film is formed on the metal surface, R<sub>t</sub> value increases and the C<sub>dl</sub> value decreases.

Systems	R <sub>t</sub> Ω cm <sup>2</sup>	C <sub>dl</sub> F cm <sup>-2</sup>	Impedance, Log (Z ohm <sup>-1</sup> )
60 ppm Cl <sup>-</sup>	20.19	5.235 × 10 <sup>-5</sup>	0.973
60 ppm Cl <sup>-</sup> + 50 ppm Ni-HUF	316.88	3.335 × 10 <sup>-6</sup>	2.098

Table 3. The AC impedance spectra of mild steel immersed in aqueous solution containing 60ppm of Cl<sup>-</sup> in the absence and presence of Ni-HUF inhibitor system.

When mild steel is immersed in aqueous solution containing 60ppm of Cl<sup>-</sup>, R<sub>t</sub> value is 20.19 Ω cm<sup>2</sup> and C<sub>dl</sub> value is 5.235 × 10<sup>-5</sup> F cm<sup>-2</sup>. When Ni-HUF are added to the aqueous solution containing 60ppm of Cl<sup>-</sup> R<sub>t</sub> value increases from 20.19 Ω cm<sup>2</sup> to 316.88 Ω cm<sup>2</sup> and the C<sub>dl</sub> value decreases from 5.235 × 10<sup>-5</sup> F cm<sup>-2</sup> to 3.335 × 10<sup>-6</sup> F cm<sup>-2</sup>. The impedance value increases from 0.973 to 2.098. This account for the high inhibition efficiency of Ni-HUF 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 to 63.73 ° (Fig.3).

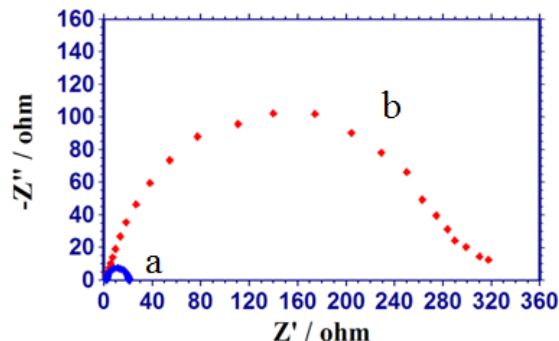


Figure 2.AC impedance spectra (Nyquist plots) of mild steel immersed in various test solutions a) aqueous solution containing 60ppm of Cl<sup>-</sup>. b) aqueous solution containing 60ppm Cl<sup>-</sup> + 50 ppm Ni-HUF

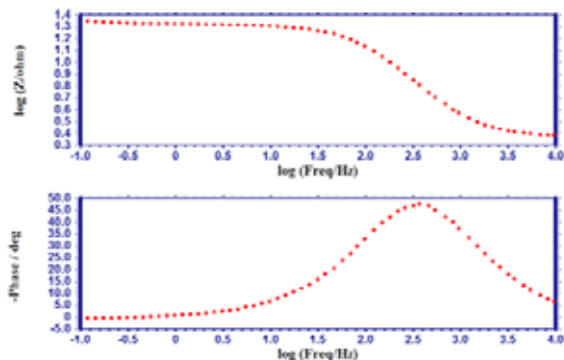


Figure 3a. AC impedance spectra (Bode Plot) of mild steel immersed in aqueous solution containing 60ppm of Cl<sup>-</sup>

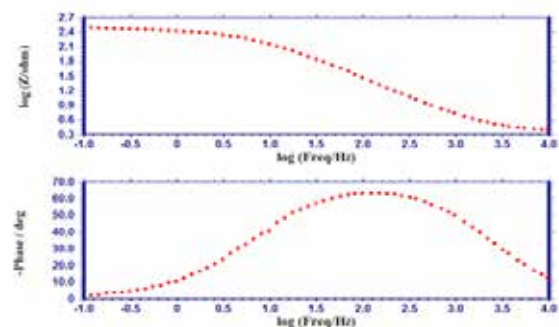


Figure 3b. AC impedance spectra (Bode Plot) of mild steel immersed in solution containing 60ppm of Cl<sup>-</sup> + 50ppm of Ni-HUF

**Analysis of the UV-Visible spectra:**

The UV-Visible absorption spectrum of an aqueous solution containing HUF is shown in figure 4. A peak appears at 356nm. When Fe<sup>2+</sup> solution is added to the solution the intensity of the UV-Visible spectra increases at 584nm. This peak is due to formation of Fe<sup>2+</sup>-HUF complex in solution [24, 25].

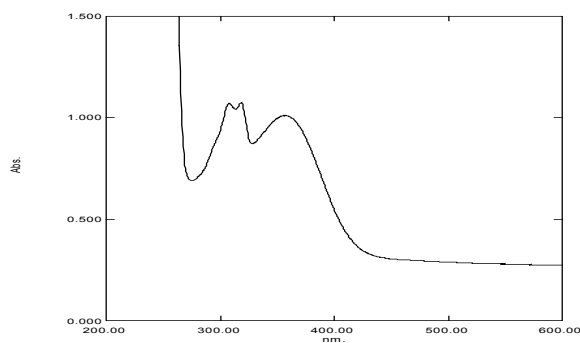


Figure 4a. UV-absorption spectrum solution containing Ni-HUF

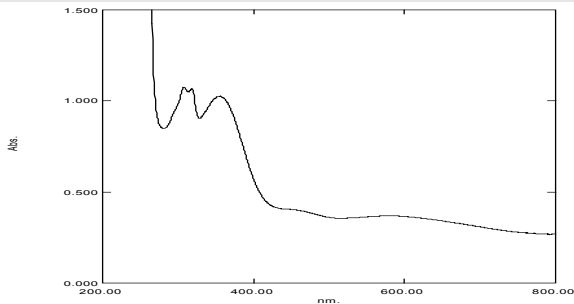


Figure 4b. UV-absorption spectra solution containing HUF-Fe<sup>2+</sup>

**Fluorescence spectra:**

The emission spectrum (λ<sub>ex</sub>: 380nm) of solution containing HUF-Fe<sup>2+</sup> solution is shown in Figure 5a. A peak appears at 400nm. This is due to HUF-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-HUF is shown in figure 5b. Hence it is concluded that the protective film consists of HUF-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 [26].

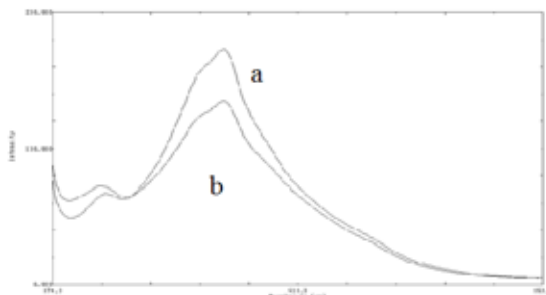


Figure 5. a) Fluorescencespectrum of Ni-HUF solution b) Fluorescence spectra of solution containing HUF-Fe<sup>2+</sup> complex.

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 HUF-Fe<sup>2+</sup> complex is shown in figure 6.

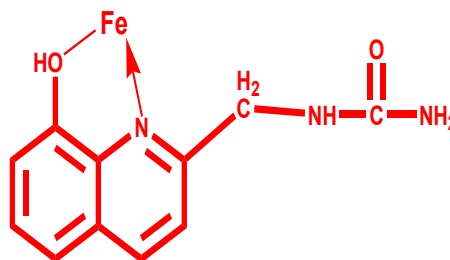


Figure 6. Structure of Fe<sup>2+</sup> complex

This view is in agreement with the structure proposed by Albrecht et al. for zinc complex [27].

**Conclusion:**

The conclusion drawn from the results may be given as: the formulation consisting of 50 ppm of Ni-HUF has 74% inhibition efficiency. Polarization study suggests that cathodic reaction is controlled predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. Fluorescence and UV-Visible spectra show that the protective film consists of HTF-Fe<sup>2+</sup> complex formed on metal surface.

## REFERENCE

- [1] Cepak L, Adam J, Grygar T, Bulanek R, Vradman L, Kosava-Kucerova G, Cicmanec P, Knotek P, Oxidative dehydrogenation of ethane over vanadium supported on mesoporous materials of M41S family, *Appl.Catal. A* 342 (2008) 99-106. | [2] Pereira C, Rosa Silva A, Paula Carvalho APires J, Freire C, Vanadyl acetylacetonate anchored onto amine-functionalised clays and catalytic activity in the epoxidation of geraniol, *J. Mol. Catal. A* 283 (2008) 5-14. | [3] Pereira C, Patricio S, Rosa Silva A, Magalhaes A L, Paula Carvahlo A, Pires J, Cristina Freire, Copper acetylacetonate anchored onto amine-functionalised clays, *J. Colloid interf. Sci.* 316 (2007) 570-579. | [4] Fujihara S, Sol-gel processing of fluoride and oxyfluoride materials, in: H. Kozuka (Ed.), *Handbook of Sol-Gel Science and Technology: Volume 1- Sol-Gel Processing*, Kluwer Academic Publishers, 2005, p. 219. | [5] Cernea M, Monnereau O, Llewellyn P, Tortet L, Galassi, C Sol-Gel synthesis and characterization of Ce doped- BaTiO<sub>3</sub>, *J. Eur.Ceram.Soc.*26 (2006) 3241-3246. | [6] Tangwivat S, Milne S J, Barium titanate sols prepared by a diol – based sol-gel route, *J.Non-Cryst. Solids* 351 (2005) 976-980. | [7] Harms H, Volkland H P, Repphun G, Hiltolt A, Wanner O, Zehnder A.J.B, Action of chelators on solid iron in phosphate-containing aqueous solutions, *Corros. Sci.* 45 (2003) 1717-1732. | [8] Hettiarachchi S, Palladium acetylacetonate solution, European Patent EP0651073, 1995. | [9] Gerloch M, Constable E G, *Transition Metal Chemistry*, VCH Verlagsgesellschaft mbH, Weinheim, 1994, p. 176. | [10] Saremi M, Parsi N, Dehghanian C, *Corrosion* 65 (2009) 778-784. | [11] Oblonsky L J, Ryan M P, Isaacs H S, *Corros.Sci.*42 (2000) 229-241. | [12] Touir R, Cenoui M, Bakri M El, Touhami M Ebn, *Corros.Sci.*50 (2008) 1530-1537. | [13] Singh I B, Venkatachari G, Balakrishnan K, *J.Appl. Electrochem.* 24 (1994) 179-183. | [14] Lahodny-Sarc O, Kapor F, Halle R, *Mater.Corros.*51 (2000) 147-151. | [15] Nagalakshmi. R., Rajendran. S., Sathiyabama, J., Pandiarajan, M., Lydia Christy, J., *Eur. Chem. Bull.* 1(17), 2012, 238. | [16] Sahayaraja A., Nagalakshmi, R., Rajendran. S., Angelin Thangakani, J., Pandiarajan, M., *Eur.Chem. Bull.* 1(3), 2012, 130. | [17] Agiladevi, S., Rajendran, S., Jayasundari, J., Pandiarajan, M., *Eur.Chem.Bull.* 2(2), 2013, 503. | [18] Rajendran, S., Sridevi, S. P., Antony, N., John Amalraj, A., Sundaravadivelu, N., *Anto.Corros. Methods Mater.* 52,2005, 102. | [19] Felicia Rajammal Selvarani, Santhanalakshmi, S., Wilson sahayaraja, J., John Amalraj, A., and Rajendran, S., *Bull. Electrochem.* 20,2004, 561. | [20] Sathiyabama, J., Rajendran, S., Arockia Selvi, J., Jayasundari, J., *Open Corrs. J.* 2 2009, 84. | [21] Shyamala Devi, B., Rajendran, S., *Eur. Chem.Bull.* 1, 2012, 150. | [22] Rajendran, S., Paulraj, J., Rengan, P., Jayasundari, J., Manivannan, M., *J.Dent.Oral. Hyg.* 1, 2009, 1. | [23] Rajendran, S., Anuradha, K., Kavipriya, K., Krishnaveni, A., Andelin Thangakani, J., *Eur.Chem.Bull.* 1, 2012, 503. | [24] Rajendran, S., Maria Joany, R., Apparao, B. V. and Palaniswamy, N., *Indian J.Chem.Technol.* 9,2002, 197-200. | [25] Rajendran s., Earnest John Peter, B. R., Peter Pascal Reces, A., John Amalraj, A. and Sundaravadivelu, M., *Trans. SABST.* 38(1), 2003, 11-15. | [26] Rajendran, S. and John Amalraj, A., *Bull. Electrochem.* 21, 2005, 185-191. | [27] Markus Albrecht., Karen Witt., Patrick Weis., Elina Wegelius., Roland Frohlich., *Inorganica Chimica Acta.* 341 (2002) 25-32.