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Electrochemical behavior of Zinc Complex of 1-(8-hydroxy quinolin-2ylmethyl) urea as Corrosion Inhibitor for Mild Steel S. S. Syed Abuthahir^{1,2}, A. Jamal Abdul Nasser¹ and S. Rajendran^{2*}

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ABSTRACT

The Corrosion inhibition of a inhibitor namely Zn complex of 1-(8-hydroxy quinolin-2ylmethyl) urea (Zn-HUF) in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm Cl⁻ has investigated using weight loss method. The corrosion inhibition efficiency offered by 50 ppm of Zn-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.

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Keywor ds

Corrosion inhibition, EIS, Mild Steel, Transition metal complex.

Introduction

The corrosion of metals is a serious problem in many industries, installations, and civil services such as water and sewage supplies. One of the most useful and practical methods that used to control and protect metals against corrosion is the use of inhibitors, especially in neutral media. Not only the costs due to corrosion increase rapidly, but also the efficiency of the plants and the quality of the products is also reduced. Most inhibitors are organic compounds containing polar groups strongly adsorbed on the metal surface [1,2]. Metal complexes are widely used as catalyst of chemical reactions, e.g. Oxidative dehydrogenation (ODH) of ethane and epoxidation of geraniol [3-5] and as stabilizer or precursor in sol-gel processes [6-8]. They are used in polymeric coatings as stabilizer of cross linking reaction [9], catalyst of drying process [10,11] and toughening agent [12]. Very few works have been performed to study anticorrosive behavior of metal complexes. Harms et al.[13] 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 [14]. 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 [15]. 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 [16-19]. Mild steel, highly applicable and most widely used alloy of iron comes in contact with chloride ions very frequently under numerous conditions and circumstances in

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industries. Chloride ions are known to be aggressive towards mild steel and cause severe corrosion problems. Various inorganic compounds viz. nitrates, sulphates, silicates, chromates etc [20] have been reported as inhibitors for controlling corrosion of mild steel in water containing chloride ions but the inhibitive efficiency of such compounds when used alone was found to be very less. Zinc ions as inhibitor of the corrosion of steel in water have been known since 19th century. Many examples exist of their use in combination with other inhibitors to improve the protection of metals [21-27]. Electrochemical impedance spectroscopy (EIS) as powerful non destructive test could be used to extract electrochemical parameters involved in corrosion process. Extracted parameters are useful to evaluate corrosion protection performance of inhibitors, organic and inorganic coating [28-31]. The aim of the present work is to evaluate corrosion inhibitive performance of zinc complex of 1-(8-hydroxy quinolin-2yl-methyl) urea 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 UV-Visible spectroscopy.

Materials and Methods

Mild steel specimens; (0.0261% S, 0.069% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions $1.0 \text{ cm} \times 4.0 \times 0.2 \text{ cm}$ 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 Zn complex of 1-(8-hydroxy quinolin-2yl-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 cm². 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, $\mathrm{I}_{\mathrm{corr}},\,\mathrm{E}_{\mathrm{corr}}$ 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 1×10⁵ Hz, low frequency limit was 1 Hz, amplitude =0.005V and quiet time $t_a=2$ s. The values of charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

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

Where f_{max} is maximum frequency. 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 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⁻ and also inhibition efficiencies(IE) in the absence and presence of inhibitor Zn 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. Corrosion rates (CR) of mild steel immersed in an aqueous solution containing 60 ppm Cl- in the presence and absence of Zn-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 [32-36]. 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 60ppm of Cl⁻ b) Mild steel immersed in 60ppm of Cl⁻ + 50ppm of Zn- HUF

Table 2. Corrosion parameters of mild steel in aqueous solution containing 60 ppm of Cl⁻ in the absence and presence of Zn-HUF 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 Zn-HTF shifts the corrosion potential to -506 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 cm² respectively. For the formulation of 50 ppm of Zn-HUF the corrosion density value has decreased to 2.140×10^{-4} A cm⁻² and the LPR value has increased from 25.74 ohm cm² to 130.3 ohm cm². 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 [37-40]. 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.2(Nyquist plots) and Fig.3 (Bode plots). The impedance parameters namely charge transfer resistance (R_t) double layer capacitance (C_{dl}) and impedance lg(z/ohm) are given in Table-3. If a protective film is formed on the metal surface, R, value increases and the C_{dl} value decreases.

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

CI.	Zn-HUF (ppm) CR		IE			
(ppm)		(mdd)	(%)			
60	00	34.55	-			
60	50	8.98	74			
60	100	12.09	65			
60	150	13.82	60			
60	200	14.51	58			
60	250	15.54	55			

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

Systems	E _{corr} (mV vs SCE)	I _{corr}	b _a (mV/dec)	b _c	LPR
		(A/cm^2)		(mV/dec)	$(ohm cm^2)$
60 ppm Cl	- 472	1.261×10^{-3}	124	187	25.74
$60 \text{ ppm} \text{Cl}^2 + 50 \text{ ppm} \text{Zn-HUF}$	- 506	2.140×10^{-4}	117	140	130.3

Table 3. The AC impedance spectra of mild steel immersed in aqueous solution containing 60ppm of Cl⁻ in the absence and presence of Zn-HUF inhibitor system.

Systems	R _t	C _{dl}	Impedance,Log
	$\Omega \text{ cm}^2$	F cm ⁻²	$(Z \text{ ohm}^{-1})$
60 ppm Cl ⁻	20.19	5.235×10^{-5}	0.973
60 ppm $\text{Cl}^2 + 50 \text{ ppm}$	203.74	5.187×10^{-6}	1.850
Zn- HUF			

When mild steel is immersed in aqueous solution containing 60ppm of Cl⁻, R_t value is 20.19 Ω cm² and C_{dl} value is 5.235 \times 10⁻⁵ F cm². When Zn-HUF are added to the aqueous solution containing 60ppm of Cl⁻ R_t value increases from 20.19 Ω cm² to 203.74 Ω cm² and the C_{dl} value decreases from 5.235 \times 10⁻⁵ F cm⁻² to 5.187 \times 10⁻⁶ F cm⁻². The impedance value increases from 0.973 to 1.850. This account for the high inhibition efficiency of Zn-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 60.60 ° (Fig.3).



Figure 2.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 Zn-HUF



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



Figure 3b. AC impedance spectra (Bode Plot) of mild steel immersed in solution containing 60ppm of Cl⁻ + 50ppm of Zn- HUF

Analysis of the UV-Visible spectra:

The UV-Visible absorption a spectrum of an aqueous solution containing HUF is shown in figure 4. A peak appears at 350nm. When Fe^{2+} solution is added to the solution the intensity

of the UV-Visible spectra increases at 590nm. This peak is due to formation of Fe^{2+} -HUF complex in solution [41, 42].



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



Figure 4b.UV- absorption spectra solution containing HUF- Fe^{2+}

Fluorescence spectra:

The emission spectrum (λ_{ex} : 300nm) of solution containing HUF-Fe²⁺ solution is shown in Figure 5a. A peak appears at 350nm. This is due to HUF-Fe²⁺ complex formed in solution. The emission spectrum of the film formed on the metal surface after immersion in solution containing 50 ppm of Zn-HUF is shown in figure 5b. Hence it is concluded that the protective film consists of HUF-Fe²⁺ complex. The number peak obtained is only one. Hence it is confirmed that the complex of somewhat highly symmetric in solution [43].



Figure 5. a)Fluorescencespectrum of Zn-HUF solution b) Fluorescence spectra of solution containing HUF-Fe²⁺ complex.

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 HUF- $Fe^{2+}\,complex$ is shown in figure 6.



Figure 6. Structure of Fe²⁺ complex

This view is in agreement with the structure proposed by Albrecht et al. for zinc complex [44].

Conclusion:

The conclusion drawn from the results may be given as: the formulation consisting of 50 ppm of Zn-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-Fe²⁺ complex formed on metal surface.

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