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Research Article

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Corrosion inhibition of mild steel in sodium chloride solution by copper complex of 1-(8-hydroxy quinolin-2yl-methyl) urea

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ABSTRACT

The Corrosion inhibition of a inhibitor namely Cu complex of 1-(8-hydroxy quinolin-2yl-methyl) urea (Cu-HUF) in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm Cl^- has been investigated using weight loss method. The corrosion inhibition efficiency offered by 50 ppm of Cu-HUF is 80 %. 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.

Key words: Corrosion inhibition, Mild Steel, EIS, Transition metal complex

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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]. They are used in polymeric coatings as stabilizer of cross linking reaction [7], catalyst of drying process [8-9] and toughening agent [10]. Very few works have been performed to study anticorrosive behavior of metal complexes. Harms et al[11] 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[12]. It is reported that palladium acetylacetonate decomposes and deposits palladium on the oxide surface. Cerium, terbium, praseodymium acetylacetonate complexes are used to design non-toxic corrosion protection pigments3]. 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 [14]. 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 [15-18]. 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 [19]. 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 [20-23]. Most of these organic compounds contain nitrogen, sulphur, oxygen, and multiple bonds in the molecules which are adsorbed on the metal surface and the organic compound [24]. The aim of the present work is to evaluate corrosion inhibitive performance of copper 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.

EXPERIMENTAL SECTION

2.1. Mild steel specimens

(0.0261% S, 0.069% 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.

2.2. 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 Cu 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.

2.3.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.

2.4. 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 1×10^5 Hz, low frequency limit was 1 Hz, amplitude =0.005V and quiet time t_q=2 s. The values of charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

$$C_{dl} = ½ \pi R_t f_{max}$$

Where f_{max} is maximum frequency.

2.5. 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.

2.6. 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.

2.6. 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 Cu 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 Cu-HUF shows 80 % inhibition efficiency.

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

Cl^- (ppm)	Cu-HUF (ppm)	CR (mdd)	IE (%)
60	0	34.55	-
60	50	6.91	80
60	100	8.98	74
60	150	10.36	70
60	200	12.78	63
60	250	14.51	58

Analysis of Polarization Curves

The polarization study has been used to investigate the formation of protective film on metal surface [25-29]. 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.

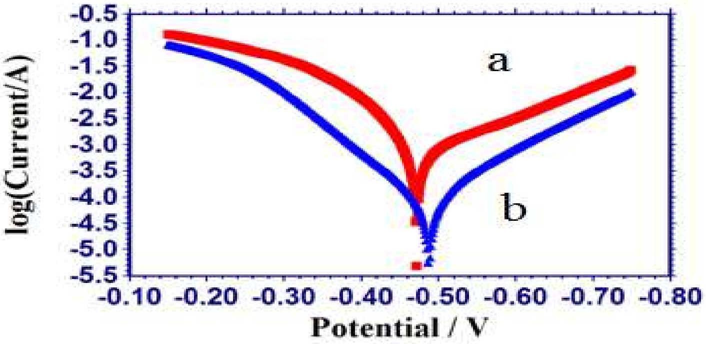

Figure 1. Polarization curves of mild steel immersed in various test solutions: a) Mild steel immersed in aqueous solution containing 60ppm of Cl^- b) Mild steel immersed in 60ppm of Cl^- + 50 ppm of Cu- HUF

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

Systems	E_{corr} (mV vs SCE)	I_{corr} (A/cm^2)	b_a (mV/dec)	b_c (mV/dec)	LPR (ohm cm^2)
60 ppm Cl^-	- 472	1.261×10^{-3}	124	187	25.74
60 ppm Cl^- + 50 ppm Cu-HUF	- 487	9.273×10^{-5}	084	125	237.7

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 Cu-HTF shifts the corrosion potential to -487 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 Cu-HUF the corrosion density value has decreased to 9.273×10^{-5}A cm^{-2} and the LPR value has increased from 25.74 ohm cm^2 to 237.7 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.

Table2. The AC impedance spectra of mild steel immersed in aqueous solution containing 60ppm of Cl^- in the absence and presence of Cu-HUF inhibitor system

Systems	R_t Ω cm^2	C_{dl} F cm^{-2}	Impedance, Log (Z ohm^{-1})
60 ppm Cl^-	20.19	5.235×10^{-5}	0.973
60 ppm Cl^- + 50 ppm Cu- HUF	182.11	5.804×10^{-6}	1.944

AC impedance spectra

AC impedance spectra [electrochemical impedance spectra] have been used to confirm the formation of protective film on the metal surface [30-33]. The AC impedance spectra of mild steel immersed in aqueous solution containing

60 ppm 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_t value increases and the C_{dl} value decreases.

When mild steel is immersed in aqueous solution containing 60ppm of Cl^-, R_t value is 20.19 Ω cm^2 and C_{dl} value is 5.235×10^{-5} F cm^{-2}. When Cu-HUF are added to the aqueous solution containing 60ppm of Cl^- R_t value increases from 20.19 Ω cm^2 to 182.11 Ω cm^2 and the C_{dl} value decreases from 5.235×10^{-5} F cm^{-2} to 5.804×10^{-6} F cm^{-2}. The impedance value increases from 0.973 to 1.944. This account for the high inhibition efficiency of Cu-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 62.10 ° (Fig.3).

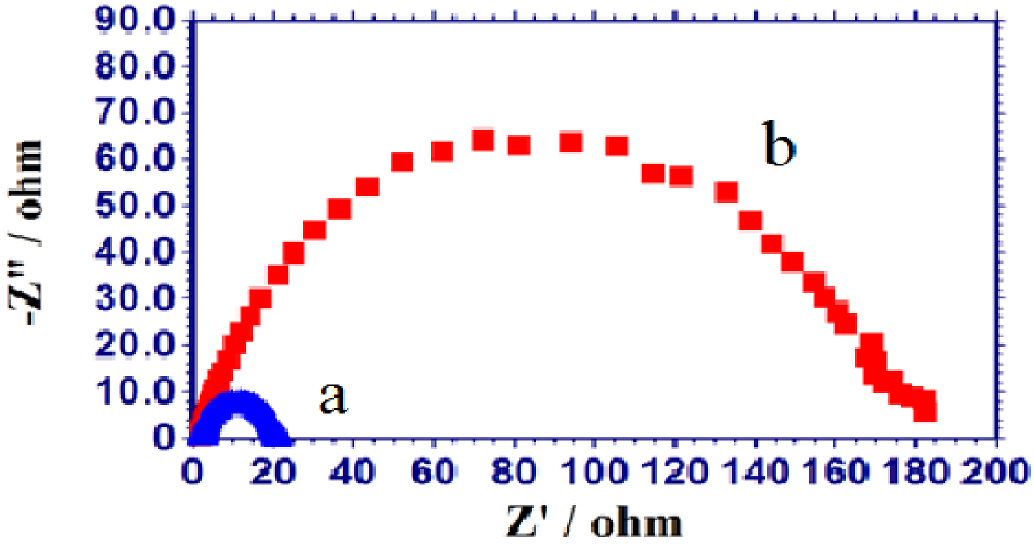

Figure 2.AC impedance spectra (Nyquist plots) of mild steel immersed in various test solutions a) aqueous solution containing 60ppm of Cl^-. b) aqueous solution containing 60ppm Cl^- + 50 ppm Cu-HUF

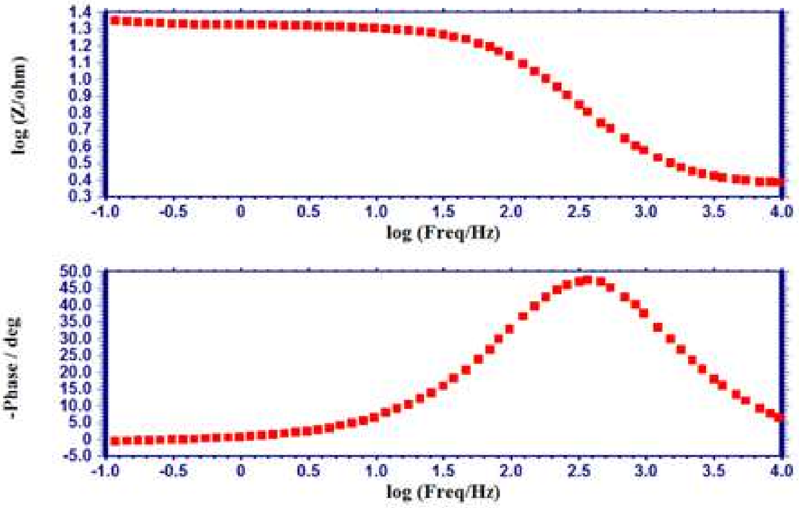

Figure 3a. AC impedance spectra (Bode Plot) of mild steel immersed in aqueous solution containing 60ppm of Cl^-

Fig 2a & 2b shows the Nyquist plots of mild steel immersed in an aqueous solution containing 60ppm of Cl^- and aqueous solution containing 60 ppm Cl^- + 50 ppm Cu-HUF respectively. The impedance spectra exhibit one single depressed semicircle, which indicates that the corrosion of mild steel is mainly controlled by a charge transfer process. When comparing with the blank solution, the shape is maintained uniformly, indication that almost no change in the corrosion mechanism occurs due to the inhibitor addition [34]. These semicircles are perfect which can be attributed to the frequency dispersion effect as a result of the roughness and homogeneous of electrode surface[35].

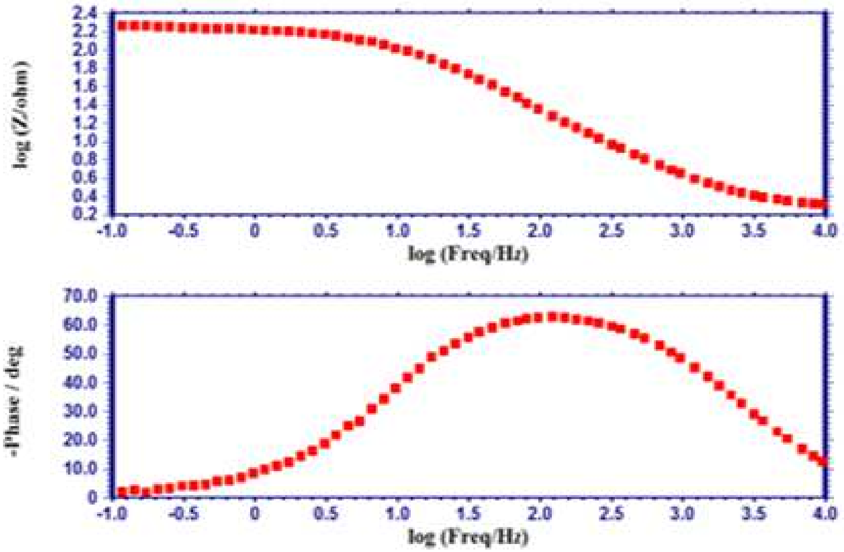

Figure 3b. AC impedance spectra (Bode Plot) of mild steel immersed in solution containing 60ppm of Cl^- + 50ppm of Cu- HUF

Electrochemical impedance spectra of the inhibitor systems were analyzed using the equivalent circuit diagram 4 which represents a single charge transfer reaction and fits well with our experimental results. R_{ct} represents the charge transfer resistance whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate [36]. The equivalent circuit diagram for the corroding system is shown in figure 4.

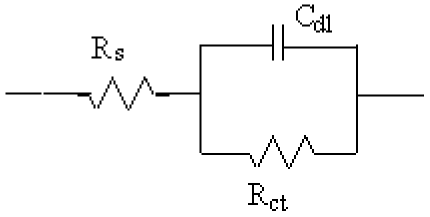

Figure-4
C_{dl} – Double layer capacitance, R_s – Solution resistance, R_{ct} – Charge transfer resistance

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 350 nm. When Fe^{2+} solution is added to the solution the intensity of the UV-Visible spectra increases at 590 nm. This peak is due to formation of Fe^{2+}-HUF complex in solution 37-38].

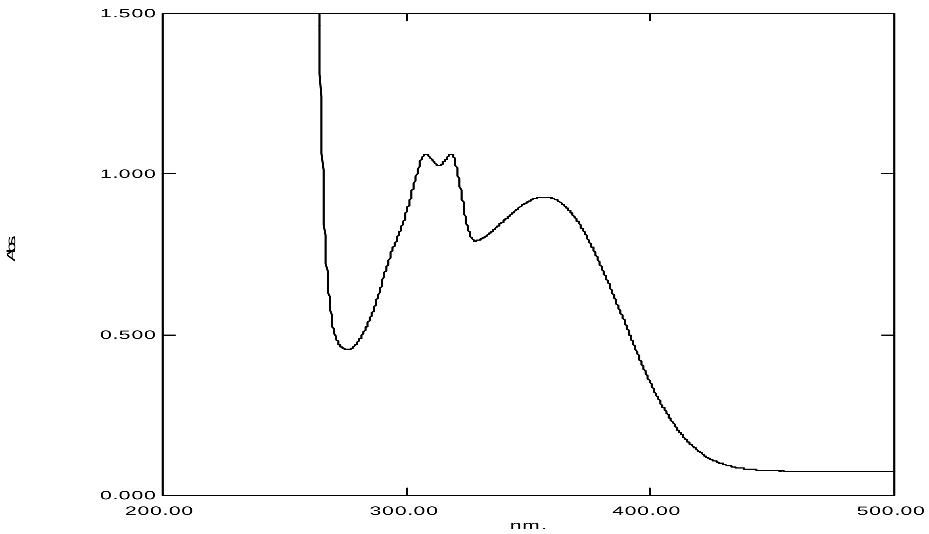

Figure 4a.UV-absorption spectrum solution containing Cu-HUF

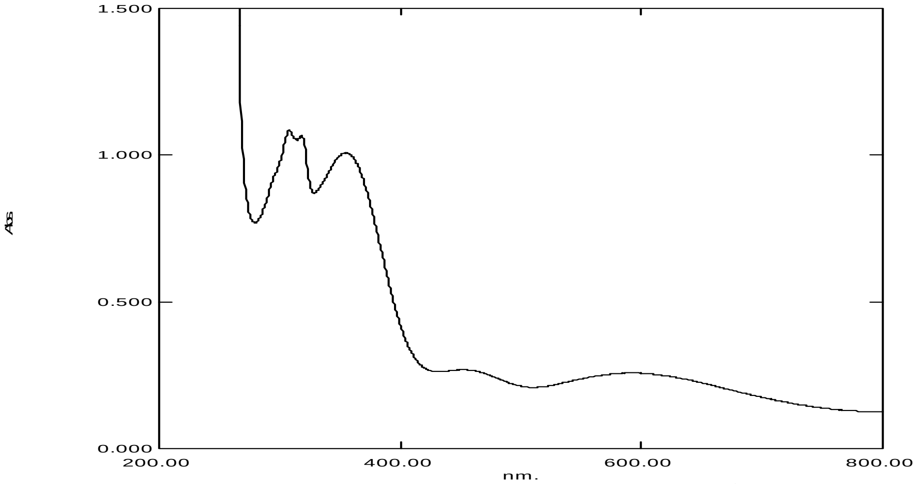

Figure 4b.UV- absorption spectra solution containing HUF-Fe^{2+}

Fluorescence spectra

The emission spectrum (λ_{ex}: 300nm) of solution containing HUF-Fe^{2+} solution is shown in Figure 5a. A peak appears at 350nm. This is due to HUF-Fe^{2+} complex formed in solution. The emission spectrum of the film formed on the metal surface after immersion in solution containing 50 ppm of Cu-HUF is shown in figure 5b. Hence it is concluded that the protective film consists of HUF-Fe^{2+} complex. The number peak obtained is only one. Hence it is confirmed that the complex of somewhat highly symmetric in solution [39].

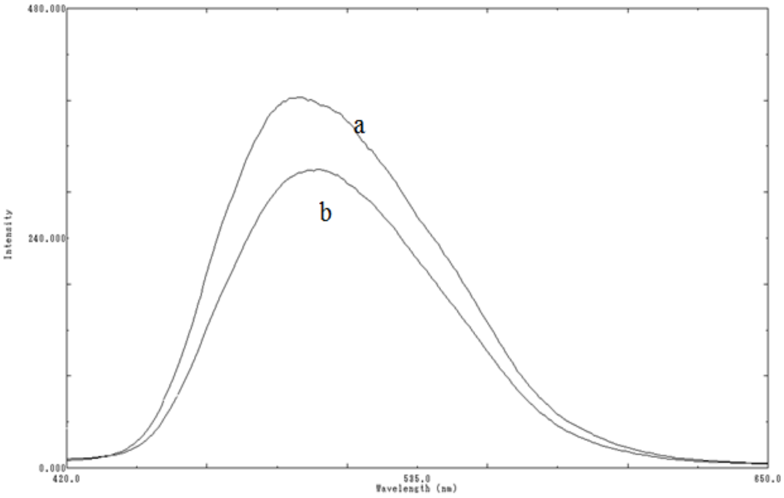

Figure 5. a)Fluorescencespectrum of Cu-HUF solution b) Fluorescence spectra of solution containing HUF-Fe^{2+} complex

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.

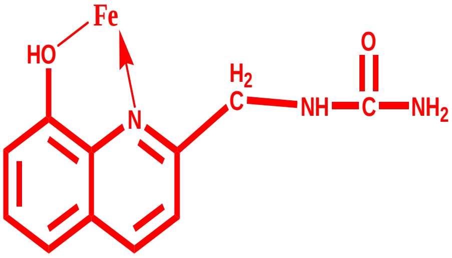

Figure 6. Structure of Fe^{2+} complex

This view is in agreement with the structure proposed by Albrecht et al. for zinc complex [40].

CONCLUSION

The conclusion drawn from the results may be given as: the formulation consisting of 50 ppm of Cu-HUF has 80% 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 HUF-Fe^{2+} complex formed on metal surface.

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