INHIBITION OFCORROSION OF CARBON STEEL IN SEA WATER BY HYDROXY PROLINE – Ni^{2+} SYSTEM

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ABSTRACT: The corrosion inhibition effect of carbon steel in sea water environment by HydroxyProline (HP)-Ni^{2+} system has been investigated using weight loss method. The results show that 92% inhibition efficiency (IE) achieved with binary system consisting of 300 ppm of HP and 30 ppm of Ni^{2+}. The addition of 50 ppm of sodium gluconate (SG) on HP- Ni^{2+} system increased the IE from 92% to 98%. The influence of sodium gluconate (SG) on HP- Ni^{2+} system control the microbial corrosion. FTIR investigate the nature of the protective film formed on the metal surface. The protective film consists of Fe^{2+}–HP complex, Fe^{2+}–SG complex and $Ni(OH)_2$. SEM used to prove the formation of protective film. The mechanistic aspects of corrosion inhibition based on the results obtained from the weight-loss method and the electrochemical method viz., potentiodynamic polarization.

Keywords: [Hyroxy Proline, corrosion inhibition, carbon steel, polarization, FT-IR and SEM.]

1. INTRODUCTION

Carbon steel is the most important engineering material. Corrosion problem occurs inthese industries and can cause disastrous damage to metal and alloy structures causingeconomic consequences in terms of repair, replacement, and product losses. The protectionagainst corrosion is important for metals containing intermetallic particles, which are widelyused in industry but susceptible to pitting corrosion in the media containing chloride ions.Corrosion inhibitors are widely used in industry to prevent or to reduce the corrosion rates ofsurface of the metal from the corroding medium. The organic compounds and severalcarboxylates have been used as inhibitors[3-5]. Synergistic effect of HydroxyProline andZn^{2+} in controlling corrosion of carbon steel in sea water has been reported [6]. The approach of inhibitorswith nickel is recent trend in corrosion inhibition [7-9]. An amino acid namely HydroxyProline (HP) wasinvestigated as a corrosion inhibitor for carbon steel in thisstudy.The inhibitive properties and synergistic effect with anorganic compound viz., HydroxyProline and Ni^{2+} ions incontrolling the corrosion of carbon steel was studied in Sea water using weightloss method and electrochemical methodsviz., potentiodynamicpolarization. Fourier transform infraredspectroscopy (FTIR) and Scanning electron microscopy (SEM)were used to analyse the protective film formed on the carbonsteel surface and a suitable mechanism of corrosion inhibition isproposed[10-14].

2. EXPERIMENTAL
2.1. Preparation of Specimen

Carbon steel (0.026%S, 0.06%P, 0.4%Mn, 0.1% C, and the rest Fe) specimen of dimension 1cm×4cm×0.2cm were used

for weight loss study. Carbon steel rod of the same composition, encapsulated in Teflon was polished to a mirror finish and degreased with trichloroethylene.

Preparation of HyroxyProline

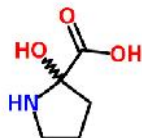1g of HyroxyProline (HP) was dissolved in distilled water and made up to 100 ml.

Figure 1- Structure of HydroxyProline

2.3. Weight-Loss Method

Two carbon steel specimens were immersed in 100 ml of test solution containing various concentrations of the inhibitors in the absence and presence of Ni^{2+} ions, for a period of one day. After exposure corrosion product were removed with Clarke's solution, and the weight of the specimens before and after immersion were determined using a metler balance.

2.4. Corrosion Inhibition Efficiency

Corrosion inhibition efficiency was calculated using the equation:

$$I.E = 100\left[1 - \frac{W_2}{W_1}\right]\%$$

where W_1= Corrosion rate in the absence of inhibitor,

W_2= Corrosion rate in the presence of inhibitor.

2.5. Surface Examination

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analysed by FTIR spectroscopic study.

2.6. FT-IR Spectra

FT-IR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

2.7. Potentiodyanmic Polarization

Polarization studies were carried out in an H&CH electrochemical work station impedance analyser model CHI760D. a three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

3. RESULTS AND DISCUSSION
3.1. Weight Loss Study

The corrosion rates of carbon steel immersed in various test solution for a period of one day are presented in the table 2.

Synergistic Effect of HydroxyProline – Ni^{2+} System

Inhibitor system: HP-Ni^{2+} Immersion period: 1 day

HP (ppm)	Ni^{2+}= 0 ppm		Ni^{2+} = 15 ppm		Ni^{2+} = 30 ppm	
	IE%	CR (mmpy)	IE%	CR (mmpy)	IE%	CR (mmpy)
0	-	0.1572	11	0.1399	23	0.1210
50	7	0.1462	18	0.1289	44	0.0880
100	10	0.1415	26	0.1163	59	0.0645
150	16	0.1321	33	0.1053	72	0.0440
200	21	0.1242	41	0.0927	83	0.0267
250	27	0.1148	47	0.0833	89	0.0173
300	33	0.1053	52	0.0755	92	0.0126

Table 1- Inhibition Efficiencies (IE%) and corrosion rates (CR) Obtained from HP-Ni^{2+} systems when carbon steel immersed in Sea water.

The calculated inhibition efficiencies of carbon steel immersed in Sea water, for a period of one day in the absence and presence of Ni^{2+} ion are given in table 2. the calculated value indicates the ability of HP to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Ni^{2+} ion. HP alone shows some IE. But the combination of 300 ppm HP and 30 ppm Ni^{2+} shows 92% IE. this suggests a synergistic effect exists between HP and Ni^{2+}[15-16].

Influence of Immersion Period on IE of HP-Ni^{2+} System

System	Immersion period (days)			
	1	3	5	7
Sea water CR (mmpy)	0.1572	0.1624	0.1659	0.1713
Sea water + HP(300ppm) + Ni^{2+}(30ppm); CR (mmpy)	0.0126	0.0260	0.0365	0.0480
IE %	92	84	78	72

Table 2- Influence of immersion period (IP) on IE of HP (250ppm) - Ni^{2+} (30ppm) system

The influence of immersion period on the IE of HP (300ppm) – Ni^{2+} (30ppm) system is given in table 3 is found that as the Immersion Period increases, the IE decreases. This due to the fact as the Immersion Period increases the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as chloridepresent in Sea water. There is a competition between two processes, namely, formation of $FeCl_2$ and Fe^{2+}-HP complex on the anodic sites of the metal surface. It appears that the formation of iron chlorides is more favoured than the formation of Fe^{2+}-HP complex film formed on the metal surface is converted into iron chlorides which go into solution and hence, the IE decreases as the IP increases.

Influence ofSodium Gluconate(SG) on Inhibition Efficiency of HP-Ni^{2+} System

HP (ppm)	Ni^{2+} (ppm)	SG (ppm)	CR (mmpy)	IE (%)
0	0	0	0.1572	-
300	30	0	0.0126	92
300	30	50	0.0110	93
300	30	100	0.0079	95
300	30	150	0.0031	98
300	30	200	0.0008	100
300	30	250	0.0007	100
300	30	300	0.0005	100

Table 3- Influence of SG on inhibition efficiency (IE%) of carbon steel immersed in Seawater

SG is a cationic surfactant. It is a biocide. The IE and biocidal efficiency (BE) of HP-Ni^{2+}-SGsystem is given here. It is observed from the results that 50 ppm of SG in combination with HP-Ni^{2+} system has increased IE from 92% to 93%. However, a decrease in IE of HP-Ni^{2+} System is noticed when the SG concentration increases from 100 ppm to 250 ppm. This is due to the formation of micelles at higher concentration of surfactant.

3.2. Analysis of Polarization Curves for HP-Ni^{2+} System

Description	E_{corr} mV/decade	b_a mV/decade	b_c mV/decade	I_{corr} A/cm^2
Sea Water	-609	185	229	8.354×10^{-5}
Sea Water + 30 ppm Ni^{2+} + 250 ppm HP	-490	183	179	1.492×10^{-5}

Table 4- corrosion potential (E$_{corr}$), Tafel slopes (anodic slope b$_a$ and cathodic slope b$_c$) and corrosion current (I$_{corr}$) values are absence and presence of inhibitors
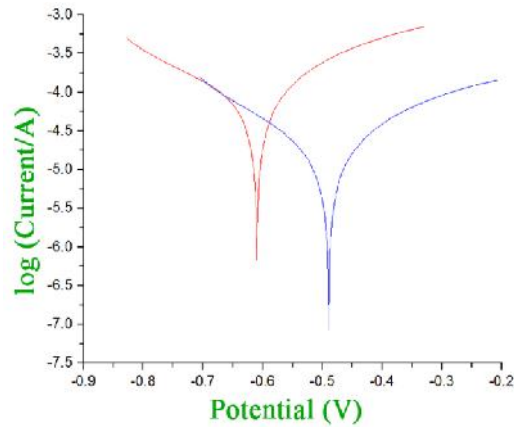
Figure 2- Potentiodynamic polarization curves of carbon steel in various test solution
a) Sea Water b) Sea Water + 30 ppm Ni^{2+} + 250 ppm HP

The calculated corrosion parameters such as corrosion potential (E_{corr}), Tafel slopes (anodic slope b_a and cathodic slope b_c) and corrosion current (I_{corr}) values are absence and presence of inhibitors are shown table 5. When carbon steel is immersed in Sea water,the corrosion potential is -609 mV vs saturated calomel electrode (SCE). The corrosion current is 8.354×10^{-5} A/cm^2. When HP (300 ppm) and Ni^{2+} (30 ppm) are added to the above system the corrosion potential is shifted to the anodic side. This suggests that the anodic reaction is controlled predominantly. Moreover, in presence of the inhibitor system, the corrosion current decreases from 8.354×10^{-5} A/cm^2 to 1.492×10^{-5} A/cm^2. These observations indicate the formation of protective film on the metal surface [17-20].

3.4. Surface Analysis
The structure of HydroxyProline is shown in fig 3. It contains N-H, C=O and O-H stretching vibrations.The protective film formed on the surface of the metal in the presence of Thiomalic acid system and HydroxyProline–Ni^{2+} system in Sea water has been analysed by FT-IR spectroscopy.

3.4.1. Analysisof FT-IR Spectra
FTIR spectrum (KBr) of pureHydroxyProline (HP) is shown in Fig. 3a.   The C=O stretching frequency of carboxyl group appears at 1700 cm^{-1}. The O-H stretching frequency of HydroxyProline appears at 3489 cm^{-1}. The FTIR spectrum (KBr) of film formed on the surface of metal after immersion in Sea water containing 300 ppm of HydroxyProline and 30 ppm of Ni^{2+} is shown in Fig. 3b. The C=O stretching frequency of carboxyl group has shifted from 1601 cm^{-1} to 1588 cm^{-1}. The O-H stretching frequency of HydroxyProline has shifted from 3489 cm^{-1} to 3429 cm^{-1}. The N-H stretching frequency of HydroxyProline has shifted from 1405 cm^{-1} to 1384 cm^{-1}. This indicates that these groups has coordinated with Fe^{2+}, resulting in the formation of Fe^{2+}-HydroxyProline complex on the cathodic sites of the metal surface. The peak at 1221 cm^{-1} is due to Ni(OH)$_2$ formed on the cathodic sites of the metal surface. Thus FTIR spectra study leads to the conclusion that the Fe^{2+}-HydroxyProline complex formed on anodic sites of the metalsurface controlled the anodic reaction and Ni(OH)$_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction   [21-24].
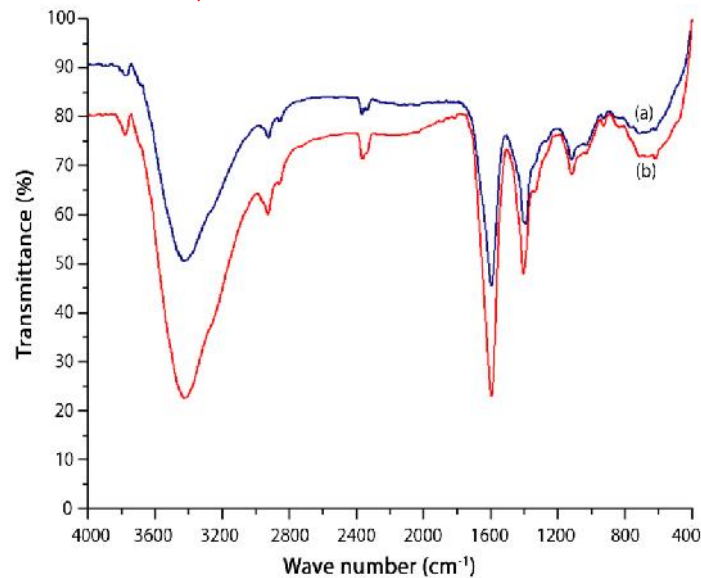
Figure 3- a) FT-IR Spectra of Pure HP b) FT-IR Spectra of Sea Water+250ppm of HP+30ppm of Ni^{2+}

3.4.2. Scanning electron microscopy (SEM)

The scanning electron micrographs of carbon steel are shown in Fig 5. The SEM micrograph of polished carbon steel surface (control) is shown in Fig 5a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of carbon steel immersed in Seawater is shown in Fig 5b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Fig 5c shows that the presence of 300 ppm of HP and 30 ppm of Ni^{2+} in Seawater gives the formation of thick films on the carbon steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to block the active site present on the carbon steel surface [25-28].
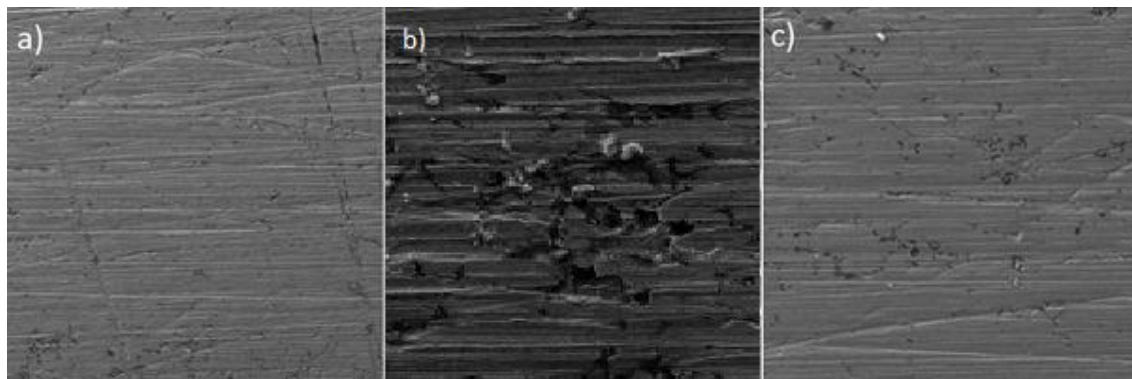

Figure 4- SEM images of carbon steel surface (a) Polished metal (b) Sea water (c) Sea water+ 30 ppm of Ni^{2+} + 300 ppm HP

3.5. Mechanism of corrosion inhibition

The results of weight loss study show that the formulation consists of 300 ppm HP and 30 ppm Ni^{2+} has 92% IE, in controlling corrosion of carbon steel in Sea water. A synergistic effect exists between HP and Ni^{2+}. Polarization study reveals that HP–Ni^{2+} system functions as anodic inhibitor controlling anodic reaction

predominantly and controls anodic reaction to some extent. FTIR spectra reveal that the protective film consists of Fe^{2+}-HP complex and $Ni(OH)_2$. SEM studies confirm the formation of protective film on the metal surface. The effective synergistic formulation consists of 300 ppm of HP, 30 ppm of Ni^{2+} and 50 ppm of SG shows IE 93% BE. Also the effective synergistic formulation consists of 300 ppm of HP, 30 ppm of Ni^{2+} and 200 ppm of SG shows IE 100% BE. The addition of HP reduces metal dissolution in an aqueous environment and this may be due to adsorption and complex formation at the metal surface with the combined application of HP and Ni^{2+}. Hence the corrosion process is inhibited.

The mechanism can be generalized as follows.
When the formulation consists of HP (300 ppm) and Ni^{2+} (30 ppm) is added in Sea water there is a formation of HP – Ni^{2+} complex in solution.
When carbon steel is immersed in this solution, HP – Ni^{2+} complex diffuses from the bulk of the solution towards the metal surface.

HP – Ni^{2+} complex is converted into HP – Fe^{2+} complex on the anodic sites of the metal surface with the release of Ni^{2+} ion.

$$HP – Ni^{2+} + Fe^{2+} \quad HP – Fe^{2+} + Ni^{2+}$$
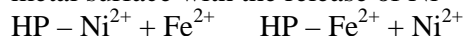
The released Ni^{2+} combined with OH^- to form $Ni(OH)_2$ on the cathodic sites of the metal surface.

$$Ni^{2+} + 2\,OH^- \quad Ni(OH)_2$$

Thus the protective film consists of HP – Fe^{2+} complex and $Ni(OH)_2$.

In near neutral aqueous solution, the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of HP – Fe^{2+} on the anodic sites of the metal surface. The cathodic reaction is the generation of OH^-. It is controlled by the formation of $Ni(OH)_2$ on the cathodic sites of the metal surface.

$$Fe \quad Fe^{2+} + 2\,e^- \text{ (anodic reaction)}$$

$$H_2O + \tfrac{1}{2}\,O_2 + 2\,e^- \quad 2\,OH^- \text{ (cathodic reaction)}$$

$$Fe^{2+} + HP \quad HP – Fe^{2+} \text{ complex}$$

$$Ni^{2+} + 2\,OH^- \quad Ni(OH)_2$$

This accounts for the synergistic effect of HP – Ni^{2+} system.

4. CONCLUSION

The Weight–loss study reveals that the formulation consisting of 30ppm of Ni^{2+} and 300ppm of HP has 92%inhibition efficiency, for one day system and explains the Synergistic effect between HP and Ni^{2+} complexes.

The protective film consists of Fe^{2+}-HP and $Ni(OH)_2$ is explained by FT-IR spectroscopy.

The results of polarization study show that the anodic reaction is controlled predominantly indicating the reduction of resolution metal as more HydroxyProline molecules are transported to the cathodic sites in the presence Ni^{2+} ions.
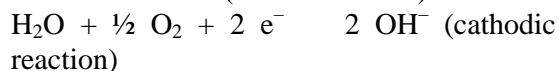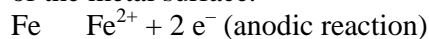
SEM confirms the presence of a protective film on the metal surface.

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