

SYNERGISTIC INHIBITION BEHAVIOUR OF HYDROXY PROLINE – Zn²⁺ SYSTEM ON MILD STEEL IN WELL WATER

¹Dr.S.K.Selvaraj, K.Karthik Kumar, X.Joy Pradeep & ²Dr.A.John Amalraj

¹PG and Research Department of Chemistry, G.T.N. Arts College, Dindigul, Tamil Nadu, India

²PG and Research Department of Chemistry, Periyar E.V.R College (A), Tiruchirappalli, Tamil Nadu, India

Abstract

The inhibition effect of Hydroxy Proline (HP)–Zn²⁺ system controls the corrosion of mild steel has been studied by weight–loss method. The weight–loss study that the formulation consisting of 30 ppm of Zn²⁺ and 250 ppm of Hydroxy Proline has 94% inhibition efficiency. Synergistic effect exists between Hydroxy Proline–Zn²⁺ system. The influence of N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) on the HP–Zn²⁺ system control the microbial corrosion. The protective film consists of Fe²⁺-Hydroxy Proline and Zn(OH)₂ by FTIR spectroscopy. Scanning electron microscopy (SEM) were used to investigate the nature of protective film formed on the Mild steel surface and for explaining the mechanistic aspects of the inhibition process.

Keywords: Hydroxy Proline, corrosion inhibition, Mild steel, FT-IR and SEM.

Introduction

Mild steel finds many applications in industries due to its easy of availability, fabrication, low cost and good tensile strength besides various other desirable properties [1-3]. It suffers from severe corrosion when it comes in contact with aqueous solutions during cleaning, transportation, de-scaling, storage of acids and other chemical processes etc [4-5]. The heavy loss of metal whenever it contact with aqueous solution can be minimized to a great extent by the use of corrosion inhibitors [6-7]. It was found out that some kind of compounds is chemically adsorbed on the metal surface forming barrier for mass and charge transfer and consequently decreasing the rate of corrosion. Unfortunately, most of these compounds are harmful for both human being and environments [8-9].

An amino acid namely Hydroxy Proline (HP) was investigated as a corrosion inhibitor for mild steel in this study. The inhibitive properties and synergistic effect of Hydroxy Proline and Zn²⁺ ions in controlling the corrosion of mild steel was studied in Well water using weight-loss method and electrochemical methods. Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) were used to analyse the protective film formed on the mild steel surface and a suitable mechanism of corrosion inhibition is proposed [10-14].

Experimental

Preparation of Specimen

Mild 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. Mild steel rod of the same composition, encapsulated in Teflon was polished to a mirror finish and degreased with trichloroethylene.

Preparation of HydroxyProline

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

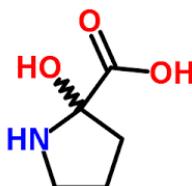


Fig.1 Structure of HydroxyProline

Weight-Loss Method

Two mild steel specimens were immersed in 100 ml of test solution containing various concentrations of the inhibitors in the absence and presence of Zn^{2+} ions, for a period of three days. 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.

Corrosion Inhibition Efficiency

Corrosion inhibition efficiency was calculated using the equation:

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

Where W_1 – Corrosion rate in the absence of inhibitor,

W_2 – Corrosion rate in the presence of inhibitor

Surface Examination

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

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.

Potentiodynamic Polarization

Polarization studies were carried out in an electrochemical work station impedance analyser model CHI 660A. a three electrode cell assembly was used. The working electrode was mild steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

Results and Discussion

Weight Loss Study

The corrosion rates of mild steel immersed in various test solution for a period of three days are presented in the table 1.

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

Table 1 Inhibition Efficiencies (IE%) and Corrosion Rates (CR) Obtained From HP- Zn^{2+} Systems when mild Steel Immersed in Well Water

Inhibitor system: HP- Zn^{2+} Immersion period: 3 days

HP (ppm)	$Zn^{2+} = 0$ ppm		$Zn^{2+} = 15$ ppm		$Zn^{2+} = 30$ ppm	
	IE%	CR (mmpy)	IE%	CR (mmpy)	IE%	CR (mmpy)
0	-	0.1137	13	0.0989	29	0.0807
50	10	0.1023	22	0.0887	59	0.0466
100	14	0.0978	31	0.0785	73	0.0307
150	18	0.0932	37	0.0716	77	0.0262
200	25	0.0853	43	0.0648	82	0.0205
250	33	0.0762	49	0.0580	94	0.0068

The calculated inhibition efficiencies of mild steel immersed in Well water, for a period of three days in the absence and presence of Zn^{2+} ion are given in table 1. 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 Zn^{2+} ion. HP alone shows some IE. But the combination of 250 ppm HP and 30 ppm Zn^{2+} shows 94% IE. this suggests a synergistic effect exists between HP and Zn^{2+} [15-16].

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

Table 2 Influence of Immersion Period (IP) on IE of HP (250ppm) - Zn^{2+} (30ppm) System

System	Immersion period (days)			
	1	3	5	7
Well water CR (mmpy)	0.1098	0.1137	0.1159	0.1173
Well water + HP(250ppm) + Zn^{2+} (30ppm); CR (mmpy)	0.0022	0.0068	0.0128	0.0211
IE %	98	94	89	82

The influence of immersion period on the IE of HP (250ppm) – Zn^{2+} (30ppm) system is given in table 2 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 chloride present in Well water. There is a competition between two processes, namely, formation of $FeCl_2$ (and also $FeCl_3$) 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 of N-Cetyl-N, N, N-Trimethyl Ammonium Bromide (CTAB) on Inhibition Efficiency of HP- Zn^{2+} System

Table 3 Influence of CTAB on inhibition efficiency (IE%) of mild steel immersed in Wellwater

HP (ppm)	Zn^{2+} (ppm)	CTAB (ppm)	CR (mmpy)	IE (%)
0	0	0	0.1137	-
250	30	0	0.0068	94
250	30	50	0.0054	95
250	30	100	0.0049	95
250	30	150	0.0010	100
250	30	200	0.0008	100
250	30	250	0.0007	100

CTAB is a cationic surfactant. It is a biocide. The IE and biocidal efficiency (BE) of HP- Zn^{2+} CTAB system is given here it is observed from the results that 50 ppm of CTAB in combination with HP- Zn^{2+} system has increased IE from 94% to 95%. However, an increase in IE of HP- Zn^{2+} System is noticed when the CTAB concentration increases from 100 ppm to 250 ppm. This is due to the formation of micelles at higher concentration of surfactant.

Analysis of Polarization Curves for HP-Zn²⁺ System

Table 4 Corrosion Potential (E_{corr}), Tafel Slopes (Anodic Slope b_a and Cathodic Slope b_c), Linear Polarization Resistance (LPR) and Corrosion Current (I_{corr}) Values are Absence and Presence of Inhibitors

Description	E_{corr} mV/decade	b_a mV/decade	b_c mV/decade	LPR ohm cm ²	I_{corr} A/cm ²
Well Water	-528	184	200	3929	1.062×10^{-5}
Well Water + 30 ppm Zn ²⁺ + 250 ppm HP	-485	206	175	5592	7.45×10^{-6}

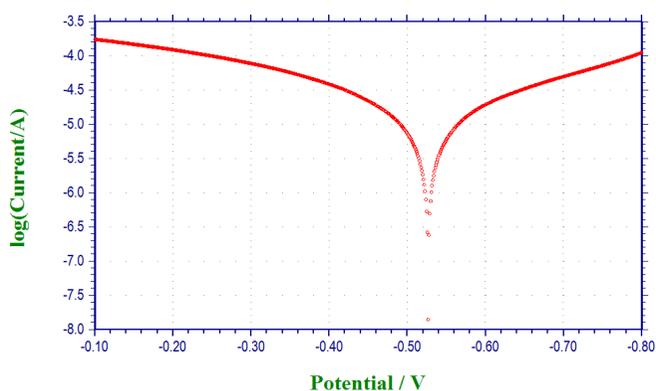


Fig.2.a) Potentiodynamic polarization curves of mild steel in Well Water

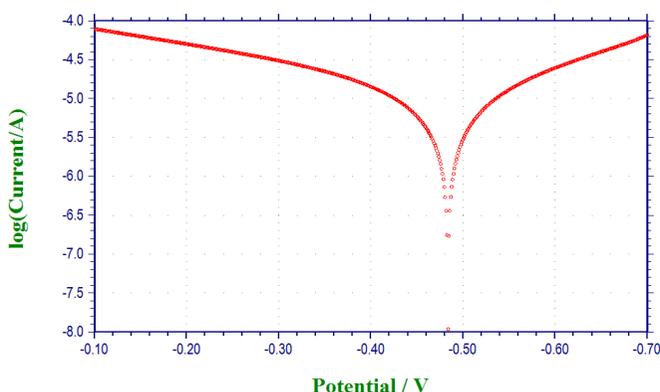


Fig.2.b) Potentiodynamic Polarization Curves of Mild Steel in Well Water + 30 ppm Zn²⁺ + 250 ppm HP

The calculated corrosion parameters such as corrosion potential (E_{corr}), Tafel slopes (anodic slope b_a and cathodic slope b_c), linear polarization resistance (LPR) and corrosion current (I_{corr}) values are absence and presence of inhibitors are shown in table 4. When mild steel is immersed in Well water the corrosion potential is -528 mV vs saturated calomel electrode (SCE). The corrosion current is 1.062×10^{-5} A/cm². When HP (250 ppm) and Zn²⁺ (30 ppm) are added to the above system the corrosion potential is shifted to the anodic side (from -528mV). This suggests that the anodic reaction is controlled predominantly. Moreover, in presence of the inhibitor system, the corrosion current decreases from 1.062×10^{-5} A/cm² to 7.45×10^{-6} A/cm²

and LPR value increases from 3929 ohm cm² to 5592 ohm cm². These observations indicate the formation of protective film on the metal surface [17-20].

Surface Analysis

The structure of HydroxyProline is shown in fig 3. It contains C=O, CN, NH and OH stretching vibrations. The protective film formed on the surface of the metal in the presence of HydroxyProline–Zn²⁺ system in Well water has been analysed by FT-IR spectroscopy.

Analysis of FT-IR Spectra

FTIR spectrometer is a power instrument that is used to determine the formation of bonds for amino acid inhibitors absorbed on the metal surface. FTIR spectra have been used to analyse the protective film formed on the metal surface. The structure of HydroxyProline is shown in Fig. 1. FTIR spectrum of pure HydroxyProline is given in Fig. 3a. The CN stretching frequency appears at 1327 cm⁻¹. The C=O stretching frequency of carboxyl group appears at 1642 cm⁻¹. The NH stretching frequency appears at 3429 cm⁻¹.

The FTIR spectrum (KBr) of film formed on the surface after immersion in well water for 3 days containing 250 ppm of HydroxyProline and 30 ppm of Zn²⁺ is shown in Fig. 3b. The CN stretching frequency has shifted from 1327 to 1302 cm⁻¹. The C=O stretching frequency of carboxyl group has shifted from 1642 cm⁻¹ to 1629 cm⁻¹. The N-H stretching frequency of HydroxyProline has shifted from 3429 cm⁻¹ to 3417 cm⁻¹. This indicates that the nitrogen atom of HP has coordinated with Fe²⁺ formed on the metal surface resulting in the formation of Fe²⁺-HydroxyProline complex on the anodic sites of the metal surface. The peak at 1382 cm⁻¹ is due to Zn-O stretching. The stretching frequency due to –OH appears at 3690 cm⁻¹. Thus FTIR study leads to the conclusion that the protective film consists of Fe²⁺-HydroxyProline complex and Zn(OH)₂ formed on the metal surface [21-24].

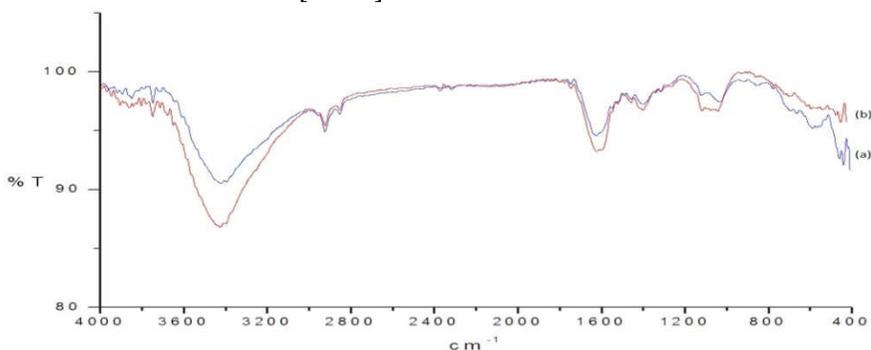


Fig.3 FT-IR Spectra of a) Pure HP b) Well Water+250ppm of HP+30ppm of Zn²⁺ Scanning Electron Microscopy (SEM)

The scanning electron micrographs of mild steel are shown in Fig 4. The SEM micrograph of polished mild steel surface (control) is shown in Fig 4a. 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 mild steel immersed in Wellwater is shown in Fig 4b. 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 4c shows that the presence of 250 ppm of HP and 30 ppm of Zn²⁺ in Wellwater gives the formation of thick films on the mild 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 mild steel surface [25-28].

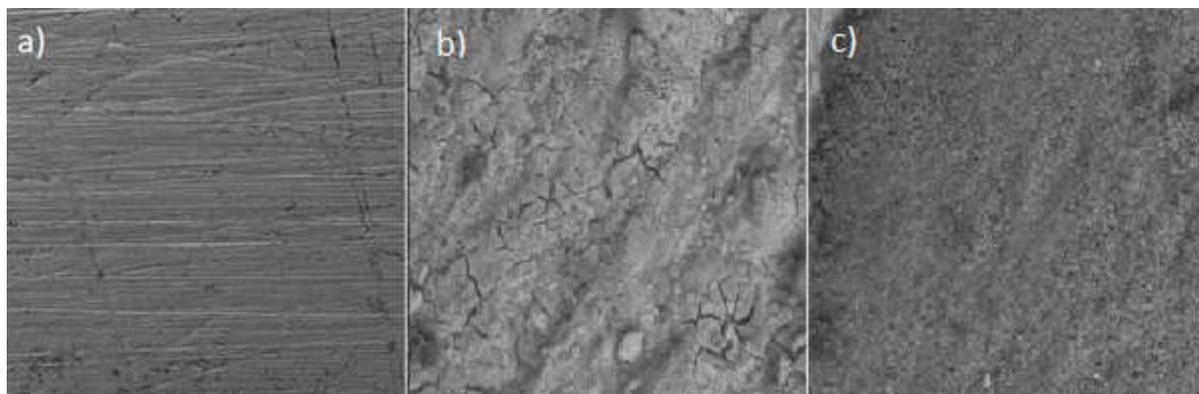


Fig.4 SEM Images of Mild Steel Surface (a) Polished Metal (b) Well Water (c) Well water+ 30 ppm of Zn²⁺ + 250 ppm HP

Mechanism of Corrosion Inhibition

The results of weight loss study show that the formulation consists of 250 ppm HP and 30 ppm Zn²⁺ has 94% IE, in controlling corrosion of mild steel in Well water. A synergistic effect exists between HP and Zn²⁺. Polarization study reveals that HP-Zn²⁺ 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 Fe²⁺-HP complex and Zn(OH)₂. SEM studies confirm the formation of protective film on the metal surface. The effective synergistic formulation consists of 250 ppm of HP, 30 ppm of Zn²⁺ and 50 ppm of CTAB shows IE 95% BE. Also the effective synergistic formulation consists of 250 ppm of HP, 30 ppm of Zn²⁺ and 150 ppm of CTAB shows IE 100% BE.

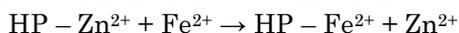
The addition of HP reduces metal dissolution in an aqueous environment and this may be due to adsorption and complex formation at the metal surface with the combined application of HP and Zn²⁺. Hence the corrosion process is inhibited.

The Mechanism can be generalized as follows

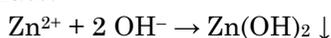
When the formulation consists of HP (250 ppm) and Zn²⁺ (30 ppm) is added in Well water there is a formation of HP – Zn²⁺ complex in solution.

When mild steel is immersed in this solution, HP – Zn²⁺ complex diffuses from the bulk of the solution towards the metal surface.

HP – Zn²⁺ complex is converted into HP – Fe²⁺ complex on the anodic sites of the metal surface with the release of Zn²⁺ ion.

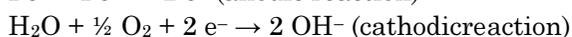
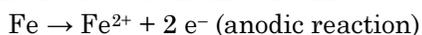


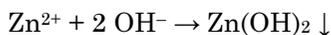
The released Zn²⁺ combined with OH⁻ to form Zn(OH)₂ on the cathodic sites of the metal surface.



Thus the protective film consists of HP – Fe²⁺ complex and Zn(OH)₂.

In near neutral aqueous solution, the anodic reaction is the formation of Fe²⁺. This anodic reaction is controlled by the formation of HP – Fe²⁺ on the anodic sites of the metal surface. The cathodic reaction is the generation of OH⁻. It is controlled by the formation of Zn(OH)₂ on the cathodic sites of the metal surface.





This accounts for the synergistic effect of HP – Zn²⁺ system.

Conclusion

- The Weight-loss study reveals that the formulation consisting of 30ppm of Zn²⁺ and 250ppm of HP has 94% inhibition efficiency, for three days system and explains the Synergistic effect between HP and Zn²⁺ complexes.
- The protective film consists of Fe²⁺-HP and Zn(OH)₂ is explained by FT-IR spectroscopy.
- Potentiodynamic polarization studies reveal that the inhibitor system is of an anodic type.
- SEM Confirm the presence of a protective film on the metal surface.

References

1. Labriti B. Dkhireche N. Touir R. EbnTouhami M. Sfaira M. El Hallaoui A., Hammouti B. and Alami A., Arab. J. Sci. Eng., 37, 1293-1303 (2012).
2. Kumar S., Sharma D., Yadav P. and Yadav M., Ind. Eng. Chem. Res., 52 (39), 14019–14029 (2013).
3. Gerengi H., Ind. Eng. Chem. Res., 51, 12835–12843 (2012).
4. Quraishi M.A., Ansari F.A. and Jamal D., Mater. Chem. Phys., 77 (3), 687-690 (2002).
5. Deng S. Li X. and Fu H., Corros. Sci., 53, 822-828 (2011).
6. Yoo S.H. Kim Y.W. Chung K. Kim N.K. and Kim J. S., Ind. Eng. Chem. Res., 52 (32), 10880–10889 (2013).
7. Ghareba S. and Omanovic S., Electrochim. Acta., 56, 3890–3898 (2011).
8. Rammelt U. Koehler S. and Reinhard G., Corros. Sci., 53, 3515-3520 (2011).
9. Demadis K.D., Mantzaridis C. and Lykoudis P., Ind. Eng. Chem. Res., 45, 7795-7800 (2006).
10. Florence G.R.H. Antony A.N. Sahayaraj.J.W, Amalraj A.J. and Rajendran S., Ind. J. Chem. Technol., 12, 472-476 (2005).
11. K. Anuradha, R. Vimala, B. Narayanasamy, J.A. Selvi and S. Rajendran, Chem. Engg. Communi., 195 (2008) 352.
12. F. Zhang, J. Pan and P.M. Claesson, ElectrochimicaActa, 56 (2011) 1636.
13. X. Zhou, H. Yang and F. Wang, ElectrochimicaActa, 56 (2011) 4268.
14. D.M. Ortega-Toledo, J.G. Gonzalez-Rodriguez, M. Casales, M.A. Neri-Florez and A. Martinez-Villafane, Mater. Che. and Phy., 122 (2010) 485.
15. F. El-TaibHeakal, A.S. Fouda and M.S. Radwan, Mater. Che. and Phy., 125 (2011) 26.
16. C. Thangavelu, M. Umarani, P. Patric Raymond and M. Sekar, Proc. 15thNational Cong. Corr. Control, Chennai, (2010) 59.
17. H. S. Awad and S. Jurgoose, British Corr. J., 37 (2002) 147.
18. ATSDR. Toxicological Profile for Chromium (update). U.S. Dept. Healthand Human services, Public Health Service, Atlanta, GA, (2000).
19. S. Ramesh, S. Rajeswari and S. Maruthamuthu, Mater. Lett., 57 (2003) 4547.
20. A.B. Tadros and Y. Abdel-Naby, J. Electroanal. Chem., 224 (1988) 433.
21. B.D. Donnelly, T.C. Downie, R. Grzeskowiak, H.R. Hamburg and D. Short, Corr. Sci., 38 (1997) 109.
22. J.G.N. Thomas, Some New Fundamental Aspects in Corrosion Inhibition: Proc. 5th Euro. Symp. Corr. Inhibitors, Italy, Univ. Ferrara, (1981) 453.
23. M.A. Pech-Canul and P. Bartolo-Perez, Surf. and Coat.Tech., 184 (2004) 133.
24. Alagta, I. Felhosi, J. Telegdi, I. Bertoti and E. Kalman, Corr. Sci., 49 (2007) 2754.

25. J.W. Sahayaraj, P. Raymond, S. Rajendran and A.J. Amalraj, *J. Electrochem. Soc.*, 56 (2007) 14.
26. G.R.H. Florence, A.N. Antony, J. W. Sahayaraj, A.J. Amalraj and S. Rajendran, *Indian J. Chem. Tech.*, 12 (2005) 472.
27. T. Umamathi, J.A. Selvi, S.A. Kanimozhi, S. Rajendran and A.J. Amalraj, *Indian J. Chem. Tech.*, 15 (2008) 560.
28. Brightson Arul Jacob Y. Sayee Kannan R. and Jeyasundari J., *Res. J. Chem. Sci.*, 3(4), (2013) 54-58.