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RESEARCH ARTICLE

Corrosion Inhibition by usage of Iso Leucine as Inhibitor on Mild Steel, Analysed by Experimental and Theoretical Methods

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ABSTRACT

This study is involves the usage of amino acid as corrosion inhibitor, as amino acids are natural compounds and are non-hazardous to environment. Amino acid Iso-leucine is picked up as an inhibitor for inhibiting corrosion on mild steel by using well water as a medium. Iso-leucine depicts the inhibition efficiency of 83% in 250ppm of Iso -leucine in well water and 30ppm of zinc, which is outlined by Gravimetric method. The contents of the inhibitor are revealed by FTIR spectral studies and polarization study insist that Iso-leucine is an anodic type of inhibitor.

Keywords: Inhibitor, corrosion, Amino acids, mild steel and Iso-leucine.

INTRODUCTION

Corrosion of metals is an electrochemical phenomena where immediate destruction of metal takes place. A good example for corrosion is rusting of steel and iron, but corrosion is also observed in ceramics and plastics. In case of metals it's a change of meta stable condition to stable condition of the mineral , where there is a decrease in free energy of the system. Corrosion can be wet and dry, wet type is due to the contact of metal with any type of solution or water and dry corrosion happens due to a touch of metal with air, moisture or oxygen in the atmosphere. As we can see a vast of steel due to its durability and strength is used in automobile industries and transportation purposes and this process of corrosion reduced the life of steel. So it has become a national issue spending lakhs of money on getting back the metal. Therefore this study relies on using environmental friendly and easily available materials as inhibitors. As we can see that these amino acids [6,7,8] are easily available and is also environmental friendly. The usage of these amino acids and its inhibition efficiency has proven to be used under normal atmospheric conditions where the metal is in direct contact with air and moisture. And further the fact also lies that these amino acids are also unreactive to water or air and also remains as such on metal surface also forming a protective coat preventing it from atmospheric deterioration.

MATERIALS AND METHOD

Mild Steel Specimen Preparation

A mild steel specimen having a composition of carbon-0.0104%, Sulphur-0.026%, phosphorus-0.035%, Manganese-0.58%, Iron-99.287% and dimension of 1.5cm X3.5cmX0.2cm is used. The surface of the specimen is polished before use[13].

Inhibitor

Iso-leucine was employed as an inhibitor, which is a type of amino acid having α-amino acid, α-carboxylic acid and a hydrocarbon side chain with a branch.

Preparation of Stock Solution

Iso-Leucine (Iso-Leu)

Iso-Leucine of 1 gm was dissolved in distilled water and made up to 100ml in a SMF and 1ml of the solution is made up to 100ml in another SMF yielding 100ppm of Iso-leucine.

Preparation of Zinc Sulphate Solution

1.09g of zinc sulphate was dissolved in double distilled water and 10ppm of Zn^{2+} ion concentrations is made up.

Gravimetric Method

The weighed specimens were allowed to stand in 100 ppm of Well water containing various concentrations of the inhibitor in the absence and presence of $Zn^{2+}$for one day of immersion. After a day of immersion, the specimens were taken out, and weighed. By change in weight of the specimen, corrosion rates were calculated using the following relationship [1,25,29,].

$$\text{Corrosion Rate (mmpy)} = \frac{87.6 \times \text{weight loss in mg}}{D \times A \times T}$$

D = Density of the Specimen
A = Surface area of the Specimen
T = Time (hr)

The inhibition efficiency (IE) was then calculated using the equation:

$$IE\ \% = \frac{W_1 - W_2}{W_1}$$

W_1 is the weight loss value in the absence of inhibitor and
W_2 is the weight loss value in the presence of inhibitor.

Electrochemical Measurements

This study was undergone by a 3 electrode cell assembly, where working electrode was carbon steel, platinum electrode was the counter electrode and saturated calomel electrode is fixed as the reference electrode. The time interval given to reach the steady state open circuit potential is around 5-10 minutes. With the help of the results , we can get E_{corr}(corrosion potential) and I_{corr}(corrosion current) values[41,43,48,50].

Tafel slopes anodic = ba and cathodic = bc and LPR value. The scan rate (V/S) was 0.01.Hold time at (Efcs) was zero and quiet time (s) was two.

AC Impedence Measurements

The AC impedence is calculated in the frequency range of 105 KHz to 101 KHz . This cell impedence gives us information about processes such as electronic or ionic conduction in electrode and electrolytes, interfacial charging at surface films or double layer. Z'(real part) and Z" (imaginary part) of cell impedence is measured in ohms. Here, $E_{(v)}$ =0, high frequency (Hz) =1x105, Low frequency (Hz) =1, Amplitude =0.005, quiet time (s) =2,
Rt=(Rs+Rt)-Rs
Rt-Charge transfer resistance
Rs= solution resistance
$C_{dl}=1/2\Pi Rt\, f_{max}$
f_{max}=maximum frequency

FTIR Spectra

FTIR spectra is used to find out chemical bonds in a molecule by producing IR spectrum[37,39], producing a molecular finger print, with which samples of different components are studied. Here, FTIR spectra enlightens about the presence of protective layer present on the metal surface. It gives out information's about various functional groups present in inhibitor and type of complex formed as a result of interaction between iron and Iso-Leucine.

RESULT AND DISCUSSION

Gravimetric method (Iso Leucine-Zn^{2+})

Corrosion rates and inhibition efficiencies of mild steel in the absence and presence of Iso-Leucine+Zn^{2+}(under 1 day suspension)

The carbon steel immersed in well water of 300ppm of Iso-Leucine without zinc , shows inhibition efficiency of 33% and by adding zinc , the inhibition efficiency is raised to about 83%for 30ppm zinc and 250ppm of Iso-Leucine. This proves the existence of synergistic effect between zinc and iso-leucine.

Synergism Parameter (S1)

The synergism parameters are used to find the interaction between inhibitors. If S1 is greater than 1, it indicates the presence of synergistic effect. If its equal to 1, then there is no interaction between the inhibitors and in case of less than 1. Then there is a negative interaction between the inhibitors.

Synergism parameter are calculated by

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}}$$

Where,
I_1 is the surface coverage of inhibitor (Iso-Leucine),
I_2 is the surface coverage of inhibitor (Zn^{2+}) and
$I'_{1+2}$is the combined surface coverage of inhibitors (Iso-Leucine) and (Zn^{2+}).

The synergistic effect prevailing between 250ppm of Iso-Leucine and 30ppm of Zn2+ are around 2.5716, that is greater than 1, reveals the synergistic effect between inhibitors.

Analysis of Variance ANOVA

F-test is used to investigate synergistic effect existing between 2 inhibitors. The analysis of variance of ANOVA is for the influence of 15ppm and 30ppm of Zn^{2+} on inhibition efficiencies of 50ppm, 100ppm, 150ppm, 200ppm, 250ppm of Iso-Leucine. For 15ppm of Zn^{2+} , F-value is 1. 6664, which is not significant as F-value is less than 5.32 for 1,8 degrees of freedom at 0.05 level of significance . Therefore, for 15ppm of Zn2+,the inhibition efficiency for various concentration of Iso-Leucine was not significant.

But in case of 30ppm of Zn^{2+}F-value is 0.0337which is also not significant, as the F-value is less than 5.32for 1,8 degrees of freedom. So various concentrations of Iso-Leucine for 30ppm of Zinc is also not significant.

Analysis by Polarization Technique

1. Well Water
2. 300 ppm of Iso-Leucine + 30 ppm of Zn^{2+} + Well Water

The carbon steel is immersed in well water [22] , the corrosion potential is around -580mV vs SCE. The shift of corrosion potential is observed in -603mV vs SCEm for 300ppm of Iso-Leucine and 30ppm of zinc. This shift is on negative side, and anodic Tafel (ba) slope for 300ppm of Iso-Leucine and 30ppm of Zn2+ was been shifted anodically 60mV/decade than cathodic Tafel (bc) slope 11mV/decade. From this observations ,its clear that Iso-Leucine –Zn^{2+} is anodic type of inhibitor.

The above result also suggest corrosion current value to be $5.5432 x 10^{-5}$ and LPR value was $963 \Omega cm^2$ for well water . And for inhibitors, corrosion current value has decreased to $1.0250 x 10^{-5} A/cm^2$ and LPR value has increased to $3130 \Omega cm^2$. The presence of inhibitor is retrieved by increase in LPR value and decrease in corrosion current value.

Analysis of AC Impedence Spectra

Fig.6.1 AC impedance of carbon steel immersed in
1. Well Water
2. 250 ppm of Iso-Leucine + 30 ppm of Zn^{2+} + Well Water

Fig.6.1 exposes AC impedence spectra [25,26,27,28,31,32,33] of carbon steel immersed in well water in presence and absence of inhibitors.
In the above Table 6.1, we can retrieve the values of Rct which is $743.22 \Omega cm^2$ and C_{dl} value is $5.3262 x 10^{-8}$ µF/cm^2. In the presence of Iso-leucine and Zn^{2+}[3]R_{ct} value increases to 1489.16Ωcm2 and C_{dl} value decreases to 0.4875 x 10^{-8} µF/cm^2. These results indicate the existence of thin layer of the inhibitor with zinc on the metal surface**.**

Analysis by FTIR Spectra

Fig.7.1. FT-IR spectra of
1. Pure Iso-Leucine
2. Protective film formed on the surface of the metal immersed in Well Water containing 300 ppm of Iso-Leucine and 30 ppm of Zn^{2+}.

The above figure insists us to believe on the existence of Iso-Leucine on the metal surface. FTIR spectra of the inhibitor Iso-Leucine dried on a glass plate, gives CN stretching frequency at 1129cm^{-1}, CO and NH stretching frequency at 3449.25cm^{-1}. Now, the spectral analysis of presence of Iso-Leucine on metal surface frequency shift from 1129.69cm^{-1} and 1109.17cm^{-1} for CN. Stretching frequency of CO is shifted from 1603.28cm^{-1} to 1631.19cm^{-1} and there is also a shift of frequency for NH from 3449.25cm^{-1} to 3469.77cm^{-1}. These spectral details indicate that nitrogen atom of Iso-Leucine coordinated with Fe^{2+} is formed on metal surface, leading to formation of Fe^{2+}-Iso-Leucine complex on anodic sites of the metal surface[39].

CONCLUSION

Iso leucine shows good inhibition efficiency in well water and the presence of inhibitor is confirmed by FTIR and weight loss method . The type of inhibitor is analysed by electrochemiscal studies.

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Gravimetric method (Iso Leucine-Zn^{2+})

Table 1. Corrosion rates and inhibition efficiencies of mild steel in the absence and presence of Iso-Leucine+Zn^{2+}(under 1 day suspension)

Iso-Leu (ppm)	IE %			CR (mmpy)		
	Zn^{2+} (ppm)			Zn^{2+} (ppm)		
	0	15	30	0	15	30
0	-	8	16	0.1051	0.0963	0.0903
50	8	33	58	0.0963	0.0700	0.0438
100	10	41	66	0.0876	0.0613	0.0350
150	25	33	75	0.0788	0.0700	0.0262
200	25	41	75	0.0788	0.0613	0.0262
250	33	41	83	0.0700	0.0613	0.0175

Table 2. Synergism parameter for Iso-Leucine-Zn^{2+} (15ppm) system in carbon steel immersed in well water for a day

Iso-Leu (ppm)	Zn^{2+} (ppm)	I_1	I_2	I''_{1+2}	S_I	IE%
50	15	0.8	0.8	0.33	2.2089	33
100	15	0.16	0.8	0.41	1.5050	41
150	15	0.16	0.8	0.33	1.3253	33
200	15	0.25	0.8	0.41	1.4745	41
250	15	0.33	0.8	0.41	1.0677	41

Table 3. Synergism parameter for Iso-Leucine-Zn2+ (30ppm) system in carbon steel immersed in well water for a day

Iso-Leu (ppm)	Zn^{2+} (ppm)	I_1	I_2	I''_{1+2}	S_I	IE%
50	30	0.8	0.16	0.58	2.1142	58
100	30	0.16	0.16	0.66	2.0752	66
150	30	0.16	0.16	0.75	3.8224	75
200	30	0.25	0.16	0.75	2.5200	75
250	30	0.33	0.16	0.83	2.5716	83

Table 4. Distribution of F-value between inhibition efficiency of various concentration of Iso-Leucine and inhibition efficiencies of Iso-Leucine in the presence of 15ppm and 30ppm

Zn^{2+} (ppm)	Source of Variance	Sum of Squares	Degree of freedom	Mean Square	F-value	Level of Significance of F
15	Between	6466	1	6466		P> 0.05
	Within	31046	8	3880	1.6664	
30	Between	4727	1	4727		P< 0.05
	Within	111947	8	13993	0.0337	

Table 5. Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor obtained by polarization method

Concentration		Tafel Parameters				
Iso-Leu (ppm)	Zn^{2+} (ppm)	E_{corr} (mV vs SCE)	I_{corr} (A/Cm²)	ba (mV/dec)	b_c (mV/dec)	LPR (Ω cm²)
0	0	-580	5.5431×10^{-5}	116.23	110.88	963
250	30	-590	0.6897×10^{-5}	185.89	180.32	3671

Table 6. Corrosion parameters of carbon steel immersed in Well Water in the presence and absence of inhibitor obtained by AC impedance spectra:

L-Proline (ppm)	Zn^{2+} (ppm)	R_{ct}(Ω cm²)	C_{dl} (μF/cm2)
0	0	391	1.3137×10^{-6}
250	30	3018	0.0253×10^{-6}

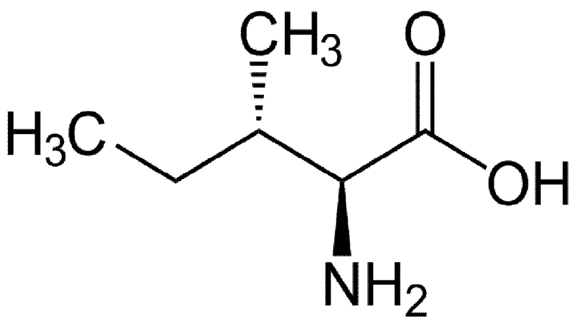

Fig. 1. Structure of Iso-Leucine

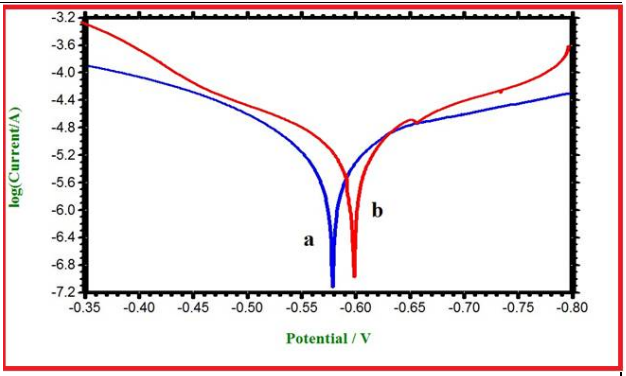

Fig.2. Analysis By Polarization Technique

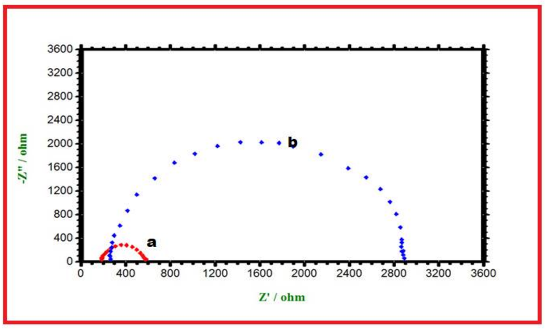

Fig.3. Analysis of AC impedence spectra

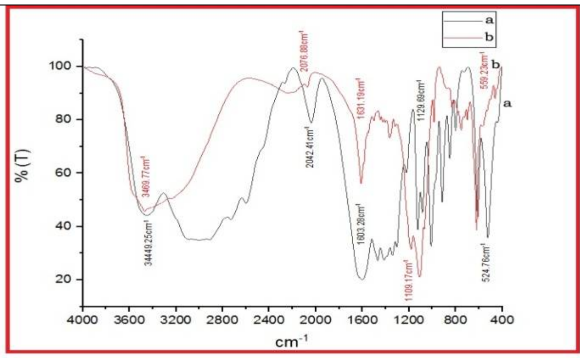

Fig.4. Analysis by FTIR spectra