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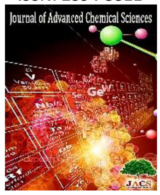

Synergistic and Antagonistic Effects of L–Alanine as Green Corrosion Inhibitor for Carbon Steel in Aqueous Medium

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ABSTRACT

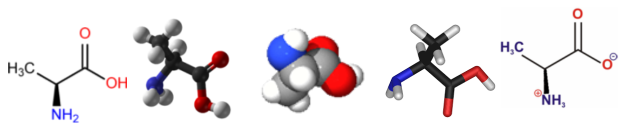
The environmental friendly inhibitor system L-alanine-Zn^{2+} has been investigated by weight loss method. A synergistic effect exists between L-alanine and Zn^{2+} system. The formulation consisting of L-alanine - Zn^{2+} offers good inhibition efficiency. Polarization study reveals that this formulation functions as an anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study and electrochemical studies. At isoelectric point, the IEs of L-alanine and also the L-alanine-Zn^{2+} systems are very low. In some cases there is acceleration of corrosion (negative IEs).

1. Introduction

Carbon Steel is widely used as the constructional material in most of the major industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. The use of inhibitors is one of the most practical methods to prevent the corrosion or to reduce the corrosion rate. The majority of well-known inhibitors are organic compounds containing heteroatom, such as O, N, S and multiple bonds [1]. Most of the organic compounds are not only expensive but also toxic to both human beings and environments [2] and therefore it is better to look for environmentally safe inhibitors. Many researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion [3-13]. This is due to the fact that amino acids are non-toxic, biodegradable, relatively cheap, and completely soluble in aqueous media and produced with high purity at low cost.

Various amino acids have been used to inhibit the corrosion of metals and alloys [3-13]. Eco–Friendly Inhibitor L–cysteine–Zn^{2+} System to control corrosion of carbon steel in aqueous medium [6]. The corrosion of SS 316L has been inhibited by glycine, leucine, valine, and arginine [7]. Sivakumar et al have used L-histidine to prevent corrosion on carbon steel [8]. Cystein, glycine, glutamic acid, and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl [9]. Amino acid such as DL-phenylalanine has been used to prevent corrosion of carbon steel [10] .The corrosion of brass in O_2-free NaOH has been prevented by methionine [11]. Sahaya Raja *et al* have used glycine along with Zn^{2+} to prevent corrosion of carbon steel in well water [12]. Arginine - Zn^{2+} system has been used to inhibit corrosion of carbon steel [13].

The environmental friendly L- alanine (Fig.1) is chosen as the corrosion inhibitor for this present work. The aim of this research is to investigate the synergistic and antagonistic effect of L- alanine. For this purpose the electrochemical studies such as potentiodynamic polarization and impedance spectroscopy have been used in the present study.



(a) (b)

Fig.1 a) various structural views of L – alanine; b) zwitter ion L – alanine at isoelectric point

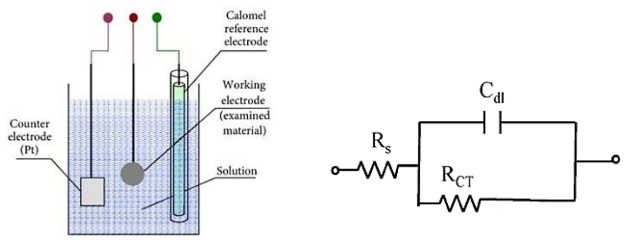
2. Experimental Methods

2.1 Determination of corrosion rate

All the weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance-AY62. Corrosion rates were calculated using the following relationship. Corrosion Rate (mm/y) = [loss in weight (mg) X 1000 / surface area of the specimen (dm^2) X period of the immersion (days)] X (0.0365/ρ).

2.2 Electrochemical and Impedance measurements

Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A) is shown in scheme 1.



(a) (b)

Scheme 1 a) Circuit diagram of three – electrode assembly; b) Equivalent circuit diagram: R_s is solution resistance, R_{ct} is charge transfer resistance, C_{dl} is double layer capacitance

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3. Results and Discussion

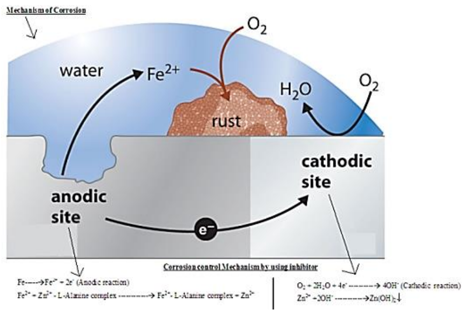
3.1 Analysis of the weight loss method

Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor (l-alanine) are given in Table 1a & 1b. The inhibition efficiencies (IEs) are also given these tables. It is observed from Table 1(a), that L-alanine shows some inhibition efficiencies. 50 ppm of L-alanine has 15 percent IE, as the concentration of L-alanine increases, IE increases.

3.2 Influence of Zn^{2+} on the inhibition efficiencies of L-Alanine

The influence of Zn^{2+} on the inhibition efficiencies of L-alanine is given in Table 1(b). It is observed that as the concentration of L-alanine increases the IE increases. Similarly, for a given concentration of L-alanine the IE increases as the concentration of Zn^{2+} increases. It is also observed that a synergistic effect exists between L-alanine and Zn^{2+}. For example, 5 ppm of Zn^{2+} has 8 percent IE; 250 ppm of L-alanine has 47 percent IE. Interestingly their combination has a high IE, namely, 83 percent. In presence of Zn^{2+} more amount of L-alanine is transported towards the metal surface. On the metal surface Fe^{2+}-L-alanine complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH^-, which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively (scheme 2). This accounts for the synergistic effect existing between Zn^{2+} and L-alanine. The corrosion rates and inhibition efficiencies of the L-alanine-Zn^{2+} systems as a function of concentrations of L-alanine are shown in Fig. 2.

$$Fe \longrightarrow Fe^{2+} + 2e^-\ \text{(Anodic reaction)}$$
$$Fe^{2+} + Zn^{2+} - \text{L-Alanine complex} \longrightarrow Fe^{2+}\text{- L-Alanine complex} + Zn^{2+}$$
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-\ \text{(Cathodic reaction)}$$
$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow$$



Scheme 2 Schematic representation of Corrosion mechanism and corrosion control mechanism for carbon steel by using inhibitors (L –alanine – Zn^{2+} system)

Table 1 Corrosion rates (CR) of carbon steel immersed in well water a) in the presence and b) in the absence of inhibitor system at various concentrations and the inhibition efficiencies (IEs) obtained by weight loss method. *(Inhibition system: L-alanine- Zn^{2+} (0 ppm and 5ppm), Immersion period : 1 day)*

Table 1a

L-Ala (ppm)	Zn^{2+} (ppm)	Corrosion Rate (mm/Y)	Inhibition Efficiency (%)
0	0	0.04730	--
50	0	0.04020	15
100	0	0.03640	23
150	0	0.02850	39
200	0	0.02740	42
250	0	0.02500	47

Table 1b

L-Ala (ppm)	Zn^{2+} (ppm)	Corrosion Rate (mm/Y)	Inhibition Efficiency (%)
0	0	0.04730	--
0	5	0.04352	8
50	5	0.01940	59
100	5	0.01609	66
150	5	0.01326	72
200	5	0.00940	79
250	5	0.00800	83

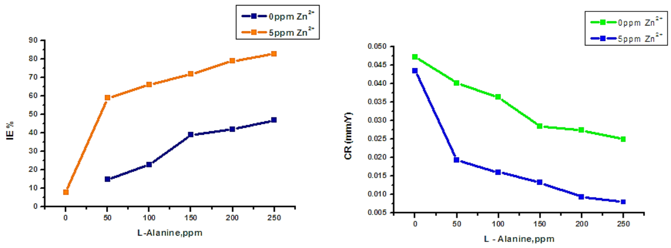


Fig. 2 Inhibition efficiencies (IEs) and corrosion rates (CR) of carbon steel immersed in various test solutions

3.3. Synergism parameters (S_I)

The synergism parameters (S_I) of L-alanine -Zn^{2+} system were found to be one and above (S_I>1, it points to synergistic effects). This indicates that the synergistic effect exist between L-alanine and Zn^{2+}.

3.4 Antagonistic Effect

3.4.1 Inhibition efficiency of L-alanine-Zn^{2+} system at the isoelectric point of alanine (pH = 6.1)

The IE of L-ala-Zn^{2+} system at the isoelectric point of alanine (pH=6.1) is given in Tables 2a and 2b. At isoelectric point, alanine exists as zwitter ion, when an electric field is applied there is no movement of ions [14, 15]. Accordingly it is observed from Tables 2a and 2b, the IEs of L-alanine and also the L-alanine-Zn^{2+} systems are very low. In some cases there is acceleration of corrosion (negative IEs). The corrosion rates and inhibition efficiencies of the isoelectric point of the L-alanine-Zn^{2+} systems as a function of concentrations of L-alanine are shown in Fig. 3.

Table.2 (a & b): Inhibition efficiency of L –alanine -Zn^{2+} system at the isoelectric point of alanine (pH = 6.1) (**Inhibition system :L-alanine- Zn^{2+} (0 ppm and 5ppm), Immersion period : 1 day)**

Table 2a

L-Ala (ppm)	Zn^{2+} (ppm)	Corrosion Rate (mm/Y)	Inhibition Efficiency (%)
0	0	0.680	--
50	0	0.638	6
100	0	0.666	2
150	0	0.734	-8
200	0	0.768	-13
250	0	0.781	-15

Table 2b

L-Ala (ppm)	Zn^{2+} (ppm)	Corrosion Rate (mm/Y)	Inhibition Efficiency (%)
0	0	0.680	--
0	5	0.659	3
50	5	0.829	-22
100	5	0.843	-24
150	5	0.924	-36
200	5	0.985	-45
250	5	1.033	-52

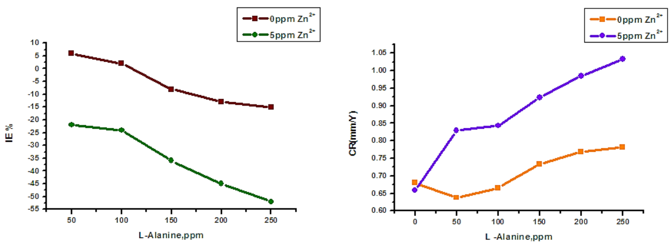


Fig. 3 Inhibition efficiencies (IEs) and corrosion rates (CR) of carbon steel immersed in various test solutions at isoelectric point (pH -6.1)

3.5 Analysis of potentiodynamic polarization study

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [6,8,10]. If a protective film is formed on the metal surface, the corrosion current value (I_{corr}) decreases. The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 4. When carbon steel was immersed in well water the corrosion potential was -673 mV vs SCE. When L-alanine (250 ppm) and Zn^{2+} (5 ppm) were added to the above system the corrosion potential shifted to the noble side-656 mV vs SCE. This indicates that a film is formed on the anodic sites of the metal surface. The corrosion current decreases from 5.980 x10^{-7} A/cm^2 to 2.832 x10^{-7} A/cm^2. Thus polarization study confirms the formation of a protective film on the metal surface.

3.5.1. Analysis of potentiodynamic polarization study at isoelectric point (pH = 6.1)

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors at isoelectric point (pH=6.1) are shown in Fig. 5. When carbon steel was immersed in well water, the corrosion potential was -652mV vs SCE. When L-alanine(250 ppm) and Zn^{2+} (5 ppm) were added to the above system, the corrosion potential shifted to -665 mV vs SCE. The corrosion potential is shifted cathodic side (active site). It is observed that I_{corr} value increases from 6.470 x10^{-7} A/cm^2 to 6.900 x10^{-7} A/cm^2, there is no protection of metal, the metal undergoes corrosion. This is in agreement with weight loss results. This is due to the fact that at isoelectric point (pH = 6.1) there is no migration of L–alanine towards the metal surface. Therefore amount of L-alanine transported towards the metal surface is reduced. So, metal is not protected by L-alanine. Hence there is no IE at isoelectric point.

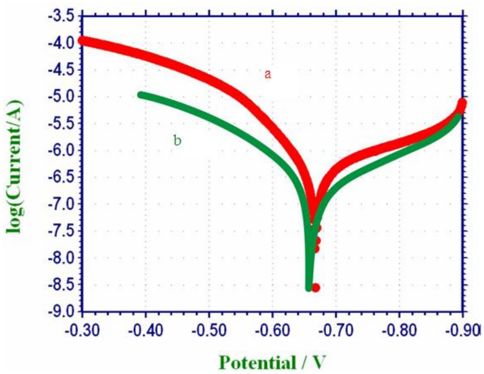


Fig. 4 Polarization curves of carbon steel immersed in test solutions a) Well water, b) well water + L-alanine (250 ppm) + Zn^{2+} (5 ppm)

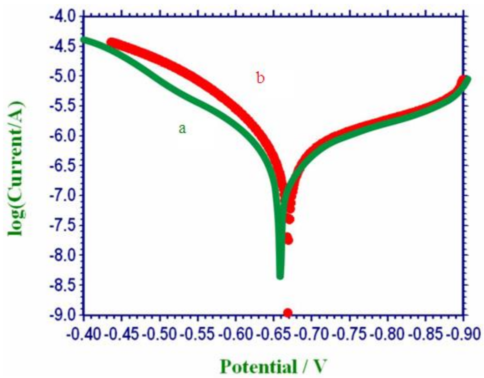


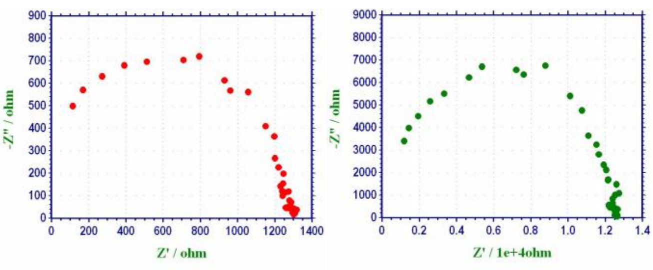
Fig. 5 Polarization curves of carbon steel immersed in test solutions at isoelectric point (pH-6.1) a) Well water, b) well water + L-alanine (250 ppm) + Zn^{2+} (5 ppm)

3.6. Analysis of AC Impedance spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface [11,13]. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L-alanine-Zn^{2+}) are shown in Fig. 6 (Nyquist plot). It is observed that when the inhibitors (L-alanine (250 ppm) +Zn^{2+} (5 ppm)) are added the charge transfer resistance (R_t) increases from 1199 Ω cm^2 to 11478 Ω cm^2. The C_{dl} value decreases from 3.8832 x 10^{-9} F/cm^2 to 4.0560 x 10^{-10} F/cm^2.

3.6.1 Analysis of AC impedance spectra at isoelectric point (pH=6.1)

The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L-alanine-Zn^{2+}) at isoelectric point are shown in Fig. 7 (Nyquist plot). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plot. It is observed that, when the inhibitors [L-ala (250 ppm) + Zn^{2+} (5 ppm)] are added, the charge transfer resistance (R_t) decreases from 1570 Ω cm^2 to 1475 Ω cm^2. The C_{dl} value increases from 2.9656 x 10^{-9} F/cm^{-2} to 3.1566 x 10^{-9} F/cm^{-2}. These results suggest that a protective film is not formed on the metal surface. When a protective film is not formed, charge transfer resistance (R_t) decreases and C_{dl} increases, there is no protection of metal, the metal undergoes corrosion. This is in agreement with weight loss results. This is due to the fact that at isoelelctric point (pH=6.1) there is no migration of L-alanine towards the metal surface. Therefore amount of L-alanine transported towards the metal surface is reduced. So, metal is not protected by L-alanine. Hence there is no IE at isoelectric point.



(a) (b)

Fig. 6 AC Impedence spectra of carbon steel immersed in test solution a) Well water, b) Well water + L-alanine(250 ppm) + Zn^{2+} (5 ppm)

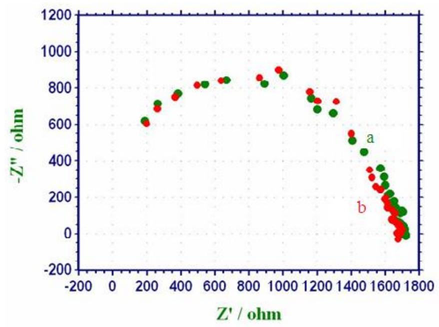
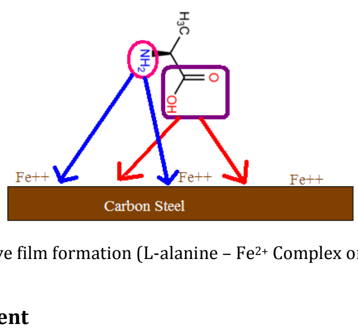


Fig. 7 AC Impedence spectra of carbon steel immersed in test solution at isoelectric point (pH-6.1) a) Well water,(b) Well water + L-alanine(250 ppm) + Zn^{2+} (5 ppm)

4. Conclusion

Weight loss study reveals that the formation consisting of 250ppm of L-alanine and 5ppm of Zn^{2+} has 83% inhibition efficiency, in controlling corrosion of carbon steel in well water (scheme 3) and the synergistic effect exists between $Zn^{2+}$and L-alanine system. Polarization study reveals that L-alanine system function as anodic inhibitors. AC impedance spectra reveal that a protective film is formed on the metal surface. At isoelectric point metal is not protected by L - alanine, the metal undergoes corrosion. Hence there is no IE.



Scheme 3 Protective film formation (L-alanine – Fe^{2+} Complex on metal surface)

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