



Corrosion and Anti-Corrosion Effect of Binary Inhibitor L-Aspartic Acid – ZnSO₄ for Carbon Steel in Aqueous Media

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ABSTRACT

The binary inhibitor system L-aspartic acid - Zn²⁺ has been investigated by weight loss method. A synergistic effect exists between L-aspartic acid and Zn²⁺ system. The formulation consisting of L-aspartic acid - Zn²⁺ offers 90% inhibition efficiency (IE). 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. At isoelectric point, the IEs of L-aspartic acid and also the L-aspartic acid - Zn²⁺ systems are very low. In some cases there is acceleration of corrosion negative IEs (-25%).

1. Introduction

Carbon steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths etc. It gets rusted when it comes in contact with any aqueous medium. The use of inhibitors is one of the best methods for protecting metals against corrosion. Corrosion is a chemical or electrochemical process in nature with four components are: an anode, a cathode, an electrolyte and some direct electrical connection between the anode and cathode, the adsorbed inhibitor then acts to slow corrosion process by either: 1. Increasing the anodic or cathodic polarization behaviour; 2. Reducing the movement or diffusion of ions to the metallic surface. Corrosion inhibitors are used to prevent the effect of corrosion in such cases. 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 the use of hazardous chemical inhibitors is totally reduced because of environmental regulations. 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 [14-17]. Eco-friendly inhibitor L-cysteine-Zn²⁺ 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 O₂-free NaOH has been prevented by methionine [11]. Sahaya Raja et al have used Glycine along with Zn²⁺ to prevent corrosion of carbon steel in well water [12]. Prathipa et al was studied corrosion inhibition of carbon steel using green inhibitor (L-alanine) [18]. Arginine - Zn²⁺ system has been used to inhibit corrosion of carbon steel [13-19]. L-alanine as inhibitor for carbon steel in well water was studied [20].

2. Experimental Methods

Chosen inhibitor L-aspartic acid is shown in Fig. 1. 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 (dm²) X period of the immersion (days)] X (0.0365/ρ). Electrochemical and Impedance measurements - Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A). All solutions were prepared using well water collected from N.S. Nagar, Dindigul, Tamil Nadu, India. The study was carried out at room temperature 303 K). The chosen environmental well water and its some physicochemical parameters are pH- 7.6, Conductivity - 1870 μmho/cm, TDS - 1329 ppm, TH - 700 ppm, Chloride - 727 ppm.

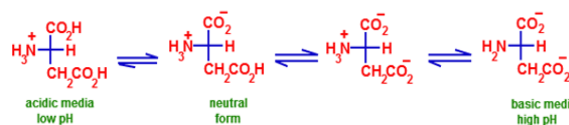


Fig. 1 Structure of aspartic acid at different pH

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-aspartic acid) are given in Table 1. The inhibition efficiencies (IE) are also given these table. It is observed that L-aspartic acid shows some inhibition efficiencies. 50 ppm of L-aspartic acid has 43 percent IE, as the concentration of L-aspartic acid increases the IE decreases. This is due to the fact that as the concentration of L-aspartic acid increases, the protective film (probably iron L-aspartic acid complex) formed on the metal surface goes into solution. That is, the system passes from passive region to active region.

Similarly, for a given concentration of L-aspartic acid the IE increases as the concentration of Zn²⁺ increases it is also observed that a synergistic effect exists between L-aspartic acid and Zn²⁺. For example, 5 ppm of Zn²⁺ has 20 percent IE; 250 ppm of L-aspartic acid has 27 percent IE. Interestingly their combination has a high IE, namely, 90 percent. In presence of Zn²⁺ more amount of L-aspartic acid is transported towards

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the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn^{2+} and L-aspartic acid.

The IE of L-aspartic acid- Zn^{2+} system at the isoelectric point of aspartic acid (pH=2.77) is given in Table 1. At isoelectric point, L-aspartic acid exists as zwitter ion. At isoelectric point, when an electric field is applied there is no movement of ions. Accordingly it is observed from Table 1, the IEs of L-aspartic acid and also the L-aspartic acid - Zn^{2+} systems are very low. In some cases there is acceleration of corrosion (negative IEs).

Table 1 Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IEs) obtained by weight loss method

At pH – 7.6			At pH – 2.77			At pH – 2.77		
L - aspartic acid ppm	Zn^{2+} (0 ppm)	Zn^{2+} (5 ppm)	L - aspartic acid ppm	Zn^{2+} (0 ppm)	Zn^{2+} (5 ppm)	L - aspartic acid ppm	Zn^{2+} (0 ppm)	Zn^{2+} (5 ppm)
IE %	CR	CR	IE %	CR	CR	IE %	CR	CR
	(mm/y)	(mm/y)		(mm/y)	(mm/y)		(mm/y)	(mm/y)
0	--	0.0874	--	--	--	0	0.1181	--
0	--	--	20	0.0699	--	3	--	0.1146
50	43	0.0498	77	0.0192	-2	1205	-9	0.1288
100	39	0.0533	83	0.0157	-4	1229	-13	0.1335
150	35	0.0568	85	0.0139	-5	1240	-17	0.1382
200	32	0.0594	87	0.0109	-8	1276	-20	0.1418
250	27	0.0638	90	0.0087	-10	1300	-25	0.1477

3.2 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, 21, 22]. 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. 2. The corrosion parameters are given in Table 2. When carbon steel was immersed in well water the corrosion potential was -670 mV vs SCE. When L-aspartic acid (250 ppm) and Zn^{2+} (5 ppm) were added to the above system the corrosion potential shifted to -640 mV vs SCE. This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from 5.779×10^{-7} A/cm² to 4.570×10^{-7} A/cm². Thus polarization study confirms the formation of a protective film on the metal surface.

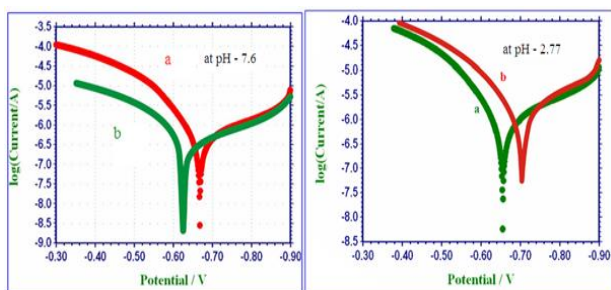


Fig. 2 Polarization curves of carbon steel immersed in various test solutions a) Well water (Blank) and b) Well water + L - aspartic acid (250 ppm) + Zn^{2+} (5 ppm)

Table 2 Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

At pH – 7.6			At pH – 2.77		
System	Tafel Results		System	Tafel Results	
	E_{corr} mV vs SCE	I_{corr} A/cm ²		E_{corr} mV vs SCE	I_{corr} A/cm ²
Well water	-670	5.779×10^{-7}	Well water	-655	7.703×10^{-7}
Well water + L - Aspartic acid (250 ppm) + Zn^{2+} (5 ppm)	-640	4.570×10^{-7}	Well water + L - Aspartic acid (250 ppm) + Zn^{2+} (5 ppm)	-700	1.052×10^{-6}

At isoelectric point, when carbon steel was immersed in well water the corrosion potential was -655 mV vs SCE. When L-aspartic acid (250 ppm) and Zn^{2+} (5 ppm) were added to the above system, the corrosion potential shifted to -700 mV vs SCE. The corrosion potential is shifted cathodic side (active site). It is observed that LPR value decreases. I_{corr} value 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 isoelectric point (pH = 2.77) there is no migration of L-aspartic acid towards the metal

surface. Therefore amount of L-aspartic acid transported towards the metal surface is reduced. So, metal is not protected by L-aspartic acid. Hence there is no IE at isoelectric point.

3.3 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, 23, 24-27]. 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-aspartic acid- Zn^{2+}) are shown in Fig. 3 (Nyquist plot). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plot are given in Table 3. It is observed that when the inhibitors (L-aspartic acid (50 ppm) + Zn^{2+} (5 ppm)) are added the charge transfer resistance (R_t) increases from $1197 \Omega\text{cm}^2$ to $11850 \Omega\text{cm}^2$. The C_{dl} value decreases from 3.7357×10^{-9} F/cm² to 4.1742×10^{-10} F/cm². These results lead to the conclusion that a protective film is formed on the metal surface.

At isoelectric point, when the inhibitors [L-aspartic acid (250 ppm) + Zn^{2+} (5 ppm)] are added, the charge transfer resistance (R_t) decreases from $1515 \Omega\text{cm}^2$ to $1320 \Omega\text{cm}^2$. The C_{dl} value increases from 3.3653×10^{-9} F/cm² to 3.8745×10^{-9} F/cm². When a protective film is not formed, charge transfer resistance (R_t) decreases and C_{dl} increases; the impedance value decreases, 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=2.77) there is no migration of L-aspartic acid towards the metal surface. Therefore amount of L-aspartic acid transported towards the metal surface is reduced. So, metal is not protected by L-aspartic acid. Hence there is no IE at isoelectric point.

Table 3 Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra

At pH – 7.6			At pH – 2.77		
System	Nyquist plot		System	Nyquist plot	
	R_t Ωcm^2	C_{dl} F/cm ²		R_t Ωcm^2	C_{dl} F/cm ²
Well water	1197	3.7357×10^{-9}	Well water	1515	3.3653×10^{-9}
Well water + L - Aspartic acid (250 ppm) + Zn^{2+} (5 ppm)	11850	4.1742×10^{-10}	Well water + L - Aspartic acid (250 ppm) + Zn^{2+} (5 ppm)	1320	3.8745×10^{-9}

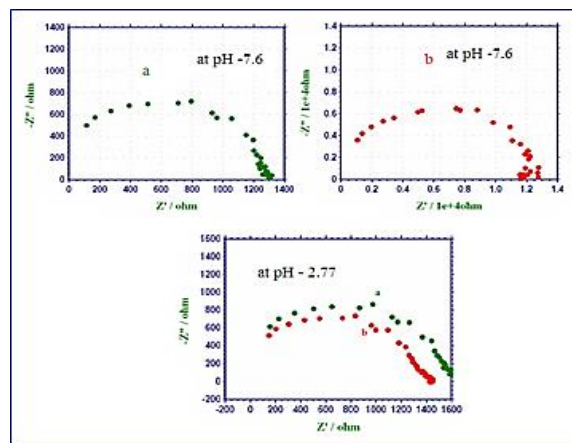


Fig. 3 AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots) a) Well water (Blank) and b) Well water + L-aspartic acid (250 ppm) + Zn^{2+} (5 ppm)

4. Conclusion

The results of the weight - loss study show that the formulation consisting of 250 ppm L-aspartic acid, 5 ppm of Zn^{2+} has 90% IE, in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and L-aspartic acid system. Polarization study reveals that the formulation functions as anodic inhibitor controlling the anodic reaction predominantly and to some extent controls the cathodic reaction. AC impedance spectra reveal that a protective film is formed on the metal surface. At isoelectric point (pH=2.77) polarization study and AC impedance spectra revealed that there is no synergistic effect exists between Zn^{2+} and L-aspartic acid and indicated that there is no protection of metal, the metal undergoes corrosion.

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