Journal of Advanced Chemical Sciences 1(2) (2015) 78–81

ISSN: 2394-5311

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com/jacs

Nano Analyses of Protective Film Formed by L-Alanine - Zinc Ion System onto Carbon Steel

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ARTICLE DETAILS

Article history:
Received 09 March 2015
Accepted 20 March 2015
Available online 24 March 2015

Keywords:
Green Inhibitor
L-alanine
Synergistic Effect
Fluorescence Spectra
Nano Film
Spectral Characterizations

ABSTRACT

We are reporting L–alanine as inhibitor for carbon steel in well water was studied using weight loss technique. The results indicate that the L-alanine functioned as a good corrosion inhibitor for the tested system. The inhibition efficiency increases with increasing L-alanine concentration. Synergistic effects increased the inhibition efficiency in the presence of zinc ions. Tafel results indicated that L-alanine is an anodic inhibitor. Adsorption of the used inhibitor led to a reduction in the double layer capacitance and an increase in the charge transfer resistance. Fluorescence spectral analysis was used in detecting the presence of an iron – inhibitor complex and the coordination sites of the metal inhibitor with iron were determined by the FT-IR spectra. Scanning electron microscopy (SEM) study confirmed that the inhibition of corrosion of carbon steel is through adsorption of the Inhibitors molecule on the surface of the metal. Energy dispersive analysis of X-rays (EDAX) shows that in the presence of inhibitors the suppression of Fe peaks, additional line of N and Zn signal & enhancement in 'C' and 'O' signal. These data show that metal surface is covered by adsorbed layer of Inhibitors molecule that protects carbon steel against corrosion. The surface morphology of the protective film (nano film) on the metal surface was characterized by using atomic force microscopy (AFM). A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study, electrochemical study and surface analysis technique. The eco-friendly inhibitor L - alanine -Zn^{2+} system may find application in cooling water system.

1. Introduction

Corrosion is a naturally occurring phenomenon which deteriorates a metallic material or its properties because of a reaction with its environment. Corrosion can cause dangerous and expensive damage to everything from pipelines, bridges and public buildings to vehicles and even home appliances. It is one of the most serious problems in the oil and gas industry. Inhibition of corrosion and scaling can be done by the application of inhibitors. It is noted that the effect of corrosion inhibitors is always caused by change in the state of surface being protected due to adsorption or formation of hardly soluble compounds with metal cations. The use of inhibitor is one of the most practical methods to protect metals from corrosion [1,2].

Most of the effective inhibitors are compounds containing in their structures nitrogen, phosphorus, and/or sulphur. Heteroatoms such as nitrogen, oxygen, and sulphur are capable of forming coordinate covalent bond with metal owing to their free electron pairs and thus, acting as inhibitor [1,3]. Many researchers were interested in biochemical compounds based on amino acids, which exhibit excellent properties such as good water solubility and rapid biodegradability [4,5]. These inhibitors used in protection against the corrosion of certain metals such as nickel, cobalt, copper, iron, and steel [6,7].

The amino acids are the building block of proteins. All amino acids have a central or alpha carbon, to which are bonded four groups; hydrogen, an amino, a carboxyl group, and a unique side chain, also known as R-group [6]. These molecules differ in their unique side chain, which can be used to classify the molecules into functional types. Various amino acids have been used to inhibit the corrosion of metals and alloys [8-12]. Eco–Friendly Inhibitor L–Cysteine–Zn^{2+} System to control corrosion of carbon steel in Aqueous Medium [13]. The corrosion of SS 316L has been inhibited by glycine, leucine, valine, and arginine [10]. Sivakumar et al have used L-histidine to prevent corrosion on carbon steel [14]. Cystein, glycine, glutamic acid, and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl [12]. Amino acid such as DL-phenylalanine has been used to prevent corrosion of carbon steel [15] .The corrosion of brass in O_2-free NaOH has been prevented by methionine [16]. Sahaya Raja et al have used Glycine along with Zn^{2+} to prevent corrosion of carbon steel in well water [17]. Arginine - Zn^{2+} system has been used to inhibit corrosion of carbon steel [18]. Perusal of several literatures reveals that there is no information regarding the use of L-alanine in combination with zinc ion (Zn^{2+}) as corrosion inhibitor. This paper focuses on the IE of L-alanine in controlling corrosion of carbon steel immersed in Well water in the absence and presence of Zn^{2+}. The investigation is performed using weight loss method, polarization technique and AC impedance spectroscopy. The morphology of the protective film (nano film) was examined by Fluorescence spectra, FTIR spectra, SEM, EDAX and AFM techniques.

2. Experimental Methods

2.1 Surface Characterization Studies

FTIR Spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco F – 6300 spectrofluoremeter. Surface morphology studies - The surface morphology measurements of the carbon steel were examined by JEOL JSM 6390 Model. All SEM micrographs of carbon steel are taken at a magnification of X=1000. The elements present on the metal surface were examined using JOEL-6390 computer-controlled Energy Dispersive Analysis of X-Rays (EDAX). Atomic force microscope (AFM) using Veeco diInnova model with the software version of SPM Lab Analysis (version 6.3.0.0) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 µm x 5 µm and the scan rate was 0.6 Hz. All solutions were prepared using well water collected from Seelapadi, Dindigul, Tamil Nadu, India. The study was carried out at room temperature (303K). The chosen environmental well water and its physicochemical parameters are given in Table 1.

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Cite this Article as: A. Sahaya Raja, N. Rajendran, V. Prathipa, S. Rajendran, Nano analyses of protective film formed by L-alanine-zinc ion system onto carbon steel, J. Adv. Chem. Sci. 1 (2) (2015) 78–81.

Table 1 Physico – chemical parameters of well water

Parameters	Value
pH	7.6
Conductivity	1860 µmhos/cm
Total Dissolved Solids	1188 ppm
Total hardness	397 ppm
Total Alkalinity	407 ppm
Magnesium	58 ppm
Calcium	74 ppm
Sodium	192 ppm
Potassium	59 ppm
Chloride	700 ppm
Sulphate	221 ppm

Table 2 Corrosion rates (CR), inhibition efficiencies (IE) and synergism parameters (SI) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations obtained by weight loss method. *(Inhibition system: L-alanine- Zn2+ (0 ppm and 5ppm), Immersion period : 1 day; pH = 7.6)*

L -alanine ppm	Zn^{2+} ppm	Corrosion Rate (mm/y)	Inhibition Efficiency IE %	coverage θ^1	Synergism Parameters S_I
0	0	0.0473	--	--	--
50	0	0.0402	15	0.15	--
100	0	0.0364	23	0.23	--
150	0	0.0285	39	0.39	--
200	0	0.0274	42	0.42	--
250	0	0.0250	47	0.47	--
0	5	0.0435	8	0.08	--
50	5	0.0194	59	0.59	1.91
100	5	0.0161	66	0.66	2.08
150	5	0.0133	72	0.72	2.00
200	5	0.0094	79	0.79	2.54
250	5	0.0080	83	0.83	2.87

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

System	Potentiodynamic Polarization study		AC impedance spectra	
	Tafel results		Nyquist plot	
	E_{corr} mV vs SCE	I_{corr} A/cm²	R_t ohm cm²	C_{dl} F/cm²
Well water	-673	5.980 x10^{-7}	1199	3.8832 x 10^{-9}
Well water + L-alanine (250 ppm) + Zn^{2+} (5 ppm)	-656	2.832 x10^{-7}	11478	4.0560 x 10^{-10}

Table 4 Analysis of the Fluorescence spectra

Fluorescence spectra (λ_{ex} = 280nm)		
System	Wavelength (nm)	Intensity (a.u)
Fe^{2+}-L-alanine complex in solution	337	83.2
Protective film formed on the surface of carbon steel after immersion in the solution containing 250 ppm of L-alanine and 5 ppm of Zn^{2+}	333	265.7

3. Results and Discussion

3.1 Analysis of the Corrosion Rates (CR), Inhibition Efficiencies (IE) and Synergism Parameters (S_I)

Corrosion rates (CR), inhibition efficiencies (IE) and synergism parameters (S_I) of carbon steel immersed in well water in the presence and absence of inhibitor system (L-alanine –Zn^{2+}) are given in Table 2. It is observed that the concentration of L-alanine increases, 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+}. Synergism parameters (S_I) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between L-alanine and Zn^{2+} [19].

3.2 Analysis of Electrochemical Study

The Electrochemical study such as potentiodynamic polarization and AC impedance spectra [13-16,18] of carbon steel immersed in well water in the absence and presence of inhibitors are given in the Table 3 . It is observed that in the presence of inhibitor system the electrochemical parameters such as corrosion potential (E_{corr}) shifted from -673 to -656 mV vs SCE, corrosion current (I_{corr}) decreases from 5.980 x10^{-7} A/cm² to 2.832 x10^{-7} A/cm², charge transfer resistance (R_t) increases from 1199 Ω cm² to 11478 Ω cm² and C_{dl} value decreases from 3.8832 x 10^{-9} F/cm² to 4.0560 x 10^{-10} F/cm². These results lead to the conclusion that a protective film is formed on the metal surface.

3.3 Surface Characterization Study

3.3.1 Analysis of the Fluorescence Spectra

Analysis of the fluorescence spectra are given the Table 4. Fluorescence spectra have been used to detect the presence of Fe^{2+}- inhibitor complex formed on the metal surface [20-22]. The emission spectrum of the Fe^{2+}-L-alanine complex solution, a peak appears at 337 nm. The emission spectrum of the film formed on the metal surface after immersion in the solution containing 250 ppm L-alanine and 5 ppm of Zn^{2+}, a peak appears at 333 nm. This indicates that the film present on the metal surface consist of Fe^{2+}-L-alanine complex. The slight variation in the position of the peak is due to the fact that the Fe^{2+}-L-alanine complex is entailed in $Zn(OH)_2$ present on the metal surface. Further, the increase in intensity of the peak is due to the fact that the metal surface, after the formation of the protective film is very bright, the film is very thin and there is enhancement in the intensity of the peak [21,22].

3.3.2 Analysis of FTIR Spectra

FTIR spectra have been used to analyze the protective film formed on the metal surface [23-27]. The FTIR spectrum L – alanine⁺ is shown in Fig. 1a. The C=O stretching frequency of carboxyl group appears at 1571 cm⁻¹, CN stretching frequency appears at 1127 cm⁻¹ and NH stretching frequency of the amine group appears at 3090 cm⁻¹ [24-26]. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of L- alanine and 5 ppm Zn^{2+} is shown in Fig. 1b, the C=O stretching frequency has shifted from 1571 to 1592 cm⁻¹. The CN stretching frequency has shifted from 1127 to 1202 cm⁻¹. The NH stretching frequency has shifted from 3047 to 3271 cm⁻¹. This observation suggests that L-alanine has coordinated with Fe^{2+} through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe^{2+}-L-alanine complex on the anodic sites of the metal surface. The peak at 580 cm⁻¹ corresponds to Zn-O stretching. The peak at 3524 cm⁻¹ is due to OH- stretching. This confirms that $Zn(OH)_2$ is formed on the cathodic sites of metal surface [27]. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+}- L-alanine complex and $Zn(OH)_2$.

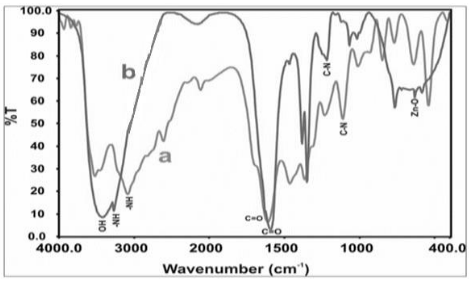

Fig. 1 FTIR spectra a) Pure L-alanine; b) Film formed on the metal surface after immersion in well water + L-alanine (250 ppm) + Zn^{2+} (5 ppm)

3.4 Surface Morphology Studies

3.4.1 SEM Analysis of Metal Surface

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined [28-30]. The SEM images of carbon steel specimen immersed in well water for one day in the absence and presence of inhibitor system are shown in Fig. 2a-c. The SEM micrographs of polished carbon steel surface (control) in Fig. 2a shows the smooth surface of the metal. This shows the absence of any corrosion products (or) inhibitor complex formed on the metal surface. The SEM micrographs of carbon steel surface immersed in well water (Fig. 2b) show the roughness of the metal surface which indicates the highly corroded area of carbon steel in well water. However in Fig. 2c indicate that in the presence of inhibitor

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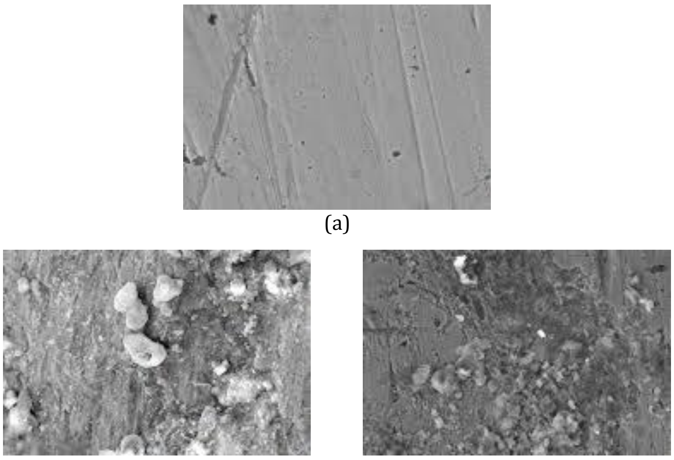
(250 ppm L-alanine and 5 ppm Zn^{2+}) the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The metal surface almost free from corrosion due to the formation of insoluble complex on the surface of the metal [28]. In the presence of L-alanine and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively controls the dissolution of carbon steel.

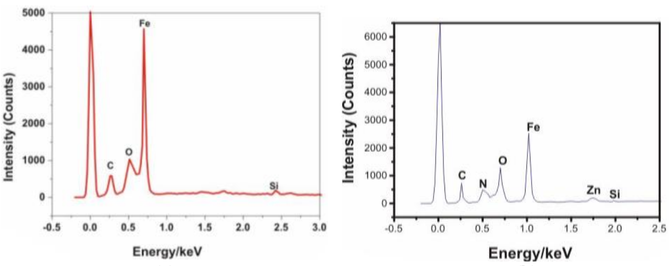


(a) (b) (c)

Fig. 2 SEM analysis: a) Carbon Steel (control), b) Carbon Steel Immersed in well Water and c) Carbon Steel immersed in well Water + 250 ppm of L-alanine + 5 ppm of Zn^{2+}

3.4.2 Energy Dispersive Analysis of X-rays (EDAX)

The EDAX survey spectra were used to determine the elements present on the metal surface before and after exposure to the inhibitor solution [28- 32]. The objective of this section was to confirm the results obtained from chemical and electrochemical measurements that a protective surface film of inhibitor is formed on the metal surface. To achieve this, EDAX examinations of the metal surface were performed in the absence and presence of inhibitors system [28-32]. EDAX spectrum of carbon steel immersed in well water is shown in Fig. 3a. They show the characteristic peaks of some of the elements constituting the carbon steel sample. The EDAX spectrum of carbon steel immersed in well water containing 250 ppm of L-alanine and 5 ppm of Zn^{2+} is shown in Fig. 3b. It shows the additional line characteristic for the existence of N and Zn. In addition, the intensity of C and O signals are enhanced. The appearance of the N and Zn signal and this enhancement in C and O signal is due to the presence of inhibitor. These data show that metal surface is covered the N, O, C and Zn atoms. This layer is undoubtedly due to the inhibitor system. The N, Zn signal and this high contribution of O and C is not present on the metal surface exposed in well water. Fig. 3b shows that the Fe peaks observed in the presence of inhibitor are considerably suppressed relative to these observed in well water (blank solution). The suppression of the Fe peaks occurs because of the overlying inhibitor film. This observation indicates the existence of an adsorbed layer of inhibitor that protects steel against corrosion. These results suggest that N, O and C atoms of L-alanine has coordinated with Fe^{2+}, resulting in the formation of Fe^{2+}-L-alanine complex on the anodic sites of metal surface and presence of Zn atoms are precipitated as $Zn(OH)_2$ on the cathodic sites of metal surface.



(a) (b)

Fig. 3 EDAX spectra: a) Carbon steel sample after immersion in well water (blank) and b) Carbon steel sample after immersion in solution containing Well water + L-alanine (250ppm) + Zn^{2+}(5ppm)

3.4.3 Atomic Force Microscopy Characterization

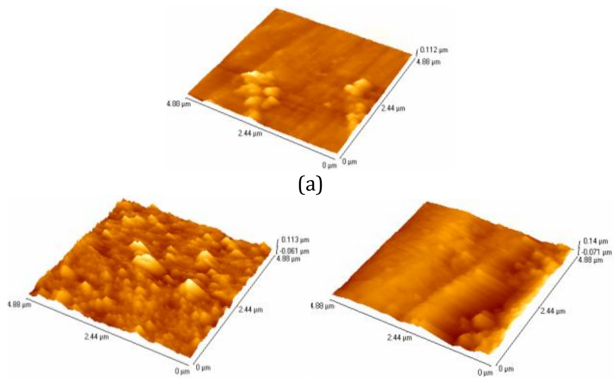
AFM is a powerful technique to investigate the surface morphology at nano–to micro–scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface [16,33-35].The three dimensional (3D) AFM morphologies for polished carbon steel surface (reference sample), carbon steel surface immersed in well water (blank sample) and carbon steel surface immersed in well water containing the formulation of L-alanine 250 ppm and 5 ppm of Zn^{2+} are shown as Fig. 4a-c. Root– mean-square roughness, average roughness and peak-to-valley value:

AFM image analysis was performed to obtain the average roughness, Ra (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) [36]. Rq is much more sensitive than Ra to large and small height deviations from the mean [37].

Table 5 is the summary of the average roughness (Ra), rms roughness (Rq) maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments. The value of RMS, Ra and P-V height for the polished carbon steel surface (reference sample) are 15 nm, 11 nm and 67 nm respectively, which shows a more homogeneous surface, with some places in which the height is lower than the average depth [16]. Fig. 4a displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The rms roughness, average roughness and P-V height values for the carbon steel surface immersed in well water are 42nm, 36 nm and 172 nm respectively. These data suggest that carbon steel surface immersed in well water has a greater surface roughness than the polished metal surface. This shows that the unprotected carbon steel surface is rougher and is due to the corrosion of the carbon steel in well water. Fig. 4b displays the corroded metal surface with few pits. The presence of 250 ppm of L-alanine and 5 ppm of Zn^{2+} in well water reduces the Rq by a factor of 19nm from 42 nm and the average roughness is significantly reduced to 17 nm when compared with 36 nm of carbon steel surface immersed in well water. The maximum peak-to-valley height also reduced to 83 nm from 172 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film (nano film) of Fe^{2+}-L-alanine complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel. Also the above parameters observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film (nano film) on the metal surface, which is protective in nature.

Table 5 AFM data for carbon steel surface immersed in inhibited and uninhibited environments

Samples RMS (Rq)	RMS (Rq) Roughness (nm)	Average (Ra) Roughness (nm)	Maximum peak-to-valley height (nm)
Polished carbon steel (control)	15	11	67
Carbon steel immersed in well water(Blank)	42	36	172
Carbon steel immersed in well water L-alanine (250 ppm) + Zn^{2+} (5 ppm)	19	17	83



(a) (b) (c)

Fig. 4 3D AFM Images of the Surface: a) Polished Carbon Steel(Control), b) Carbon Steel Immersed in Well Water(Blank) and c) Carbon Steel Immersed in Well Water containing L-alanine(250ppm)+Zn^{2+} (5ppm)

3.5 Mechanism of Corrosion Inhibition

The results of the weight-loss study show that the formulation consisting of 250 ppm L-alanine and 5 ppm of Zn^{2+} has 83% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and L-alanine. Polarization study reveals that this formulation functions as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+}–L-alanine complex and $Zn(OH)_2$. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

* When the solution containing well water, 5 ppm of Zn^{2+} and 250 ppm of L-alanine is prepared, there is formulation of Zn^{2+}–L-alanine complex in solution. When carbon steel is immersed in this solution, the Zn^{2+} - L-alanine complex diffuses from the bulk of the solution towards metal surface.
* Zn^{2+}-L-alanine complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe^{2+}-L-alanine complex, which is more stable than Zn^{2+}-L-alanine .
* On the metal surface Zn^{2+} - L-alanine complex is converted in to Fe^{2+} - L-alanine on the anodic sites. Zn^{2+} is released.
* Zn^{2+} - L-alanine + Fe^{2+} ----------> Fe^{2+} - L-alanine + Zn^{2+}
* The released Zn^{2+} combines with OH- to form $Zn(OH)_2$ on the cathodic sites.
* $Zn^{2+} + 2OH^-$ -------------> $Zn(OH)_2 \downarrow$
* Thus the protective film consists of Fe^{2+}-L-alanine complex and $Zn(OH)_2$.
* The EDAX analysis SEM micrographs and AFM images confirm the formation of protective layer (nano film) on the metal surface.

4. Conclusion

The results of the Mass- loss study show that the formulation consisting of 250 ppm L-alanine, 5ppm of Zn^{2+} has 83% IE, in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and L-alanine 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. FTIR spectral study reveals that the protective film consists of Fe^{2+} - L-alanine complex and $Zn(OH)_2$. The EDAX, SEM micrographs and AFM images confirm the formation of protective layer on the metal surface.

Acknowledgement

The authors are thankful to their respective management, Principal, G.T.N. Arts College, Dindigul, Tamil Nadu, India for providing the required facilities for completion of the work.

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