Corrosion Inhibition Performance of Mild Steelusing L-Tryptophan with Sodium Potassium Tartrate in 0.1 M HCL

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Abstract - The corrosion inhibition characteristics of nitrogen containing amino acid tryptophan (250ppm)with 0.05g of SPTon mild steel in0.1M HCl, was studied by various techniques. Weight loss method analysis showed that there is an increase in inhibition efficiency by increasing the concentration of inhibitor. Polarization and impedance studies indicated that the present inhibitor system as acathodic type inhibitor. EDAX spectra confirm the presence of inhibiting elements on the metal surfaceand SEM analysis indicated the smoothness of the layer formed on the surface of the metal.

Key words: Mild steel, tryptophan, SPT, EIS, SEM, EDAX, AFM.

I. INTRODUCTION

'Corrosion' and 'rust' are almost synonymous terms since iron and its alloys are the most commonly used material by mankind and corrosion of iron must have been the one of the first serious corrosion problems affected humans. Most of the metals and alloys have a natural tendency to combine with water and oxygen present in its environment and return to its most stable state [1].In the last few decades, mild steel (MS) is widely applied as a constructional material in a large number of industries due to its excellent mechanical properties and it's exceptionally low cost [2, 3].Corrosion of reinforcement has been established as the predominant factor causing widespread premature deterioration of concrete construction worldwide [4]. Corrosion of bridges is a major problem of the age and requires replacement [5]. Corrosion is a cancer of metal and alloys and causes direct and indirect losses. The cost of direct loss due to corrosion has been estimated to be about 3 to 4% of GNP (Gross National Product) in developed countries. In India, the amount is calculated to be roughly 2-3% of GNP. The estimated cost of losses in India is about more than hundred crore rupees every year [6]. Corrosion inhibitors have long been used for daily operation of recirculating cooling water system, industrial acid cleaning, oil well acidification, and descaling due to their economical and efficient properties [7-9].Amino acids are nontoxic, relatively cheap, and easy to produce with purities greater than 99%. Recently, with respect to amino acid as corrosion inhibitor, many achievements have been gained in laboratory studies [10-15].Almost 3% of the world's GDP is the annual cost of corrosion, because it has an impact upon the metallurgical, chemical, oil industries and so on. In addition, governments and industries pay little attention to corrosion except in large risk areas such as aircraft and pipelines [16-18]. The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99% [19-21]. The high efficiency of organic compounds as corrosion inhibitors is due to the polar functions from the presence of S, O, or N atoms, which are used as centers to establish the adsorption process [22,23, 24,25,26].Hence, the present system (L-tryptophan with Sodium Potassium tartrate) consisting the hetero atoms present in theshows their corrosion inhibition performance in acid medium.

II. MATERIALS AND METHODS

The Mild steel specimens were chosen from the same sheet of the following composition: Carbon - 0.1 %, Sulphur – 0.026 %, Phosphorus - 0.06 %, Manganese - 0.4 % and the balance iron. Mild steel specimen of the dimension 3x2x0.2cm were polished to mirror finish, degreased with

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acetone and used for mass – loss and surface examination studies.

Electrochemical studies:

Potentiodynamic polarization study:

Polarization and AC impedance study was carried out in Electrochemical Impedance analyzer model CHI 660A three electrode cell assembly was used. The working electrode was used as a rectangular specimen of mild steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded after doing ire compensation. The corrosion parameters such as corrosion potential (Icorr), corrosion current (Icorr) and Tafel slopes (anodic = b_a and cathodic =b_c) and Linear polarization resistance (LPR) were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at Eve(s) was zero and quite time (s) was 2.Cdl values were calculated using the following relationship.

$$C_{dl} = \frac{1}{2 \times 3.14 \times R_t \times fax}$$

Scanning Electron Microscopic studies (SEM) and EDX:

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of the mild steel were examined using Tescon, Vega3, and USA computer controlled scanning electron microscope. The elemental analysis of the mild steel surface at the same condition was carried out using an energy dispersive X-ray analyzer (EDAX) [Brucker, Nano, GMBH, Germany] unit attached to the SEM machine.

Atomic Force Microscopy characterization (AFM):

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the mild steel surface were carried out by atomic force microscopy (AFM) using Pico SPM 9500-21 with the software version of Pico scan version 5.4.

III. RESULT AND DISCUSSION

1. Analysis of results of the weight loss method

The corrosion rates and the inhibition efficiencies(IE) of L-tryptophan(AA) and L-tryptophan withSodium Potassium tartrate(SPT) in controlling corrosion of mild steel immersed in 0.1M HClfor a period of one day in the absence of and presence of inhibitors is given in Table1.

Table1. Inhibition efficiencies (IE%) and corrosion rates (CR) obtained from AA-SPT system in controlling corrosion of mild steel immersed in 0.1M HCl

Inhibitor system: AA + SPTin 0.1M HCl
Immersion period: 1 day

Electrolytic solution	Corrosion rate mg|cm^2	Inhibition efficiency%
0.1MHCl(Blank)	0.22	77.5
50ppm AA + 0.05g SPT in 0.1MHCl	0.19	85.6
150ppm AA + 0.05g SPT in 0.1MHCl	0.17	87.4
250ppm AA + 0.05g SPT in 0.1MHCl	0.15	89.2

It is observed from Table 2 that L-tryptophan shows some inhibition efficiency. After the addition of L-tryptophan in different concentrationswith 0.05g SPT in 0.1MHClthe inhibition efficiency increases. 50ppm of AA + 0.05g SPT in 0.1MHClhas 85.6%, 150ppm of AA + 0.05g SPT in 0.1MHCl has 87.4% and 250ppm of AA + 0.05g SPT in 0.1MHCl has 89.2%. That is addition of inhibitor system in 0.1M HClincreases the corrosion protection of mild steel immersed in the solution. That is, the system passes from active to passive region.

IV. ANALYSIS OF POTENTIODYNAMIC POLARIZATION STUDY

Electrochemical study such as Polarization study has been used to confirm the formation of protective film on the metal surface during corrosion inhibition process. If a

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protective film is formed on the metal surface, the linear polarization resistance values (LPR) increases and the corrosion current value (I_{corr}) decreases.

The potentiodynamic polarization curves of mild steel immersed in 0.1M HCl in the absence and presence of inhibitor are shown in Fig 1. The corrosion parameters namely, corrosion potential (E_{corr}), Tafel slopes (anodic slope b_a and cathodic slope b_c) Linear polarization resistances (LPR) and corrosion current (I_{corr}) values are given in the Table 2.

When mild steel is immersed in 0.1M HCl the corrosion potential was-0.5190mVvs SCE (saturated calomel electrode). When AA(50ppm)+0.05g SPTwas added it shifted to -0.3684mV when AA (150ppm)+0.05g SPTwas added it shifted to -0.3373mV when AA (250ppm)+0.05g SPTwas added it shifted to -0.3271mVVs SCEthat is cathodic side as noble side. This indicates that the AA+SPT system controls cathodic reaction predominantly. This indicates that the passive film is formed on the metal surface in presence of inhibitor. Further, the LPRvalue increases When a passive film is formed on mild steel surface, in presence of inhibitor system, the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system.

Table 2:Corrosion parameters of mild steel immersed in 0.1M HCl in the absence and presence of AA + SPT system obtained from Potentiodynamic Polarization Study

System	E_{corr} mV vs SCE	b_cmV/ decade	b_a mV/ decade	LPR ohmcm^2	I_{corr}Acm^{-2}
0.1MHCl(Blank)	-0.5190	4.733	3.730	15.9	0.03232x10^{-6}
50ppm AA + 0.05g SPTin 0.1MHCl	-0.3684	5.561	3.670	2420.8	0.01946x10^{-6}
150ppm AA + 0.05g SPT in 0.1MHCl	-0.3373	6.288	3.38205	2593.9	0.01733x10^{-6}
250ppm AA + 0.05g SPT in 0.1MHCl	-0.3271	6.204	4.153	33501	0.01253x10^{-6}

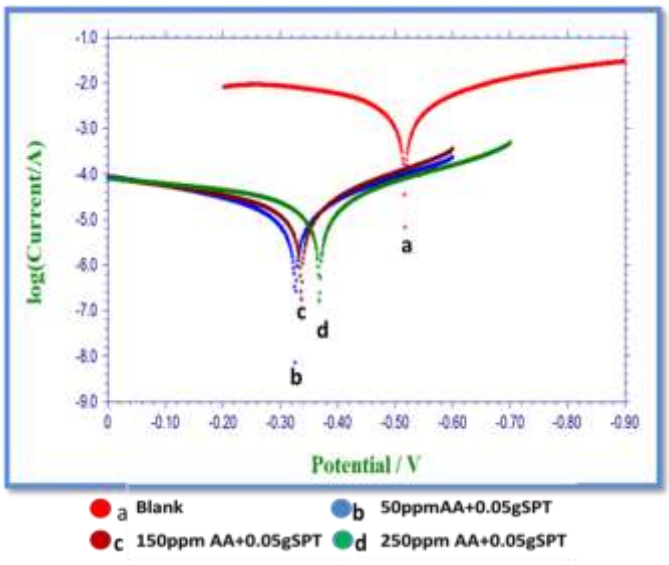

Fig 1.Polarization curves of mild steel immersed in various test solutions(Blank, 50ppmAA+SPT, 150ppm AA+SPT, 250ppm AA+SPT) prepared in 0.1MHCl

3. Analysis of AC impedance spectra:

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film formed on the metal surface. If a protective film on the metal surface, the charge transfer resistance(R_t) increases, double layer capacitance value(C_{dl}) decreases and the impedance log (z/ohm) value increases. The AC impedance spectra of mild steel immersed in 0.1MHCl in the absence and presence of inhibitor are shown as Nyquist plotin Fig 2, and Bode plots in Fig 3, Fig 4, Fig 5 and in Fig 6.The AC impedance parameters such as charge transfer resistance(R_t),double layer capacitance(C_{dl}) and impedance value log(z/ohm) are given in table 3.

Table 3: Impedance parameters of mild steel immersed in0.1M HCl in the absence and presence of inhibitor system obtained from AC impedance spectra

System	Nyquist plot		Bode plot
	R_t ohm cm^2	C_{dl} F/cm^2	Impedance value log (z/ohm)
0.1MHCl(Blank)	11.79	4.24 x10^{-9}	1.2
50ppmAA+SPT in0.1MHCl	401.62	7.55 x10^{-9}	2.7
150ppmAA+SPT in 0.1MHCl	410.48	1.24 x10^{-9}	2.8
250ppmAA+SPT in 0.1MHCl	662.19	1.22 x10^{-9}	2.9

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The Nyquist plots obtained comprise of the depressed semi-circle, which indicates that the steel dissolution is essentially a charge transfer process [27, 28]. The size of the Nyquist plots rises with respect to the blank solution and with increasing inhibitor concentration signifying that the AA+SPT system formed an inhibitor film on the mild steel surface. Moreover, it is observed that when mild steel is immersed in 0.1M HCl, R_t is 11.79 ohmcm^2 and C_{dl} value is 4.24 x10^{-9}F/cm^2. When mild steel isimmersed in 0.1M HCl $R_t$values increases and the C_{dl} value decreases as indicated in the table.3. The impedance log (z/ohm) value increases gradually as the concentration of increased inhibitor concentration asfrom 1.2 to 3.2, 3.5, and 3.6.This suggests that a protective film is formed on the metal surface.

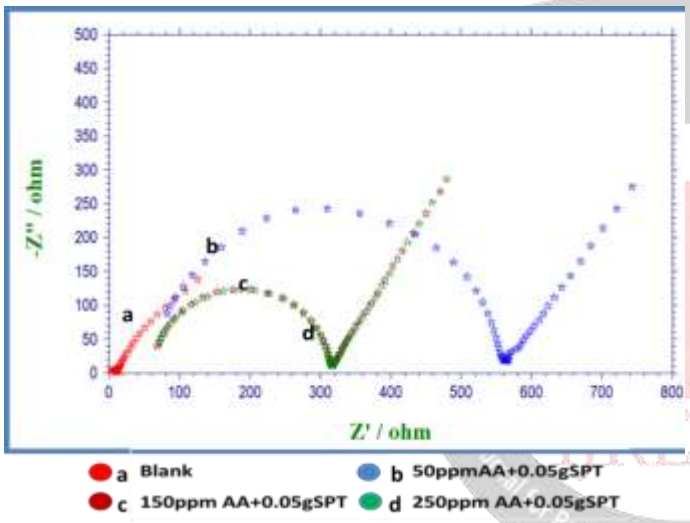

Fig 2.AC impedance spectra-Nyquist plots of mild steel immersed in various test solutions

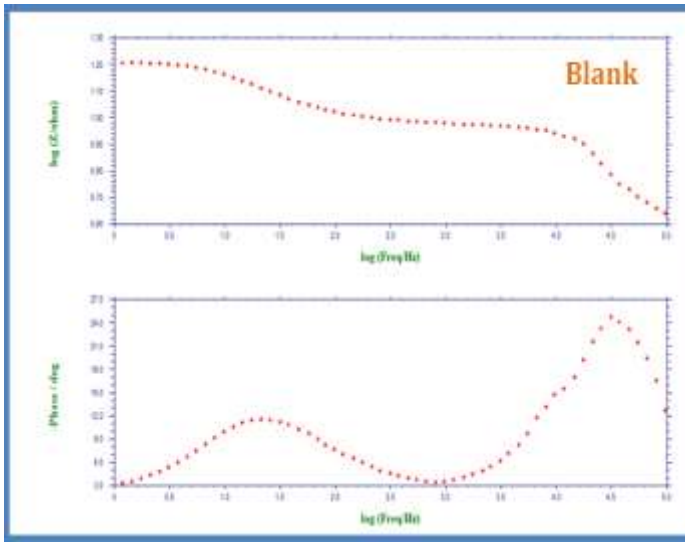

Fig 3.AC impedance spectra-Bode plot of 0.1M HCl(Blank) solution

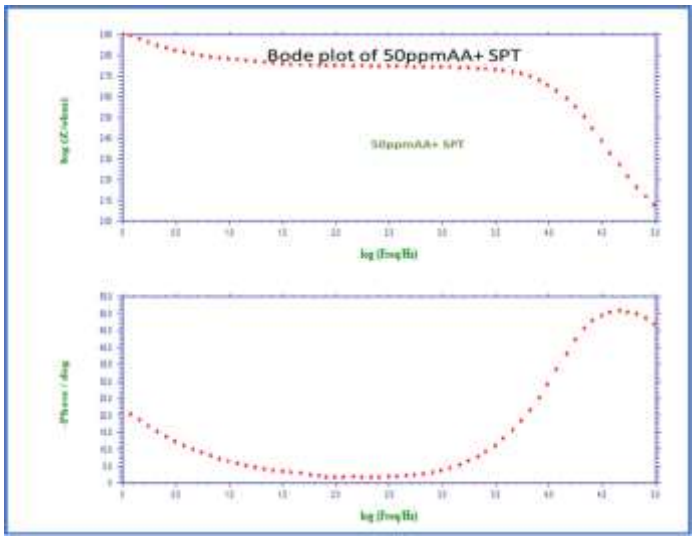

Fig 4.AC impedance spectra-Bode plot of 50ppm AA+ SPT in 0.1M HCl (Blank) solution

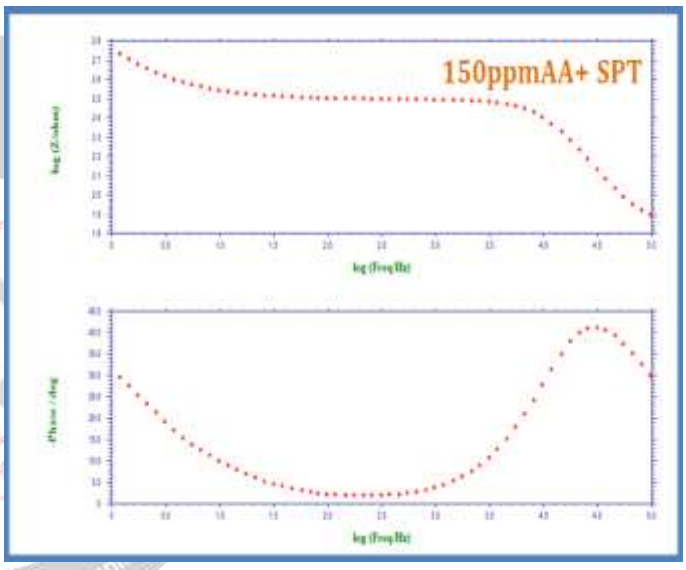

Fig 5.AC impedance spectra- Bode plot of 150ppm AA+ SPT in 0.1M HCl (Blank) solution

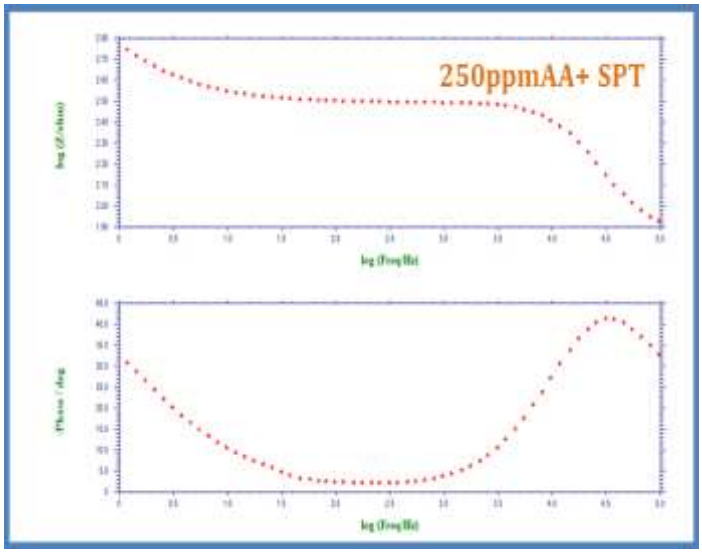

Fig 6.AC impedance spectra-Bode plot of 250ppm AA+ SPT in 0.1M HCl (Blank) solution

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V. SEM ANALYSIS OF METAL SURFACE

SEM provides a pictorial representation of the surface. To understand the nature of the film in the absence and presence of inhibitors and the extent of corrosion of mild steel, the SEM microscopes of the surface are examined.

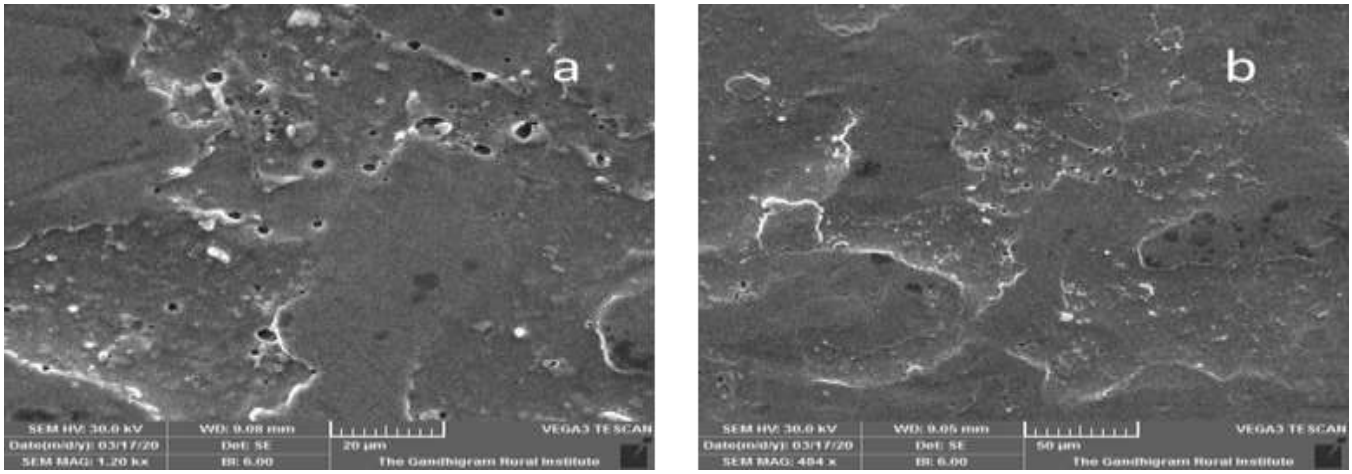

Fig 7.SEM micrographs of mild steel immersed in0.1M HCl(Blank); Magnifications X20(a),X50(b)

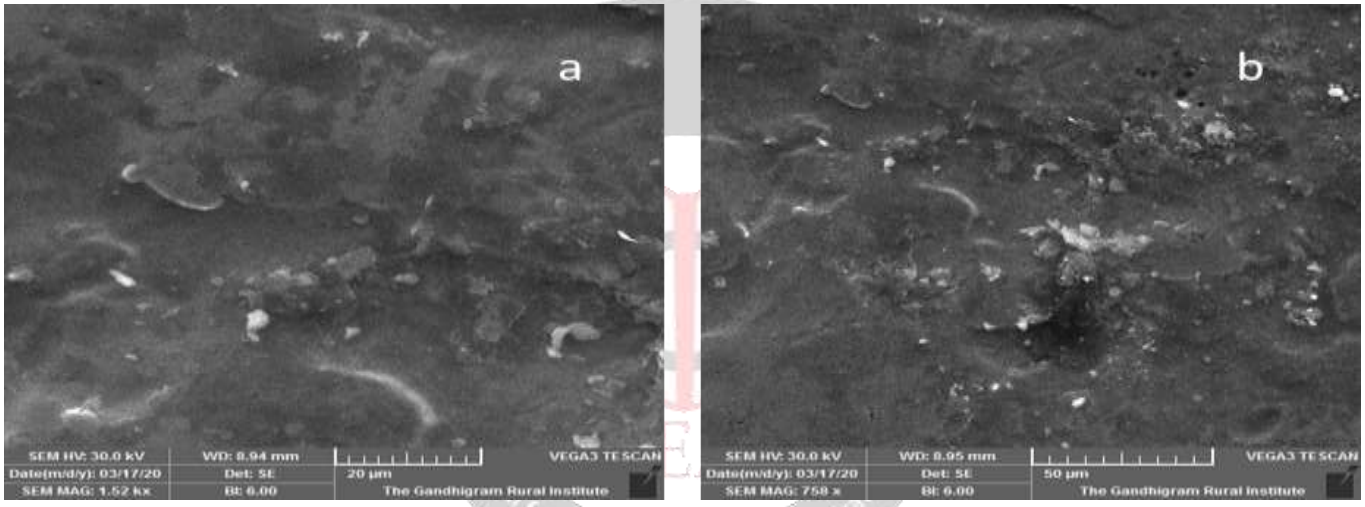

Fig 8.SEM micrographs of mild steel immersed in 250ppm AA+ 0.05g SPTin0.1M HCl; Magnification X20(a),X50(b)

The SEM images of different magnifications (X20, X50) of mild steel specimen immersed in blank and 250ppmAA+SPT in 0.1MHClfor 1 day are shown in Fig.7 (a,b) and Fig.8 (a,b) respectively.

The SEM micrographs of different magnifications of mild steel surface immersed in 0.1M HCl in Fig.7 (a,b)shows the roughness of the metal surface which indicates the highly corroded area on mild steel and Fig.8 (a,b)shows the smoothness of the metal surface which indicates the formation of protective film on the metal surface.

5. Surface analysis - Energy dispersive analysis of X-rays (EDAX)

The EDAX spectra were used to determine the elements present on the metal surface before and after exposure to the inhibitor solution. EDAX examinations of the mild steel surface were performed in blank and 250ppmAA+SPT in 0.1MHClfor 1 day are shown in Fig.9 to Fig.10respectively.

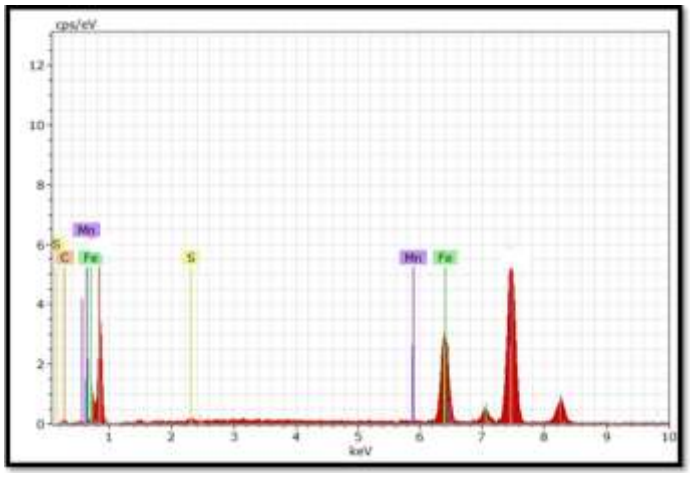

Fig.9: EDAX spectra of mild steel specimen in 0.1M HCl (Blank)

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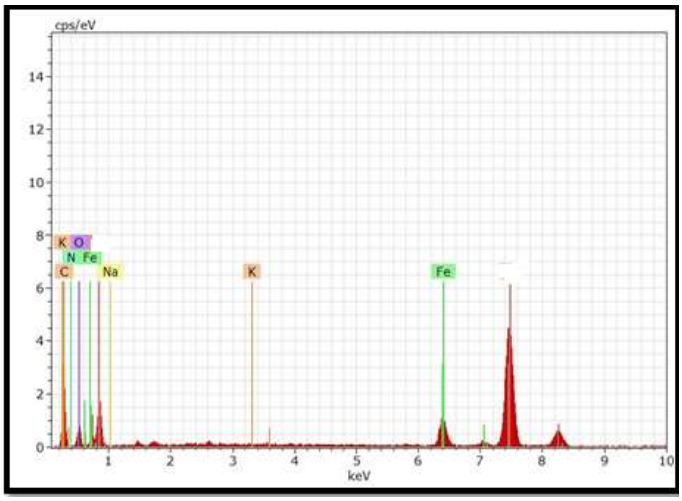

Fig.10: EDAX spectra of mild steel immersed in 250ppm AA+ 0.05g SPT in 0.1M HCl

The analysis shows the presence of (Na, K) peak, [where there is no presence of Na and K on mild steel surface in blank solution] this concludes the presence of sodium and potassium on the metal surface and notable decrease in iron peak shows the formation of protective film on the metal surface. The surface of mild steel sample is preserved to a large extent due to formation of the protective film formed of the inhibitor molecules as indicated by the decrease of iron peak in Fig:10. This leading to a high degree of ionization energy.

VI. SURFACE ANALYSIS - ATOMIC FORCE MICROSCOPY

Atomic force microscopy is a powerful technique for gathering roughness statistics from a variety of surfaces. AFM is becoming an accepted method of roughness investigation. The two dimensional (2D), three dimensional (3D) AFM morphologies, AFM cross – sectional profile and histogram images of surface for of the mild steel surface were performed in blank and in 250ppmAA+SPT in 0.1MHCl system for 1 day are shown in Fig.11 and in Fig.12 respectively.

Root – mean – square roughness, average roughness and peak – to – valley value for SPT system

AFM image analysis was performed to obtain the average roughness, R_a(the average deviation of all points roughness profile from a mean line over the evaluation length), root – mean – square roughness, R_q (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). R_q is much more sensitive than R_a to large and small height deviations from the mean.

Table - 5 AFM data for mild steel surfaces immersed in inhibited and uninhibited environments

System (Mild Steelimmersed in)	Average(R_a) Roughness (nm)	RMS(R_q) Roughness (nm)	Maximum peak –to– valley height (nm)
Blank	669.81	884.15	1.84
250ppmAA+SPT in0.1MHCl	186.32	253.25	1.62

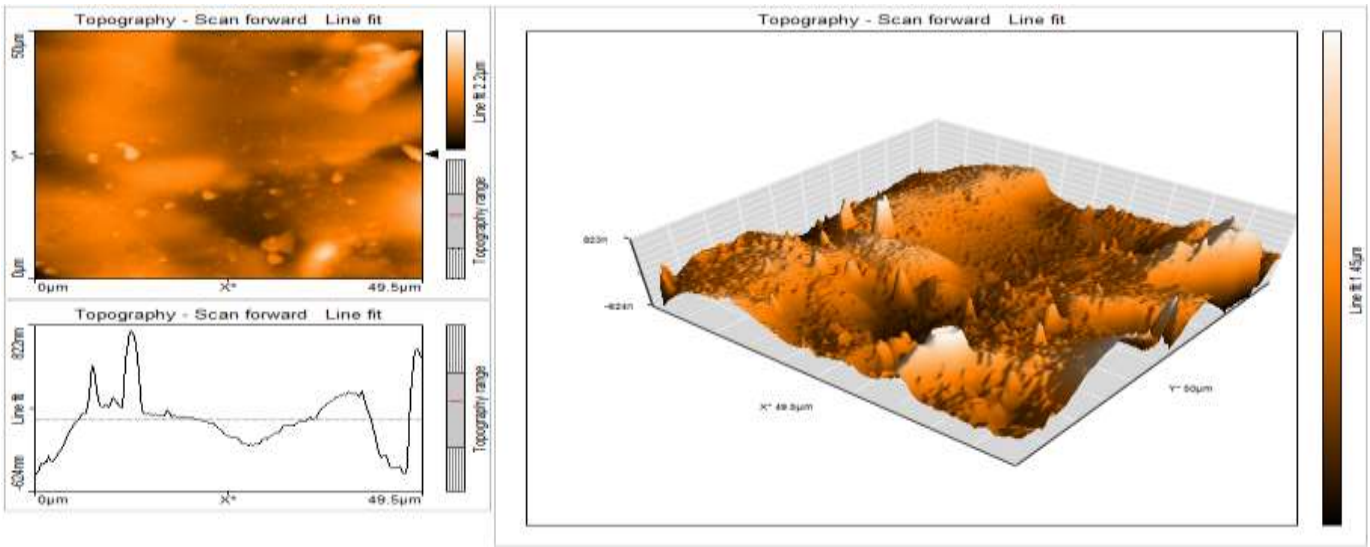

Fig 25. AFM image of mild steel specimen in 0.1M HCl (Blank)

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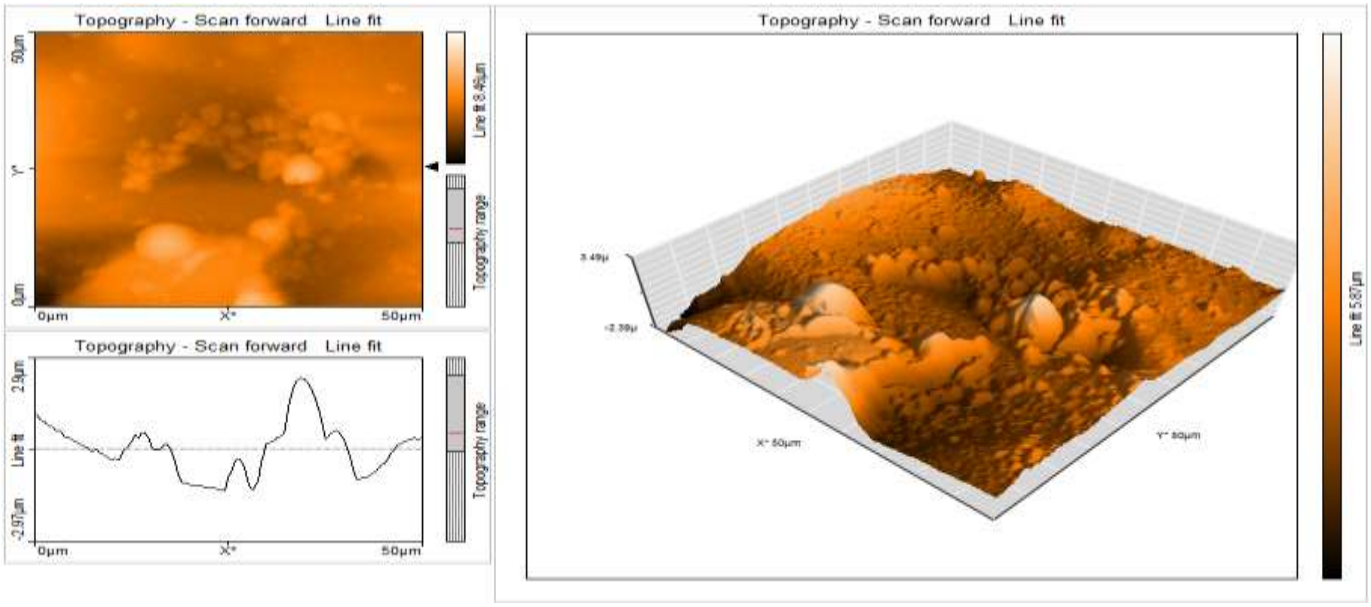

Fig 26AFM image of mild steel immersed in 250ppm AA+ 0.05g SPT in 0.1M HCl

Table – 5is the summary of the average roughness (R_a), rms roughness (R_q) maximum peak- to- valley height (P-V) value for mild steel surface immersed in different environments. The value of R_a, R_{RMS} and peak to valley height for the mild steel immersed in 0.1M HCl are669.81, 884.15 and 1.84shown in Fig.25. The slight roughness observed on the mild steel surface is due to atmospheric corrosion. These data suggest that mild steel surface immersed in 0.1M HCl displays the corroded metal surface with few pits.The presence of mild steel immersed in 0.1M HCl and 250 ppm of AA+ 0.05g SPT reduces the R_{av} by a factor of 186.32nm from 669.81nm and the RMS roughness is significantly reduced to 253.25nm, when compared with 884.15nm of mild steel surface immersed in 0.1M HCl. The maximum peak to valley height also reduced to 1.62nm from 1.84nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - SPT complex and AA on the metal surface thereby inhibiting the corrosion of mild steel, also the above parameters are observed somewhat greater than the AFM data of polished metal surface, which confirms the formation of the film on the metal surface, which is protective in nature.

VII. CONCLUSION

The corrosion study of amino acid in the presence of Sodium Potassium tartrate has revealed that the inhibition efficiency tended to increase with increasing inhibitor concentration. Polarization measurements show that they are cathodic-type inhibitors. Nyquist plots established that the inhibitors reduced the mild steel corrosion through their effective adsorption of inhibitive layer, which is further evidenced from SEM and AFM. From the above studies we are reported that 250ppm of amino acid in the presence of Sodium Potassium tartrate as a best corrosion inhibitor for Mild Steel corrosion in 0.1MHCl solution.

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