



ISSN: 0975-833X

RESEARCH ARTICLE

CORROSION INHIBITION STUDY OF IS : 1062 GRADE A - LOW CARBON STEEL IN 1M HCL BY  
L - METHIONINE -WEIGHT LOSS, ICP-OES AND SEM-EDX STUDIES

<sup>1</sup>Shanmugasundaram, P., <sup>2</sup>Sumathi, T., <sup>3</sup>Chandramohan, G. and <sup>4</sup>Ramesh Babu, G. N. K.

<sup>1</sup>TÜV Rheinland (India) Pvt.Ltd, 17B, Electronic City Phase 2, Hosur road, Bangalore-560100, India

<sup>2</sup>Department of Chemistry, B.N.M.Institute of Technology, BSK 2<sup>nd</sup> Stage, Bangalore 560 070, India

<sup>3</sup>P.G and Research Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi-613503,India

<sup>4</sup>Central Electro Chemical Research Institute, Karaikudi- 623 006.

ARTICLE INFO

Article History:

Received 06<sup>th</sup> May, 2013

Received in revised form

25<sup>th</sup> June, 2013

Accepted 08<sup>th</sup> July, 2013

Published online 23<sup>rd</sup> August, 2013

Key words:

Inhibition, L-Methionine, Carbon steel,  
Green Inhibitor, HCl Medium, ICP-OES,  
SEM-EDX

ABSTRACT

The corrosion inhibition characteristics of amino acid L- Methionine on IS : 1062 Grade A - Low carbon Steel in 1M HCl solutions at 30°C temperature was studied by using weight loss, Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) and Scanning Electron Microscope with Energy Dispersive X- Ray analyzer (SEM-EDX) techniques. Measurements were conducted without and with various concentrations of L- Methionine and the inhibition efficiency (IE %) has been studied accordingly. The addition of very small concentration Zinc and potassium iodide as synergizing agents on the corrosion inhibition behavior of L- Methionine was also studied. The highest Inhibition Efficiency (IE %) of 98.80% was observed in the presence of L- Methionine (10<sup>-1</sup> moles) with Zinc (15 milli moles) and KI (10 milli moles) as synergizing agents at 30°C for an exposure duration of 1hr. These measurements were complemented with ICP-OES examinations of the electrolyte solution, SEM and EDX characterization of the electrode surface. The effect of Zinc and KI as synergizing agents on inhibition efficiency along with combined synergizing effect (Zn+ KI) was also studied.

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INTRODUCTION

Low carbon steel is one of the best preferred materials for construction applications due its easy availability and its excellent properties including ductility and toughness. But its use restricted in acidic environments because of its susceptibility towards corrosion. The use of inhibitors is one of the best-known methods of corrosion protection. The addition of heterocyclic organic compounds containing nitrogen, sulfur and oxygen have been widely used as potential corrosion inhibitors in acid solutions [1-4] is one of the most practical and well proven methods of achieving this. These compounds prevent corrosion either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface, thus blocking the active corrosion sites. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, oil-well acidizing, etc. However, most of the commercially available inhibitors are synthetic chemicals, expensive and hazardous in nature (CMR Cat 1&2) to both human beings and the environments, and need to be replaced by non toxic and environmental friendly green organic compounds. In recent years, number of eco-friendly compounds such as extract of common plants which contain many organic compounds, e.g., amino acids, alkaloids, fatty acids, carbohydrates, tannins and pigments, have been exploited as green alternative to toxic and hazardous compounds [5]. This proved to be an efficient and inexpensive method of corrosion protection of metals. The amino acid which contains carboxyl and amino functionalities bonded to the same carbon atom are non-toxic,

relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitutes to conventional corrosion inhibitors that are usually toxic [6-10]. The corrosion inhibition of Fe in 1M HCl using twenty two different common amino acids and four related compounds has been investigated by using potentiodynamic polarization curves [11].

Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. A literature survey shows that most of the organic inhibitors will act upon adsorption onto the metal surface. The adsorption of inhibitors takes place through heteroatom such as nitrogen, oxygen, phosphorus and sulfur, as well as through triple bonds or aromatic rings. The inhibition efficiency is reported to increase in the order O < N < S < P [12]. Synergistic inhibition is an effective means to improve the inhibitive force of the inhibitor, to decrease the amount of usage of inhibitor and to diversify the application of the inhibitor in acidic media. It is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. Many investigations in regard to synergistic inhibition have been carried out and are being investigated. Abdel Rehim *et al.* [13] have studied the synergistic inhibition between adenine and iodide ions for low carbon steel corrosion in sulfuric solutions. They have found that the inhibition efficiency of adenine is greatly enhanced in the presence of KI because of synergism. They have also reported that the inhibition mechanism involves the electrostatic adsorption of protonated adenine molecules on the low carbon steel surface charged with a negative layer of chemisorbed I<sup>-</sup> ions. Amara *et al.* [14] have investigated the synergistic inhibition offered by Zn<sup>2+</sup> and piperidin-

\*Corresponding author: Sumathi, T., Department of Chemistry,  
B.N.M.Institute of Technology, BSK 2<sup>nd</sup> Stage, Bangalore 560 070, India

l-yl-phosphonic acid (PPA) to the corrosion. Armco iron in 3% chloride solution. They have observed that the combination of PPA and  $Zn^{2+}$  shows excellent inhibition efficiency. Their system of  $Zn^{2+}$ -PPA shows a synergistic effect toward iron corrosion in 3% chloride medium. They have found that the anodic reaction is delayed by the formation of  $Fe^{2+}$ -PPA, whereas the cathodic reaction is also delayed by the formation of  $Zn(OH)_2$  on the cathodic sites of the metal surface. Li *et al.* [15] have reported the synergistic inhibition effect of rare earth cerium(IV) ions and 3,4-dihydroxybenzaldehyde (DHBA) on the corrosion of cold rolled steel (CRS) in  $H_2SO_4$  solution. They have observed that the combination of  $Ce^{4+}$  with DHBA improves the inhibition performance significantly and produces a strong synergistic inhibition effect. They have reported that the new complex of  $Ce^{4+}$ -DHBA could be formed and adsorbed onto the CRS surface in  $H_2SO_4$  for  $Ce^{4+}$  in combination with DHBA. Umoren *et al.* [16] have studied the synergistic inhibition effect of iodide ions and polyacrylamide (PA) on the corrosion of pure iron in 0.5 M  $H_2SO_4$  solution. They have reported that the inhibition efficiency of PA was enhanced by the addition of iodide ions because of synergistic effects. The synergistic effect of iodide ions and PA is due to the co-adsorption of iodide ions and PA molecules, which is synergistic in nature. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups which increased electron density on alpha amino group also increased the inhibition efficiency.

The nitrogen and sulphur containing amino acid L- Methionine's molecular structure suggests that it has strong potential to become an effective corrosion inhibitor. Synergism is an effective method to improve the inhibitive action of an inhibitor in presence of another substance in corrosive medium and to decrease amount of usage [17 & 18]. The addition of Zinc and / or halide salts to some inhibitor solution results in synergistic effect. Recently, several studies have been reported to explain role of synergism on corrosion inhibition mechanism of steel in sulphuric acid ( $H_2SO_4$ ) medium [19-24] and Steel in Saline water medium [25]. The synergistic effect of different halide ions with pyrazoles on corrosion of low carbon steel in  $H_2SO_4$  have been reported [26]. The inhibitive effect of halide ions found to be in the order  $I^- > Br^- > Cl^-$ . Jeyaprabha *et al.* [22] reported the highest synergistic effect of iodide ions is due to its chemisorptions with metal surface and its larger size and low electro negativity. At present, weight loss measurement is the mostly employed method to acquire the corrosion rate data for metal coupons at natural environmental corrosion test stations in many countries. However, it is time consuming, which makes the corrosion rate obtained only a long-term average. Hence few details about the corrosion process during the experimental period are revealed. In this section, experimental corrosion rates for Low carbon steel in 1M HCl were determined by a chemical method other than weight loss. The chemical method of corrosion rates measurements involved determination of the dissolved cation using ICP-OES (inductively coupled plasma optical emission spectrometry) method of analysis. The advantages offered by ICP-OES method of analysis includes a multi-element measurement capability (72 elements in a single scan), high stability, optimum selectivity and superior dynamic range for concentration as well as calculation, data reporting and data reprocessing. This makes the ICP-OES instrument is superior in the trace and environmental analysis in aqueous and organic media in complex samples. In the corrosion studies, such sophisticated instrument provides an excellent continuous chemical monitoring and robust analytical method for corrosion rate. (ICP-OES) provides therefore the most reliable results concerning the efficiency of a given inhibitor compound, so that the corresponding corrosion data obtained from them approach service conditions more accurately than the data obtained with any other test.

Scanning Electron Microscope was applied to confirm that the self-assembled films on the low carbon steel surface can protect the metal from corrosion. The SEM micrographs with surface morphologies of the as polished, Bare (without inhibitor) and L- Methionine modified low carbon steel sheets after exposed for 1 hr in 1M HCl solutions.

The composition of protective film formed on low carbon steel surface was analyzed in a non- destructive method by using EDX. The present work was undertaken to investigate the corrosion inhibition behavior of L- Methionine on IS : 1062 Grade A - Low carbon Steel in 1M HCl solution. The effect of the addition of various concentrations of metallic Zinc and potassium iodide, as synergizing agent on the corrosion inhibition behavior of L- Methionine were also studied. The techniques used are weight loss, Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) and Scanning Electron Microscope with Energy Dispersive X- Ray analyzer (SEM-EDX)

## MATERIALS

In the present work, commercial grade low carbon steel specimens equivalent to IS: 2062 Grade A specification having composition (weight %): 0.04 % C, 0.24 % Mn, 0.01 % S, 0.03 % Si and 0.001 % P, and balance Fe, with a dimension of 4.7 cm (L) × 1.0 cm (W) × 0.29 cm (T) were used for corrosion Inhibition studies. L-Methionine (SD fine) was used as such. Other chemicals and reagents such as hydrochloric acid and potassium iodide were (Merck) of analytical grade with 99.9% purity. The stock solutions of HCl were prepared using double distilled water.

## METHODS

### Weight loss measurements

This is the simplest and most widely used method for evaluating corrosion rated and the component materials. The specimens were cut into rectangular shape with a dimension of 4.7 cm (L) × 1.0 cm (W) × 0.29 cm (T) were used for weight loss measurements. To remove the last traces of impurities, scales or rust, the specimens were polished with Silicon carbide emery papers of grade 1/0, 2/0, 3/0 and 4/0 followed with a velvet cloth polishing in an alumina medium. The polished specimen with mirror finish finally washed and degreased using acetone, and dried up. To hold the specimens a hole of 1.7 mm diameter was made near the edge. The weight loss studies were carried out at 30°C in 1 M HCl. The test solution was made of AR grade 35% HCl using double distilled water. The concentration of L-Methionine was kept in the range of  $10^{-4}$  to  $10^{-1}$  M in 1M HCl. The weight loss experiments were performed after an exposure of 1hr and 2 hr separately. The weight loss of pre-cleaned low carbon steel specimens were determined after 1h and 2 hr of immersion at 30°C by weighing metal samples before and after immersing in 1M HCl, absence and presence of various concentration of L- Methionine, Zinc and potassium iodide. The specimens were weighed by electronic digital analytical balance (Make: Essae Teroka, Range: 1mg to 220mg) with four decimal accuracy before and after exposure. The inhibition efficiency (%IE) was calculated by using the following equation:

$$\text{Inhibition Efficiency, \%} = (1 - w_1/w_2) \times 100$$

Where  $w_1$  &  $w_2$  are the weight losses (mg) for low carbon steel in the presence and absence of inhibitor respectively.

$$\text{Corrosion rate (mmpy)} = (K \times W) / D \times A \times T$$

Where W is the weight loss in mg, D is the density in g/cc, A is the area of exposure in  $cm^2$ , T is the time in hour and K is constant with a value of  $8.76 \times 10^{-6}$  mmpy

### Inductively coupled plasma optical emission spectroscopy (ICP-OES) method

The chemical method of corrosion inhibition efficiency measurements are involved in determination of the dissolved cation using ICP-OES (Inductively Coupled Plasma optical emission spectrometry, Make: Perkin Elmer Model Optima 7000DV). ICP-OES is one method of optical emission spectrometry. When plasma energy is given to a sample solution from outside, the component elements (atoms) is excited. When the excited atoms return to low energy position,

emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity. as

$$E = h \nu = \frac{hc}{\lambda}$$

Where,  $E_2 - E_1 = E$ ,  $h$  - Planck's constant  $6.626068 \times 10^{-34} \text{ m}^2 \text{ kg} / \text{s}$ ,  $c$ -Velocity of light  $3 \times 10^8 \text{ meters per second}$ ,  $\lambda$  - wavelength of light.

**Scanning Electron Microscope examinations (SEM)**

SEM is a powerful magnification tool that utilizes focused beams of electrons to obtain information. The high-resolution, three-dimensional images produced by SEM to provide topographical, morphological and compositional information make them very useful in a variety of science and industrial applications. Samples for SEM experiments were used steel sheets of dimension of 4.7 cm (L) × 1.0 cm (W) × 0.29 cm (T). The polishing procedure was the same as that mentioned above. The immersion time was 1hr. Scanning Electron Microscope EVO 18 from Carl Zeiss was used to observe the morphology of the low carbon steel sheets, including the bare low carbon steel sheet, L- Methionine modified sheet, with Zinc and potassium Iodide as synergizing agent after corrosion in 1M HCl for 1hr.

**Energy dispersive X-ray analysis (EDX)**

EDX from Oxford Instruments with INCA 250 Energy Microanalysis System attached with Carl Zeiss EVO 18 Scanning Electron Microscope was used for elemental analysis or chemical characterization of the film formed on steel surface. As a type of spectroscopy, it relies on the investigation of sample through interaction between electromagnetic radiation and the matter. So that, a detector was used to convert X-ray energy into voltage signals. This information is sent to a pulse processor, which measures the signals and passed them into an analyzer for data display and analysis. Energy Dispersive X-ray Spectroscopy (EDS, EDX or XEDS) is a qualitative and quantitative X-ray microanalytical technique that can provide information on the chemical composition of a sample for elements with atomic number (Z) >3. The detection limit of EDX analysis in the SEM depends on the composition of the sample being

analyzed, but is in the range 0.1-0.5 wt%. It is an effective technique for major and minor element analysis, but lacks trace-element analysis.

**RESULTS AND DISCUSSION**

**Weight loss measurements**

The corrosion of low carbon steel in 1M HCl in the absence and the presence of different concentrations of amino acid L- Methionine were studied at 30<sup>0</sup> C with an exposure time of 1hr and 2 hr using weight loss technique. Table: I shows the calculated values of weight loss, inhibition efficiency and corrosion rate at different concentrations of L- Methionine at 30<sup>0</sup> C temperatures with an exposure period of 1 hr and 2 hr respectively. From these data, it is clearly seen that the corrosion rate of low carbon steel in 1M HCl depends mainly upon inhibitor concentration. The corrosion rates are significantly reduced in the presence of L- Methionine. The maximum increase in IE of 92.17% was observed (Table: I) & (Fig 1-3) at a concentration of 10<sup>-1</sup>M at 30<sup>0</sup>C with an exposure of 1hr. The corrosion inhibition exhibited by organic molecules is through adsorption on corroding metal. This adsorption is not always a direct

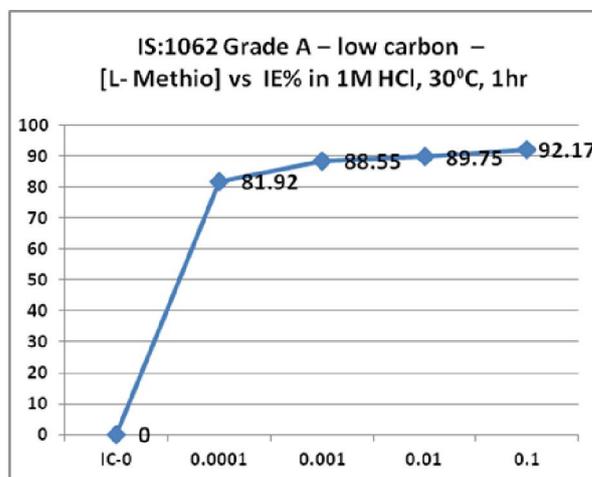


Fig. 1. Concentration of L- Methionine in mole

Table 1. Effect of concentration of L- Methionine on IS: 1062 Grade A - low carbon steel in 1M HCl

| Sl.No | [L- Methio] M    | Exposure time | Length (L), mm | Width (W),mm | Thickness (T), mm | Initial weight (A) g | Final weight (B) G | Weight Loss, W = (A-B) g | IE %  | Corrosion rate mmpy |
|-------|------------------|---------------|----------------|--------------|-------------------|----------------------|--------------------|--------------------------|-------|---------------------|
| 1     | 0                | 1hr           | 46.71          | 10.29        | 2.88              | 10.5424              | 10.5258            | 0.0166                   |       | 14.28               |
| 2     | 10 <sup>-1</sup> |               | 47.02          | 9.91         | 2.87              | 10.3411              | 10.3398            | 0.0013                   | 92.17 | 1.15                |
| 3     | 10 <sup>-2</sup> |               | 46.73          | 9.90         | 2.87              | 10.3305              | 10.3288            | 0.0017                   | 89.75 | 1.51                |
| 4     | 10 <sup>-3</sup> |               | 47.10          | 9.86         | 2.85              | 10.3147              | 10.3128            | 0.0019                   | 88.55 | 1.68                |
| 5     | 10 <sup>-4</sup> |               | 47.12          | 9.94         | 2.86              | 10.3023              | 10.2993            | 0.0030                   | 81.92 | 2.64                |
| 6     | 0                | 2hr           | 47.19          | 10.25        | 2.84              | 10.6291              | 10.5876            | 0.0415                   |       | 17.8                |
| 7     | 10 <sup>-1</sup> |               | 47.29          | 10.25        | 2.88              | 10.5313              | 10.5273            | 0.0040                   | 90.36 | 1.71                |
| 8     | 10 <sup>-2</sup> |               | 47.47          | 9.98         | 2.86              | 10.3816              | 10.3768            | 0.0048                   | 88.43 | 2.09                |
| 9     | 10 <sup>-3</sup> |               | 46.97          | 9.90         | 2.87              | 10.2098              | 10.2016            | 0.0082                   | 80.24 | 3.62                |
| 10    | 10 <sup>-4</sup> |               | 46.24          | 9.94         | 2.86              | 9.9174               | 9.9064             | 0.011                    | 73.49 | 4.92                |

Inhibitor: L- Methionine, Exposure time: 1 hr & 2hr, Temp: 30<sup>0</sup>C, [HCl] : 1M Inhibition Efficiency, I.E% = (1- w<sub>1</sub> / w<sub>2</sub>) x 100, w<sub>1</sub>= Weight loss with inhibitor,

Table-II. Effect of [Zn] + [KI] on Inhibition efficiency of 0.1 M L- Methionine on IS: 1062 Grade A - low carbon steel in 1M HCl

| Sl.No | [L- Methi], M    | Zn mM | KI mM | Length (L), mm | Width (W), mm | Thickness (T), mm | Initial weight (A) g | Final weight (B) G | Weight Loss, W = (A-B) g | IE %  | Corrosion rate, mmpy |
|-------|------------------|-------|-------|----------------|---------------|-------------------|----------------------|--------------------|--------------------------|-------|----------------------|
| 1     | 0                | 0     | 0     | 46.71          | 10.29         | 2.88              | 10.5424              | 10.5258            | 0.0166                   |       | 14.28                |
| 2     | 10 <sup>-1</sup> | 0     | 0     | 47.02          | 9.91          | 2.87              | 10.3411              | 10.3398            | 0.0013                   | 92.17 | 1.15                 |
| 3     | 10 <sup>-1</sup> | 15    | 0     | 46.98          | 9.97          | 2.85              | 10.2894              | 10.2881            | 0.0013                   | 92.16 | 1.14                 |
| 4     | 10 <sup>-1</sup> | 0     | 10    | 47.20          | 10.07         | 2.89              | 10.3410              | 10.3398            | 0.0012                   | 92.77 | 1.04                 |
| 5     | 10 <sup>-1</sup> | 15    | 10    | 46.90          | 9.93          | 2.87              | 10.2970              | 10.2968            | 0.0002                   | 98.80 | 0.18                 |

Inhibitor: 0.1M L- Methionine, exposure time: 1hr, Temp: 30<sup>0</sup>C, [HCl] : 1M

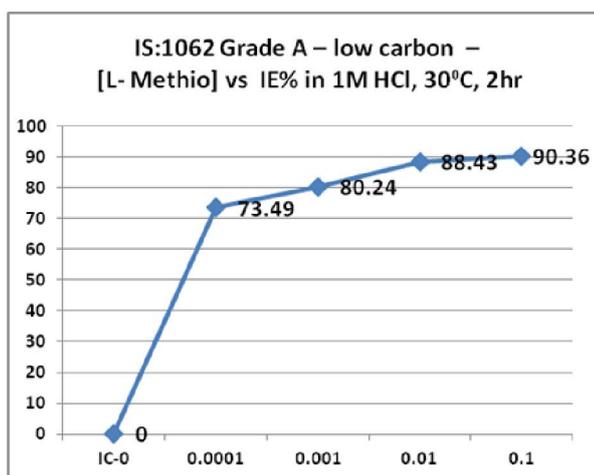


Fig. 2. Concentration of L- Methionine in mole

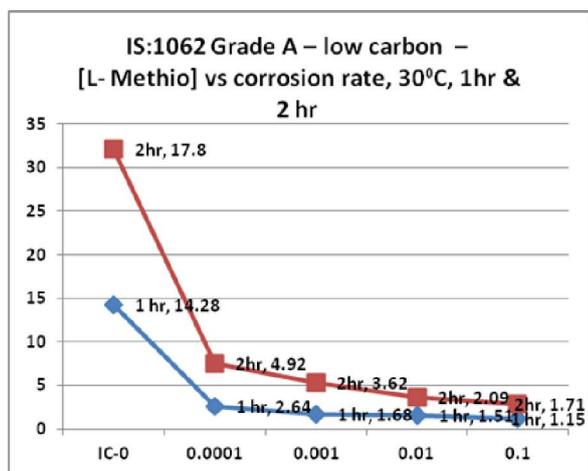


Fig. 3. Concentration of L- Methionine in mole

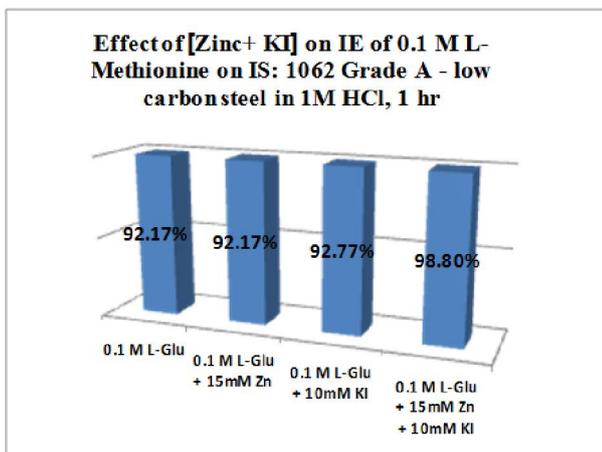


Fig. 4. Concentration of L- Methionine in mole

combination of organic molecules with the metal surface, but in some cases, the adsorption of organic molecules takes place via already adsorbed anions of the media [27, 28]. The specific adsorption of anions is found to be more pronounced with those anions having a smaller degree of hydration [29]. It has been reported that the steel surface is less positively charged in HCl medium compared to H<sub>2</sub>SO<sub>4</sub> medium. The Cl<sup>-</sup> ions which are having smaller degree of hydration are specifically adsorbed on metal surface by creating an excess negative charge towards solution and favor more adsorption of organic cations leading to greater inhibition [25- 29]. To avoid the excess use of inhibitors, various concentrations of Zinc and KI were

introduced along with 10<sup>-1</sup>M L-Methionine individually and combined together (Table: II). The corrosion rates are significantly reduced in the presence of L- Methionine with Zinc and KI. The maximum increase in IE of 98.80 % was observed at a concentration of 10<sup>-1</sup>M L-Methionine with Zn (15 millimole) and KI (10 milli mole) at 30°C with an exposure of 1hr Table – II & Fig 4.

**Inductively Coupled Plasma Optical emission spectroscopy (ICP-OES) method**

At present, weight loss measurement is the mostly employed method to acquire the corrosion rate data for metal coupons at natural environmental corrosion test stations in many countries. However, it is time consuming, which makes the corrosion rate obtained only a long-term average. Hence few details about the corrosion process during the experimental period are revealed. In this section, experimental corrosion rates for iron in HCl were determined by a chemical method other than weight loss. The chemical method of corrosion rates measurements involved determination of the dissolved cation using ICP-OES (inductively coupled plasma optical emission spectrometry) method of analysis. The advantages offered by ICP-OES method of analysis includes a multi-element measurement capability (72 elements in a single scan), high stability, optimum selectivity and superior dynamic range for concentration as well as calculation, data reporting and data reprocessing. These make the ICP-OES instrument is superior in the trace and environmental analysis in aqueous and organic media in complex samples. In the corrosion studies, such sophisticated instrument provides an excellent continuous chemical monitoring and robust analytical method for corrosion rate. (ICP-OES) provides therefore the most reliable results concerning the efficiency of a given inhibitor compound, so that the corresponding corrosion data obtained from them approach service conditions more accurately than the data obtained with any other test [30]. The corrosion rate was determined here separately by determination of dissolved Fe ions in 1.0 M HCl solutions without and with 10<sup>-1</sup>M L- Methionine, 15 millimole Zn and 10millimole KI at 30°C for 1hr and 2hr exposure using the (ICP-OES) technique. The [L- Methionine] vs dissolved iron content is shown in Fig 5.

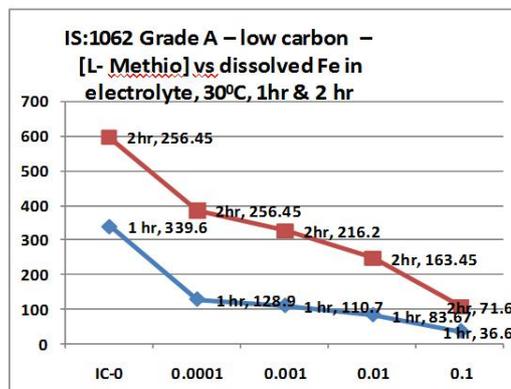


Fig. 5. shows the plots of [L- Methio] vs dissolved Fe in electrolyte, 30°C, 1hr & 2 hr

Fe 234.349

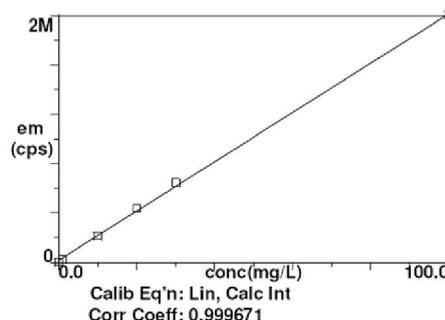


Fig.6. ICP-OES Calibration curves for Iron content analysis

The trend clearly indicates that increase in inhibitor concentration reduces the dissolution of iron from electrode. The calibration curves for iron content estimation by ICP-OES were shown in Fig. 6. Known aliquots of the solution containing dissolved Fe ions were withdrawn and total dissolved iron were analyzed. It follows from the data of Table III that the corrosion rate is suppressed and the corrosion inhibition strengthened with increase in inhibitor concentration.

**Table III. Dissolved Fe content in 1M HCl solutions without and with various concentrations of L- Methionine at 30°C, using the (ICP-OES) technique**

| Sl.No | [L- Methi], M    | Exposure time, hr | Fe concentration in mg/L | Corrosion Rate, R <sub>corr</sub> , g m <sup>-2</sup> hr <sup>-1</sup> |
|-------|------------------|-------------------|--------------------------|--|
| 1     | 0                | 1                 | 339.6                    | 263.3351   |
| 2     | 10 <sup>-1</sup> |                   | 36.6                     | 29.07728   |
| 3     | 10 <sup>-2</sup> |                   | 83.67                    | 66.91939   |
| 4     | 10 <sup>-3</sup> |                   | 110.7                    | 88.31385   |
| 5     | 10 <sup>-4</sup> |                   | 128.9                    | 102.0482   |
| 6     | 0                | 2                 | 842.2                    | 325.512  |
| 7     | 10 <sup>-1</sup> |                   | 71.6                     | 27.51993   |
| 8     | 10 <sup>-2</sup> |                   | 163.45                   | 64.04202   |
| 9     | 10 <sup>-3</sup> |                   | 216.2                    | 86.03675   |
| 10    | 10 <sup>-4</sup> |                   | 256.45                   | 103.3572   |

Inhibitor: L- Methionine, Exposure time: 1 hr & 2 hr, Temp: 30°C, [HCl]: 1M  
 R<sub>corr</sub> = m/(S x t) 'm' = Mass of the corroded metal (can be calculated from the dissolved iron content in solution, g S = Area of test metal in m<sup>2</sup>, t = exposure time in hour

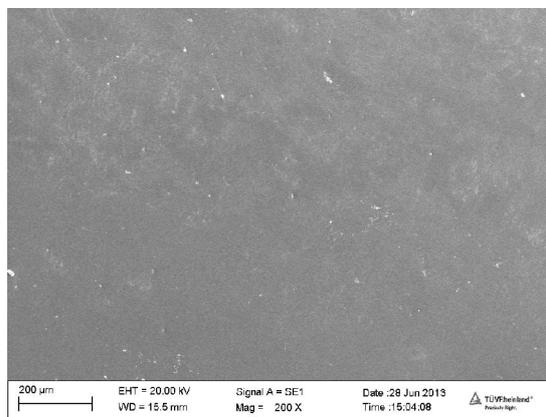
**Table-IV. Dissolved Fe content in 1M HCl solutions without and with 10<sup>-1</sup>M concentrations of L- Methionine and various concentration of Zn, KI and Zn+KI at 30°C, for 1hr using the (ICP-OES) technique**

| Sl.No | [L- Methi],M     | Exposure time, hr | [Zn],mM | [KI],Mm | Fe concentration in mg/L | Corrosion Rate,R <sub>corr</sub> , g m <sup>-2</sup> hr <sup>-1</sup> |
|-------|------------------|-------------------|---------|---------|--------------------------|---|
| 1     | 0                | 1                 | 0       | 0       | 339.6                    | 263.34  |
| 2     | 10 <sup>-1</sup> |                   | 15      | 0       | 10.3                     | 8.17  |
| 3     | 10 <sup>-1</sup> |                   | 0       | 10      | 35.53                    | 27.72   |
| 4     | 10 <sup>-1</sup> |                   | 15      | 10      | 3.665                    | 2.91  |

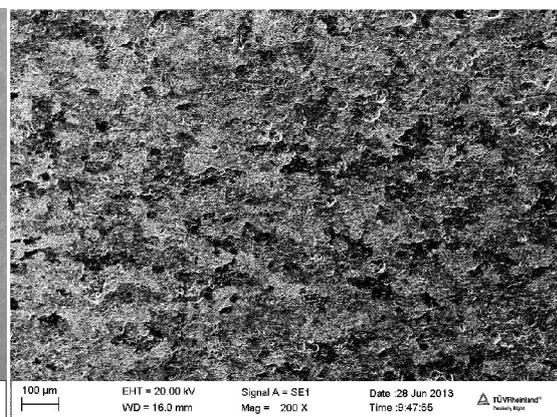
This trend may result from the fact that adsorption and surface coverage increases with the increase in inhibitor concentration; thus the surface is efficiently separated from the medium [30-33]. The reduction in dissolved iron content and corrosion rate reveals that 10<sup>-1</sup>M L- Methionine +15 millimole Zinc + 10 millimole KI at 30°C with an exposure time 1hr posses better inhibition efficiency and corrosion rate (Table IV). The critical inhibitor concentration with better efficiency including exposure duration was identified.

### SEM Analysis

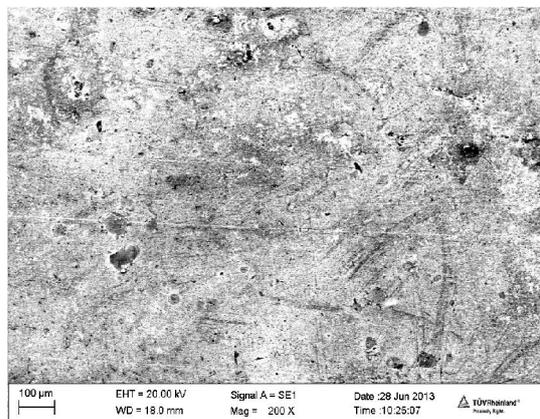
SEM was applied to confirm that the self-assembled films on the iron surface which can protect the metal from corrosion. The SEM micrographs with surface morphology details of the as polished, bare (without inhibitor) and L- Methionine modified low carbon steel sheets after corrosion for 1hour and 2 hour in 1M HCl solutions are shown in Fig. 7 (a-e). It can be observed that there are distinct differences between the five SEM microphotographs. The bare one had suffered more severe corrosion than inhibitor protected one. The surface of the bare low carbon steel sheets were completely damaged after exposure time of 1hr and 2 hrs respectively Fig.7(b) & 7(d), while the L- Methionine modified steel sheet was not so severely damaged. This means the presence of L-Methionine films can partially protect low carbon steel sheets surface from corrosion. SEM photographs obtained from low carbon steel sheets surface after the



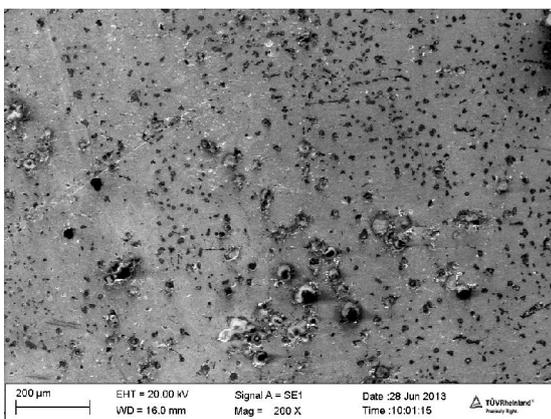
**Fig. 7 (a) As polished**



**Fig. 7(b) Bare with 1M HCl, 2hr**



**Fig. 7(c) 1M HCl+ 10<sup>-1</sup> M [L- Methio], 2 hr**



**Fig. 7(d) Bare with 1M HCl, 1hr**

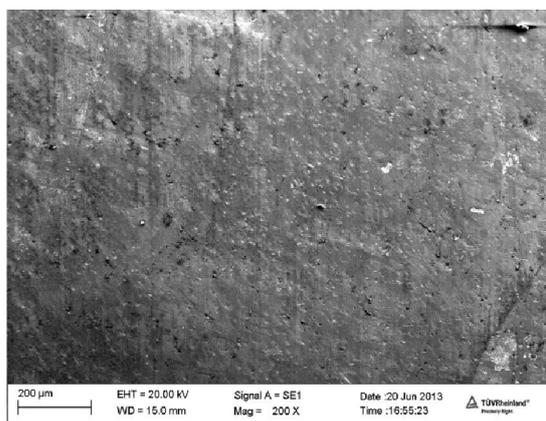
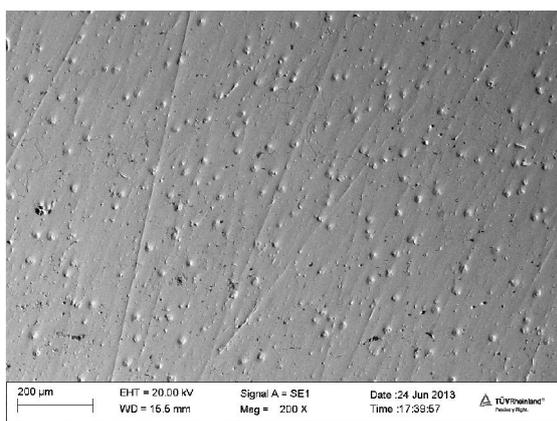
Fig. 7(e) 1M HCl+ 10<sup>-1</sup> M [L- Methio], 1 hrFig. 7(f) 1M HCl+ 10<sup>-1</sup> M [L- Methio] + 15millimole Zn +10 millimole KI , 1hr

Fig. 7 (a-i) SEM Micrographs of low carbon steel surface

Table V. Electrode composition without and with various concentrations of L- Methionine, Zn and KI at 30°C in 1M HCl using SEM- EDX technique, Exposure time 1hr &amp; 2 hr

| Sl.No | Description of the sample                                      | Exposure time, hr | Weight, % |      |         |          |        |      |
|-------|--|-------------------|-----------|------|---------|----------|--------|------|
|       |  |                   | Fe        | C    | Sulphur | Nitrogen | Oxygen | Mn   |
| 1     | As polished  |                   | 98.14     | 0.43 | 0.30    | 0.0      | 0.0    | 1.13 |
| 2     | 1M HCl , without inhibitor                                     | 1hr               | 90.13     | 4.8  | 0.36    | 0.0      | 3.72   | 0.14 |
| 3     | 1M HCl + L- Methi, 10 <sup>-1</sup> M                          |                   | 84.59     | 7.93 | 0.22    | 0.0      | 6.42   | 0.39 |
| 4     | 1M HCl + 10 <sup>-1</sup> M L- Methi + 15milli mole Zn         |                   | 86.08     | 5.47 | 0.0     | 0.23     | 7.39   | 0.22 |
| 5     | 1M HCl + L- Methi 10 <sup>-1</sup> M + 10milli mole KI         |                   | 88.97     | 5.3  | 0.01    | 0.10     | 4.14   | 0.31 |
| 9     | L- Glu, 10 <sup>-1</sup> M + 15milli mole Zn + 10milli mole KI |                   | 78.94     | 8.67 | 0.44    | 1.90     | 7.24   | 0.45 |
|       | 1M HCl , without inhibitor, 2hr                                | 2hr               | 91.04     | 4.44 | 0.10    | 0.0      | 3.83   | 0.18 |
|       | 1M HCl + L- Methi, 10 <sup>-1</sup> M, 2hr                     |                   | 85.80     | 6.02 | 0.13    | 1.39     | 5.43   | 0.28 |

specimens immersed in 1M HCl for 1hr in the presence of 10<sup>-1</sup> M L-Methionine + 15 millimole Zinc + 10 millimole KI at 30°C is shown in Fig. 7(f). It could be seen that in presence of the inhibitor, along with Zinc and KI as synergizing agents, the rate of corrosion was suppressed; it further revealed that there was a good protective film adsorbed on specimen surface, which was responsible for the inhibition of corrosion. This synergism is due to increased surface coverage as a result of ion-pair interactions between organic cation and halide anion. The halide ions present in an inhibiting solution adsorb on corroding electrode surface by creating oriented dipoles and facilitates the adsorption of inhibitor cations on the dipoles. It could be observed from Fig. 7 (b & d) that the specimen surface was strongly damaged in the absence of the inhibitor.

#### Energy dispersive X-ray analysis (EDX)

The composition of protective film formed on low carbon steel surface was analyzed using EDX as shown in Fig. 8 (a-h). The EDX spectrum of polished carbon steel sample in Fig. 8(a) shows good surface properties, while the spectrum in case of low carbon steel sample immersed in 1M HCl solution without inhibitor molecules (blank) was failed because it is severely weakened by external corrosion as shown in Fig. 7 (b). By adding 10<sup>-1</sup> M of L- Methionine the decrease of iron band and appearance of carbon, Sulphur and oxygen band was observed due to the formation of a moderately strong protective film of the inhibitor molecules on the surface of low carbon steel sample Fig 7(c) & 7(e). The action of inhibitor is related to adsorption and formation of a barrier film on the electrode surface. The formation of such a barrier film is confirmed by SEM and EDX examinations of the electrode surface. Fig 8(c & e) and Table V. The EDX survey spectra presented in Fig. 8 (b & c) & Table V showed that in uninhibited HCl solutions, iron oxide is present, as indicated by the Fe and O signals. However, in inhibited HCl solutions with Zn and KI as synergizing agents (in presence of 10<sup>-1</sup> M L- Methionine + 15 millimole Zinc + 10 millimole KI at 30°C, with

1hr exposure as a representative example), Fig.8(d-h) the EDX spectra showed an additional line characteristic of the existence of C (due to the carbon atoms of L- Methionine). In addition, the O and S signal is significantly enhanced due to the oxygen and sulphur atoms of the head group. These data show that a carbonaceous material containing oxygen and sulphur atoms has covered the electrode surface. This layer is undoubtedly due to the inhibitor, because the carbon signal and all the previous results plead on the favour that the corrosion inhibition effect of the L- Methionine is due to their adsorption onto the electrode surface blocking the corrosion process. It is well known that the adsorption of organic compounds can be described by two main types of interaction: physical adsorption and chemisorptions. In general, the proceeding of physical adsorption requires the presence of both electrically charged surface of the metal and charged species in the bulk of the solution. Chemisorptions process involves charge sharing or charge-transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond. This is possible in case of a positive as well as a negative charge of the surface. The presence of a transition metal, having vacant, low-energy electron orbitals and of an inhibitor with molecules having relatively loosely bound electrons or heteroatom with a lone pair of electrons is necessary. The molecular structure of the L- Methionine suggests that adsorption may occur through two lone pairs of electrons on the oxygen and sulphur atoms of the hydrophilic head group. This type of adsorption is expected to be chemical due to the possible formation of coordinate bonds between the lone electron pairs of the oxygen and sulphur atoms and the empty orbitals of iron atoms which enhance the attraction between the L- Methionine molecules and electrode surface. The chemisorbed L- Methionine molecules form a protective layer, [33] as confirmed from SEM and EDX examinations Fig 8 (d& e), covering the surface to some extent. It could be seen that in presence of the inhibitor, along with Zinc and KI as synergizing agents there was a good protective film adsorbed on specimens surface, which was responsible for the inhibition of corrosion (Fig7(f) & 8(f-h)). This synergism is due to increased surface coverage

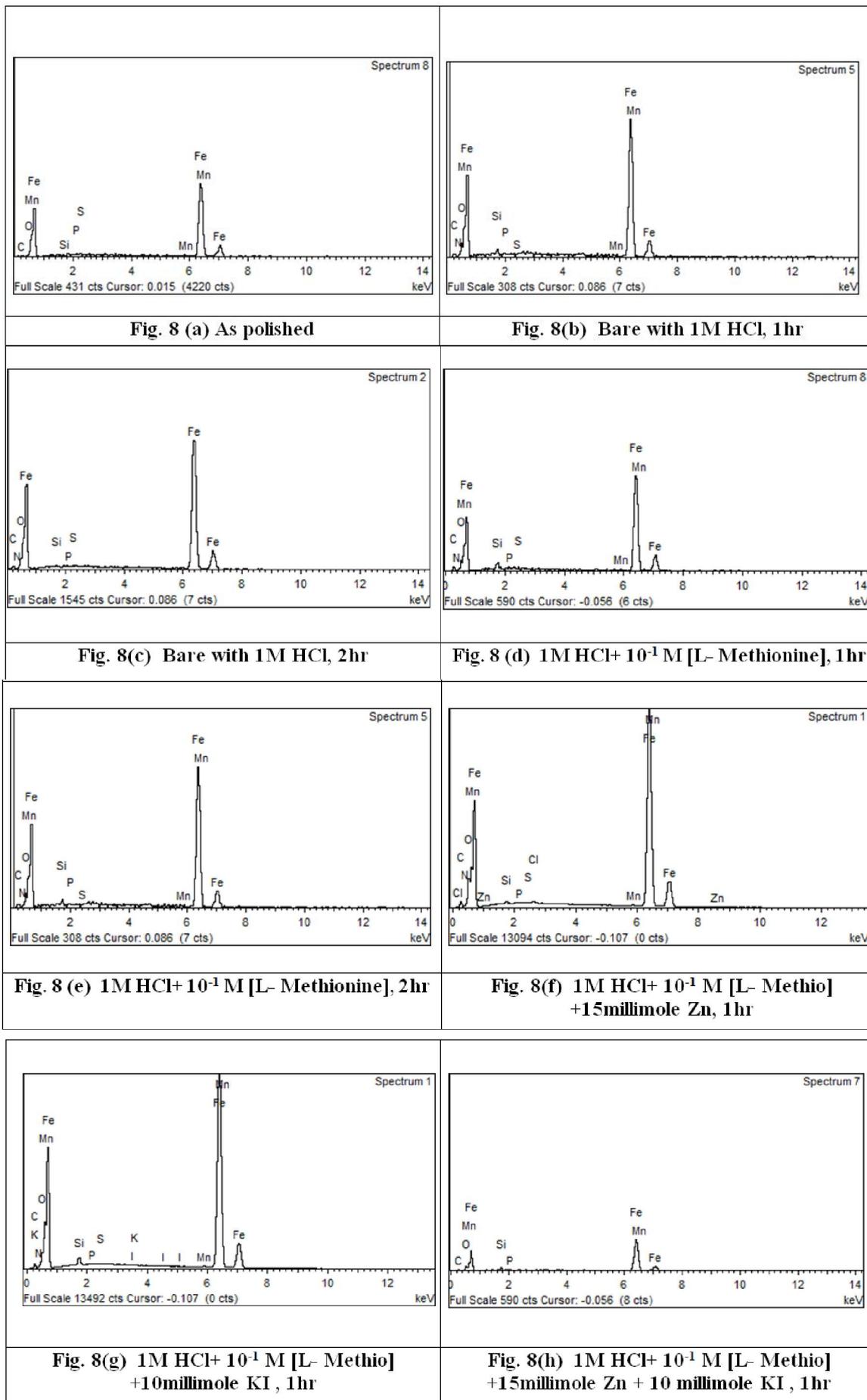


Fig. 8 (a-h) EDX graphs of duplex steel surface without and with Inhibitor

as a result of ion-pair interactions between organic cation and halide anion. The halide ions present in an inhibiting solution adsorb on corroding electrode surface by creating oriented dipoles and facilitates the adsorption of inhibitor cations on the dipoles, and possibly at the same time, blocks access to the active site of corrosion on the surface, reducing the aggressiveness of attack at these sites

## Conclusion

The main conclusions of the present study could be summarized in the following points:

- 1) In weight loss measurements L- Methionine has shown the maximum increase in Inhibition Efficiency of 92.17% at a concentration of  $10^{-1}$ M at 30°C for 1hr, which further affected by adding Zn and KI as synergizing agents. The maximum increase in IE of 98.80 % was observed at a concentration of  $10^{-1}$ M L-Methionine with Zinc (15 millimole) and potassium iodide (10milli mole) at 30°C with an exposure of 1hr
- 3) ICP-OES measurements, reconfirms that the increase in inhibitor concentration with Zn and KI as synergizing agents reduces the corrosion rate of low carbon steel surface. This is mainly due to protective film produced on the steel surface. This was further confirmed by estimating the dissolved Fe content in electrolyte solution
- 4) SEM and EDX observations of the electrode surface showed that a film of inhibitor molecules is formed on the electrode surface. This film retarded the reduction of dissolution of iron in carbon steel surface

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