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An Investigation of L-Valine and Zn^{2+} Ion as Corrosion Inhibitor for Carbon Steel in Cauvery River Water

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ABSTRACT

Corrosion of metals as age old as the origin of earth itself. In the past history, various means and methods have been employed to suppress corrosion. One of those methods to suppress corrosion is by using organic inhibitors. Since many of those organic inhibitors were found to be hazardous to the lives on earth. Hence it is the need of the time to go for eco-friendly corrosion inhibitors. Out of the various ecologically favorable inhibitors, amino acids are found to be the suitable corrosion inhibitors. In this study L-Valine has been chosen with Zn^{2+} ion to know its corrosion inhibition behavior on carbon steel in Cauvery water. Weight loss method has been employed for this investigation. The film formation has been authenticated by various electrochemical investigations such as FTIR, UV-Vis spectroscopy, Fluorometry, Potentiostatic polarization and Scanning electron microscopy. From the results of the above studies the probable mechanism for the corrosion inhibition has been proposed.

Key words: Carbon steel, cauvery water, Weight loss method, FTIR, UV-Visible spectroscopy, Polarization, Scanning electron microscopy

1. INTRODUCTION

Corrosion in general signifies the deterioration of metal when it comes into contact with the corrosive environment. In short, it is the collective range of reactions that occurs between metals and their environment [(1)]. Various methods and materials have been employed for controlling this corrosion phenomenon. Using organic inhibitors is one among them. Organic inhibitors are the chemical substances which when added by small quantities can efficiently control the corrosion process or fully arrest the same[(2)]. The classical inhibitors such as chromate, nitrate, polyphosphate and organic phosphate have been banned in most of the countries [(3, 4)]. The present scenario in the research field requires the corrosion inhibitors which are safe, non-toxic, easily biodegradable and more environmental friendly green chemicals in order to meet environmental protection requirements [(5-7)]. Amino acids are found to be non-lethal, ecologically friendly and simple to make with purities greater than 99%. So many innovative accomplishments have been made in recent times on using amino acids as corrosion inhibiting species[(8-13)].

Hence amino acids are found to be very good eco-friendly corrosion inhibitors [(14-15)]. In this study one of the effective eco-friendly amino acid, namely, L-Valine is chosen along with Zn^{2+} ion for investigation of its corrosion inhibition behavior. Literature survey elucidates some of the investigations that includes amino acids as corrosion inhibitor on various metals such as iron[(16)], Steel[(17-23)], Aluminium[(24-26)], Nickel[(27)], Copper[(28-33)], and Brass[(34)]. However this investigation probes into the corrosion inhibition efficiency of carbon steel by L-Valine and Zn^{2+} ion in cauvery water medium is being investigated. Hence this work is carried out to know

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- The effect of corrosion inhibition of L-Valine with Zn^{2+} ion on carbon steel in cauvery water medium using weight loss method.
- The effect of synergism existing between L-Valine and Zn^{2+} ion.
- The results of potentiostatic polarization study
- The characteristics of the sparingly film formed by FTIR, UV-Visible Spectroscopy, and Fluorometry.
- The confirmation of the formed protective film formed by scanning electron microscopy.

2. MATERIALS AND METHODS

CARBON STEEL AS SPECIMEN

For this study the specimen chosen was carbon steel. The dimension of the carbon steels was $1.2\times4.0\times0.1$ cm^3. The composition was as follows,

ELEMENT	COMPOSITION OF CARBON STEEL (%)
Carbon	0.1
Sulphur	0.026
Phosphorous	0.06
Manganese	0.4
Silicon	0.129
Chromium	0.022
Molybdenum	0.011
Nickel	0.013
Iron	Rest

These carbon steel metals were carefully, mechanically burnished to mirror finish and made use for the study.

WEIGHT-LOSS METHOD

The previously weighed metals were taken, hooked up in plastic hooks and were suspended in the cauvery water with and without the ecologically favorable inhibitor, namely, L-Valine with Zn^{2+} ion for 1 day. After 1 day, those metals were remove off, rinsed thoroughly in running tap water, dehydrated by drying and then weighed. From the variation in the weight before and after immersion, the corrosion rate was calculated. For calculating corrosion rate the following relation was used,

$$\text{Corrosion rate} = \frac{\text{Loss in Weight (mg)}}{\text{Surface area of the specimen (dm2)} \times \text{Period of immersion (days)}}$$

And then efficiency of corrosion inhibition by the inhibitor, namely, L-Valine and Zn^{2+} ion was determined by using following formula,

$$\text{Inhibition efficiency} = \frac{W1-W2}{W1} \times 100$$

Where,

W1 = Corrosion rate in the non-existence of inhibitor
W2 = Corrosion rate in the existence of inhibitor

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FTIR

After one day of immersion in the various environment, the carbon steel metals were removed off and dehydrated by drying. The film formation occurred was visible and that was scratched carefully and mixed thoroughly to make it uniform. And then powder was sent for FTIR analysis. Also the pure inhibitor sample, namely, L-Valine without Zn^{2+} ion was sent for FTIR analysis and the resulting graph is presented with interpretation.

UV-VIS SPECTROSCOPY

UV-Vis spectroscopy (U-Visible) is a kind of absorption spectroscopy. Absorption spectroscopy in the UV-Visible region is one of the age old classic techniques. Analysis of the substance is done by the sample produced by it. This is because of the absorption taking place in assertive wavelengths of the UV-Vis light region. Both UV and Visible light are found to behave likewise; hence both UV and Visible spectroscopy are studied together. For our study Lambda 35 UV-Visible spectrometer has been used.

FLUORESCENCE SPECTROSCOPY

Fluorometry is generally ten to thousand times more sensitive and more specific by nature than spectrophotometry. Fluorometric measurement is versatile because it combines various parameters at the same time such as excitation and emission wavelengths, fluorescence life time or fluorescence polarization[(36)]. For this study Jasco F-6300 spectrofluorometer has been used.

POTENTIOSTATIC POLARIZATION

Potentiostatic polarization is a kind of technique which controls polarization of metal surface in electrolyte; thereby paving path to pay attention to cathodic and anodic behaviors. Scrutinizing of corrosion reactions are carried out on a sample of the respective metal. These polarization experiments are being performed with the assistance of a computer controlled potentiostat.

SEM

Scanning electron micrographs (SEM) are used to comprehend the characteristics of the sparingly soluble film which was formed on the metal surface. In this study SEM was carried out in the non-existence as well as in the existence of the inhibitor formulation, namely, L-Valine and Zn^{2+} ion.

3. RESULTS AND DISCUSSION

WEIGHT LOSS METHOD

Corrosion inhibition of carbon steel in cauvery water for one day by Zn^{2+} ion, L-Valine alone and L-Valine with Zn^{2+} ion is being depicted in the tables and pie charts below.

INHIBITION BEHAVIOR OF ZN^{2+} ION IN CAUVERY WATER FOR ONE DAY

Table 1 gives the statistical data of rate of the corrosion and percentage of inhibition efficiency of Zn^{2+} ion with varied numerous concentrations with the scope of the range from 10 ppm to 60 ppm. Here it is inferred that the inhibition efficiency is up surged as Zn^{2+} ion concentration is up surged. The inhibitive resistance reached its optimum with 40% inhibition efficiency at the concentration of 50 ppm.

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Zn^{2+} SYSTEM FOR ONE DAY

S.NO	CONC. OF L-VAL (PPM)	CONC. OF ZN^{2+} ION (PPM)	INHIBITION EFFICIENCY (%)	CORROSION RATE (MMPY)
1	0	10	15	0.0810
2	0	20	20	0.0762
3	0	30	25	0.0715
4	0	40	35	0.0620
5	0	50	40	0.0574
6	0	60	17.5	0.0786

TABLE NO. 1

The same is expressed as pie chart in the figure (1) below,

RATE OF CORROSION AND PERCENTAGE OF INHIBITION EFFICIENCY OF ZN^{2+} ION IN CAUVERY WATER FOR ONE DAY

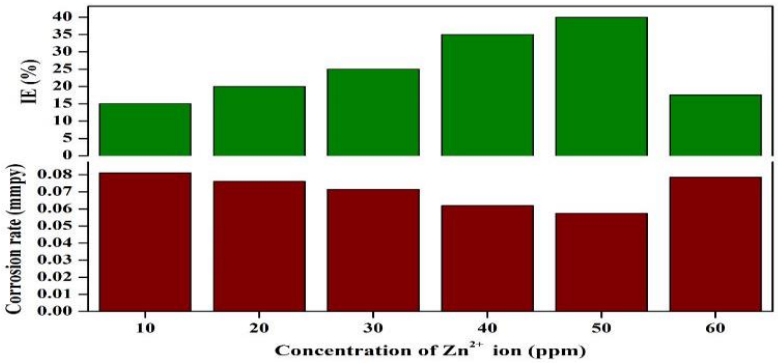

FIGURE 1

INHIBITION BEHAVIOR OF L-VALINE IN CAUVERY WATER FOR ONE DAY

Table 2 gives the statistical data of rate of corrosion and percentage of inhibition efficiency of L-Valine with various concentrations ranging from 50 ppm to 300 ppm. Here it is found that at 50 ppm itself the highest inhibition efficiency of 55% has been obtained and afterwards the inhibition efficiency is found decreasing as the concentration of L-Valine is increased.

L-VALINE SYSTEM FOR ONE DAY

S.NO	CONC. OF L-VAL (PPM)	CONC. OF ZN^{2+} ION (PPM)	INHIBITION EFFICIENCY (%)	CORROSION RATE (MMPY)
1	50	0	55	0.0429
2	100	0	40	0.0572
3	150	0	20	0.0762
4	200	0	10	0.0858
5	250	0	2.5	0.0929
6	300	0	2.5	0.0929

TABLE NO. 2

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The same is expressed as pie chart in the figure (2) below

RATE OF CORROSION AND PERCENTAGE OF INHIBITION EFFICIENCY OF L-VALINE IN CAUVERY WATER FOR ONE DAY

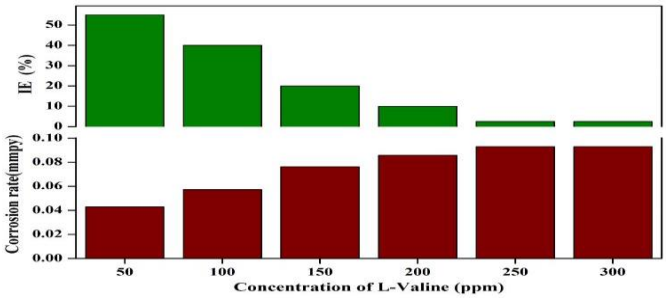

FIGURE 2

INHIBITION BEHAVIOR OF L-VALINE AND ZN^{2+} ION IN CAUVERY WATER FOR ONE DAY

Table 3 gives the statistical data of rate of corrosion and percentage of inhibition efficiency of L-Valine with various concentrations ranging from 50 ppm to 300 ppm with Zn^{2+} ion of 50 ppm concentration remaining same all through. Here it is found that concentration ratio, 50:50 ppm of L-Valine and Zn^{2+} ion respectively, exhibited the highest inhibition efficiency of 77.50 %. Afterwards the inhibition efficiency is down surged as the concentration of L-Valine is up surged.

L-VALINE AND ZN^{2+} SYSTEM FOR ONE DAY

S.NO	CONC. OF L-VAL (PPM)	CONC. OF ZN^{2+} ION (PPM)	INHIBITION EFFICIENCY (%)	CORROSION RATE (MMPY)
1	50	50	77.50	0.0214
2	100	50	75	0.0238
3	150	50	70	0.0286
4	200	50	65	0.0334
5	250	50	65	0.0334
6	300	50	62	0.0357

TABLE NO. 3

The same is expressed as pie chart in the figure (3) below,

RATE OF CORROSION AND PERCENTAGE OF INHIBITION EFFICIENCY OF L-VALINE AND ZN^{2+} ION IN CAUVERY WTAER FOR ONE DAY

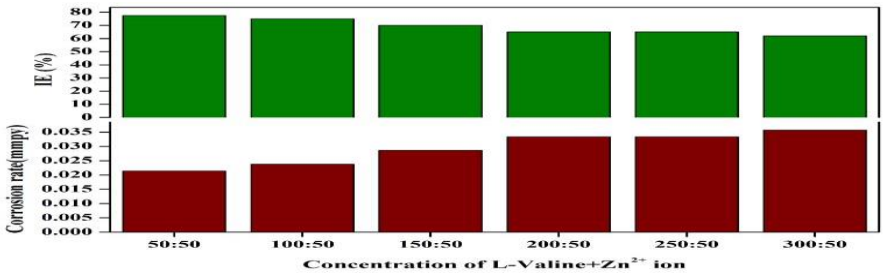

FIGURE 3

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FTIR

FTIR GRAPH FOR (A) PURE L-VALINE AND (B) L-VALINE AND ZN^{2+} ION FILM POWDER

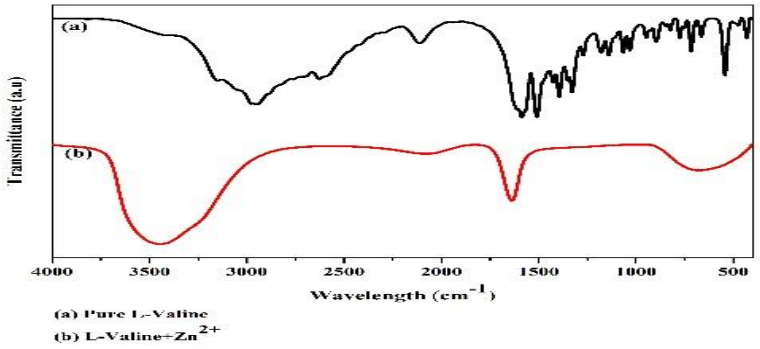

FIGURE 4

The functional groups that are present in the samples under investigation are identified using FTIR spectroscopy. This technique is also being made use to examine the film formation on metal surface [34-35]. In this study two samples have been investigated for FTIR spectroscopy, namely, L-Valine and Zn^{2+} ion film powder and pure L-Valine. On comparing these two graphs, the following observations have been made.

The FTIR spectra of Pure L-Valine and the film powder of L-Valine and Zn^{2+} ion is depicted in the above figure (4). The peak of pure L-Valine at 3149.50 cm^{-1} which was due to –NH and –OH stretching vibrations, has been shifted to 3406.61 cm^{-1} for L-Valine and Zn^{2+} film powder. The two peaks obtained at 2949.76 cm^{-1} and 2916.66 cm^{-1} for pure L-Valine which was due to two alkyl stretching, have been shifted to 2925.54 cm^{-1} and 2855.30 cm^{-1} respectively for L-Valine and Zn^{2+} ion film powder. The peak of pure L-Valine at 1587.10 cm^{-1} which was due to –NH bending of $–NH_2$ group, has been shifted to 1463.32 cm^{-1} for L-Valine and Zn^{2+} ion film powder. The carbonyl stretching at 1611.90 cm^{-1} for pure L-Valine has been shifted to 1631.96 cm^{-1} for L-Valine and Zn^{2+} ion film powder. Also the formation of –ZnO in L-Valine and Zn^{2+} ion formulation was authenticated by the peak obtained at 698.34 cm^{-1} for the same. This is expressed in the table (4).

So the formation of the protective film has been authenticated with all these diagnosed functional groups in the formulated mixture. Hence FTIR study led to the result that the film formed on metal surface contained Fe^{2+} -L-Valine mixture and $Zn(OH)_2$ on the carbon steel metal surface.

INTERPRETATION OF FTIR DATA

TYPES OF VIBRATIONS	Peaks (cm^{-1})	
	L-Val	L-Val + Zn^{2+}
-NH and –OH str	3149.50	3406.61
Alkyl str	2949.76 & 2916.66	2925.54 & 2855.30
-NH bending of –NH2	1587.10	1463.32
Carbonyl str	1611.9	1631.96
ZnO str	-	698.34

TABLE NO. 4

UV-Vis absorption spectroscopy

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UV-VIS ABSORPTION SPECTROSCOPY OF (A) L-VALINE AND ZN^{2+} ION SOLUTION AND (B) L-VALINE AND ZN^{2+} ION FILM POWDER

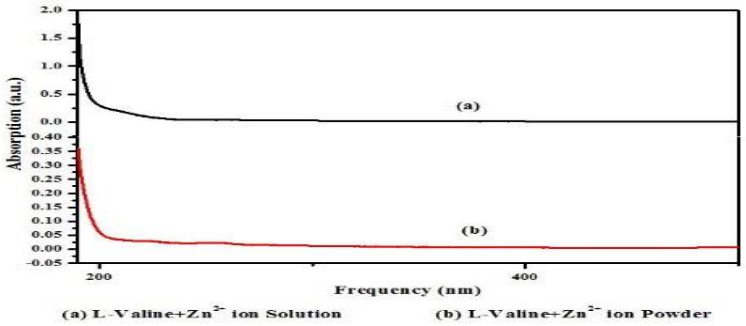

FIGURE 5

The UV-Visible absorption spectrum of the formulation of L-Valine and Zn^{2+} ion solution and the formulation of L-Valine and Zn^{2+} ion film powder is shown in the above figure (5). From the obtained spectral data, the following fact is confirmed. For the formulation of solution L-Valine and Zn^{2+} ion, a peak was obtained at 392.6 nm (0.015 a.u.). Whereas for the formulation of film powder of L-Valine and Zn^{2+} ion, a peak was obtained at 253.90 nm (0.023a.u.). In this case a reduced peak variation has occurred which indicates that a complex formation has taken place between L-Valine and Zn^{2+} ion on metal surface in the form of film. The interpretation of these data are expressed in the table (5).

INTERPRETATION OF UV-VISIBLE ABSORPTION SPECTRAL DATA

NAME	S.NO.	PEAK (NM)	PEAK(A.U)
Solution-L-Val+Zn^{2+} ion	1	392.60	0.015
Film powder-L-Val+Zn^{2+} ion	1	253.9	0.023

TABLE NO. 5

FLUORESCENCE SPECTROSCOPY

FLUORESCENCE SPECTROSCOPY OF (A) L-VALINE AND ZN^{2+} ION SOLUTION AND (B) L-VALINE AND ZN^{2+} ION POWDER

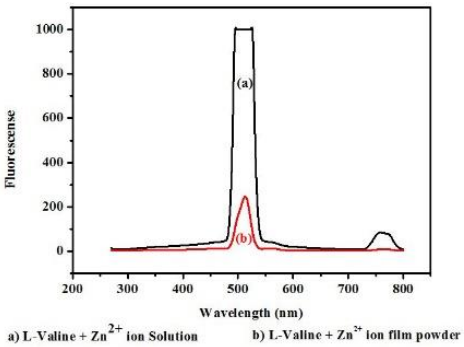

FIGURE 6

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Fluorescence spectrum is generally used to recognize the existence of the formulated inhibitor mixture upon the metal surface. From the figure (6) the following observations were made. The λmax for the emission spectrum of the solution of L-Valine and Zn^{2+} ion is 523.36 nm (1010.96 a.u.).The λ_{max} for the emission spectrum of the film powder of L-Valine and Zn^{2+} ion is 513.06 nm (246.23 a.u.).

The λ_{max} value is being reduced to a greater extent in the case of emission spectrum of film powder than the solution. This is being shifted from 523.36 nm to 513.06 nm. These shifts and variations in the spectral graphs point out that the film formation has occurred on the metal surface. The interpretation of these data are expressed in the table (6).

INTERPRETATION OF FLUORESCENCE SPECTRAL DATA

NAME	S.NO.	PEAK (NM)	PEAK(A.U)
Solution-L-Val+zn^{2+} ion	1	523.36	1010.96
Film powder-L-Val+Zn^{2+} ion	1	513.06	246.23

TABLE NO. 6

POTENTIOSTATIC POLARIZATION

POLARIZATION STUDY OF CARBON STEEL IMMERSED IN VARIOUS ENVIRONMENT: (A) CAUVERY WATER, (B) CAUVERY WATER + 50 PPM OF L-VALINE + 50 PPM OF ZN^{2+} ION

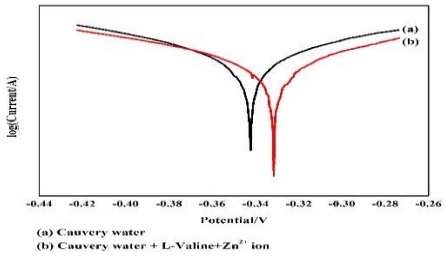

FIGURE 7

The potentiostatic polarization curves of carbon steel which was suspended in varied numerous environments are portrayed in the above figure (7). The corrosion parameters have been presented in the table (7) below. On the occasion when the carbon steel gets immersed in cauvery water, the corrosion potential is deciphered to be -341.961 mV Vs saturated calomel electrode (SCE). The mixture of 50 ppm L-Valine and 50 ppm Zn^{2+} attempts to shift the corrosion potential to -351.21 mV Vs saturated calomel electrode (SCE). This advocates that cathodic reaction is controlled prominently. The same formulated mixture, namely, L-Valine and Zn^{2+} ion attempts to shift the cathodic slopes from 148.867 mV to 178.458 mV. This gives the confirmation that the mixture functions as cathodic inhibitor controlling the cathodic reaction.

The corrosion current for cauvery water is 582.821 nA. The corrosion current for the formulated mixture containing L-Valine (50 ppm) and Zn^{2+} ion (50 ppm) has been decreased to 479.018 nA. The interpretation of these data are expressed in the table (7).

INTERPRETATION OF POTENTIOSTATIC POLARIZATION DATA

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L-Val (ppm)	Zn^{2+} ion (ppm)	E_{corr}	b_a	b_c	$I_{corr\ (nA)}$
0	0	-341.961	140.861	148.37	582.821
150	50	-351.21	148.867	178.458	479.01

TABLE NO. 7

SEM

The carbon steel metals which were suspended in cauvery water for one day in non-existence and existence of the inhibitor, namely, L-Valine and Zn^{2+} ion and they were investigated for SEM analysis. The SEM images are given below.

The SEM images in figure (8) show the various magnifications of carbon steel, namely, 1.64 KX, 2.50 KX, and 10.02 KX in cauvery water without inhibitor for one day. Here the surface of the metal is found to be very rough. This raggedness of the metal surface is because of the corrosive deterioration that took place upon it.

SEM IMAGES OF VARIOUS MAGNIFICATIONS OF CARBON STEEL, NAMELY, 1.64 KX, 2.50 KX, AND 10.02 KX IN CAUVERY WATER FOR ONE DAY

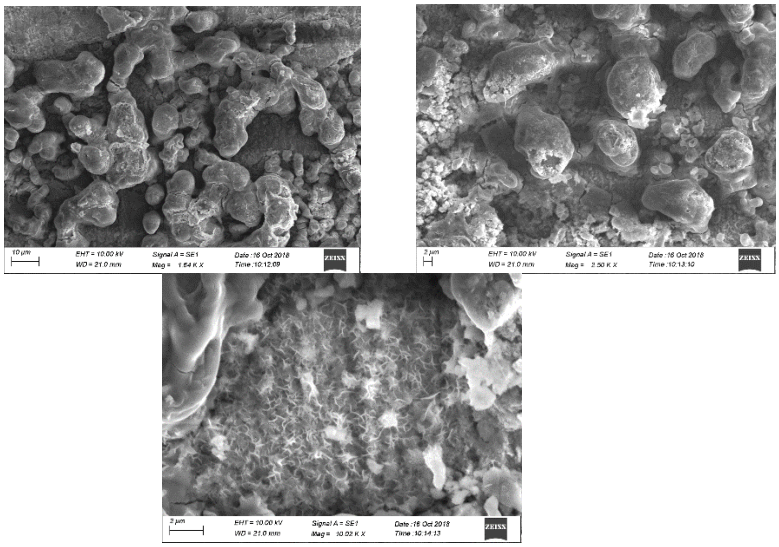

FIGURE 8

The SEM images in Figure (9) show the various magnifications of carbon steel, namely, 10.56 KX, 12.08 KX, 23.99 KX) in cauvery water with inhibitor, namely, 50 ppm L-Valine and 50 ppm Zn^{2+} ion for one day. Here the surface of the metal is found to be smoother. This is because of the film formed upon the metal surface. At the ratio of 50:50 ppm of L-Valine and Zn^{2+} ion respectively, the corrosion is suppressed and the same is evident from the decrease in corroded area. This is because of the formation of insoluble metal inhibitor complex (L-Valine and Zn^{2+} ion) on the carbon steel surface. This metal inhibitor complex has effectively controlled the corrosive deterioration of carbon steel.

SEM IMAGES OF THE VARIOUS MAGNIFICATIONS OF CARBON STEEL, NAMELY, 10.56 KX, 12.08 KX, 23.99 KX IN CAUVERY WATER WITH INHIBITOR, NAMELY, 50 PPM L-VALINE AND 50 PPM ZN^{2+} ION FOR ONE DAY.

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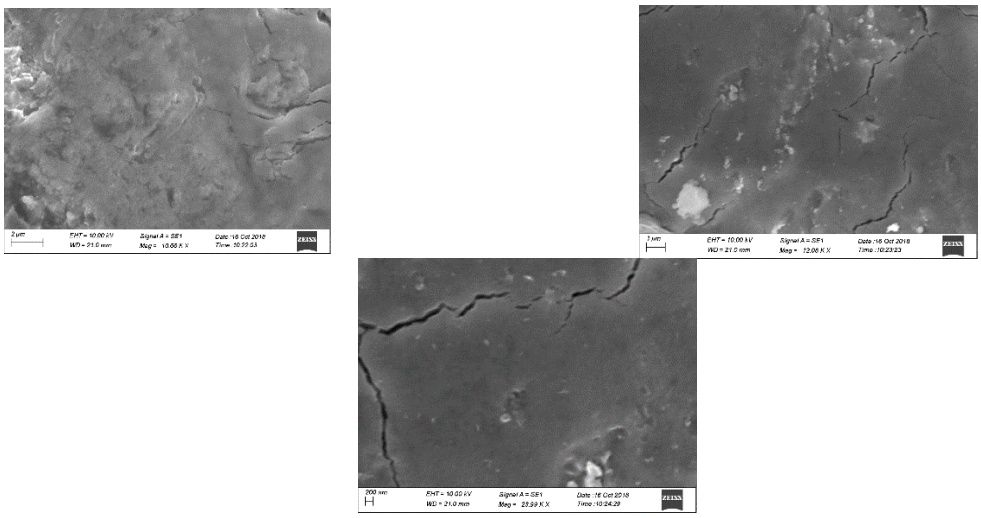

FIGURE 9

4. CONCLUSION

From the investigation of the system by chemical and electrochemical methods, the following findings have been brought into spotlight.

- Though L-Valine was considered to be one of the best corrosion inhibitors, when it was mixed with Zn^{2+} ion, a very good synergistic effect occurred between them. Due to this synergism the inhibition efficiency has increased considerably.
- Potentiostatic polarization showed that the mixture of L-Valine and Zn^{2+} ion acted as cathodic inhibitor.
- Spectral analysis such as FTIR, UV, Fluorometry confirmed the fil formation .
- Formation of insoluble metal inhibitor complex (L-Valine & Zn^{2+} ion) has been confirmed by Scanning electron microscopy.
- Complex mixture of L-Valine (50 ppm) and Zn^{2+} ion (50 ppm) was established to inhibit the corrosion of carban steel in cauvery water with the inhibition efficiency of 77.50 %.

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