Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **4(1),** 41-49, January **(2014)** *Res. J. Chem. Sci.*

Synergistic effect of Thiomalic acid and Zinc ions in Corrosion control of Carbon Steel in Aqueous Solution

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Available online at: www.isca.in, www.isca.me
Received 12th December 2013, revised 2nd January 2014, accepted 16th January 2014

Abstract

The synergistic effect has been studied in the presence of a dicarboxylic acid inhibitor with or without bivalent cation like zinc ions. A protective film has been formed on the carbon steel surface in aqueous solution using a synergistic combination of an environmentally friendly dicarboxylic acid (thiomailc acid) and zinc ions. The corrosion inhibition effect of thiomalic acid with zinc ions on carbon steel has been carried out by gravimetric studies and electrochemical techniques. Potentiodynamic polarization studies reveal that the inhibitor system is of a mixed type. Impedance studies point out that a protective film is formed on the carbon steel surface in the presence of the inhibitor formulation. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to investigate the nature of protective film formed on the carbon steel surface and for explaining the mechanistic aspects of the inhibition process.

Keywords: Corrosion, synergistic effect, carbon steel, protective film, FTIR, SEM.

Introduction

Because of its good mechanical properties, availability and relatively reasonable cost carbon steel is the most worldwide used material for industrial and domestic applications. Several techniques have been applied in order to reduce the corrosion of metals. The use of inhibitors was one of the most practical and efficient methods for protection against corrosion[1]. Corrosion inhibitors are substances added in very small concentrations that they effectively reduce the corrosion rate[2]. Generally, organic compounds having heteroatom O, N, P and S are found to have basicity and electron density, thus assist in corrosion inhibition[3]. Compounds with functional groups containing hetero-atoms which can donate a lone pair of electrons are found to be useful as corrosion inhibitors for metals[4,5]. These compounds are still continuously investigated as inhibitors for corrosion of metals in industry. The selection criteria for various inhibitors include low concentration, more adherance to environmental regulations, environmental friendliness and cost effectiveness. Carboxylic and dicarboxylic acids and salts thereof are very widely used as corrosion inhibiting agents and has been the subject of various workers[6-8]. An inexpensive way to protect the metals from corrosion is by using carboxylic acids. Carboxylic acid derivatives alone or both with other additives can effectively inhibit the corrosion of metals. One of the most important effects in inhibition process that serves as the basis for most of the modern corrosion inhibiting formulations is synergism[9]. Synergistic effect existing among dicarboxylic acids and Zn^{2+} on the inhibition of corrosion of metals has been studied by various workers[10,11].

An organic compound namely dicarboxylic acid was investigated as a corrosion inhibitor for carbon steel in this study.The inhibitive properties and synergistic effect with an organic compound viz., Thiomalic acid (TMA) and Zn^{2+} ions in controlling the corrosion of carbon steel was studied in aqueous solution using gravimetric method and electrochemical methods viz., potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) were used to analyze the protective film formed on the carbon steel surface and a suitable mechanism of corrosion inhibition is proposed. An aqueous solution of 60 ppm chloride has been chosen as control because of the water used in cooling water systems is generally either demineralized water or unpolluted surface water.

Material and Methods

Preparation of specimens: The specimens of carbon steel 0.02-0.03 % S, 0.03-0.08 % P, 0.4-0.5 % Mn, 0.1-0.2 % C and the rest iron of dimensions 3.5 cm x 1.5 cm x 0.2 cm, were polished with 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0 emery polishing papers respectively. They were degreased with acetone, dried and used for gravimetric studies, FTIR and SEM. The dimensions of the specimens used for electrochemical studies were 1.0 cm x 1.0 cm x 0.2 cm.

Gravimetric measurements: The polished carbon steel specimens in triplicate were weighed and immersed, in 100 ml test solution (control solution) and solutions containing various concentrations of TMA in the absence and presence of Zn^{2+} ions, for a period of seven days. Then after washing and drying the carbon steel specimens were reweighed. The weights of the carbon steel specimens before and after immersion were determined using Mettler Balance AE 240 model. Corrosion rates (CR) of carbon steel in the absence and presence of TMA and Zn^{2+} ions are expressed in mdd. The CR was calculated according to the following equation

$$CR(mdd) = \Delta W/St \quad (1)$$

Where ΔW (mg) is the weight loss, S (cm^2) is the surface area and t (days) is the immersion period. Inhibition efficiencies (IE) were calculated by using the equation

$$IE_g(\%) = \left[\frac{CR_0 - CR_I}{CR_0}\right] \times 100 \quad (2)$$

where CR_O and CR_I are the corrosion rate in the absence and presence of inhibitor respectively.

Electrochemical studies: Electrochemical measurements were carried out in a conventional three-electrode cell consisting of carbon steel working electrode (WE), a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode, using CH electrochemical workstation (Model No: CHI 760D, manufactured by CH Instruments, Austin, USA) at 30ºC. Before starting the experiments, the working electrodes were immersed in the test solution for 30 min before starting the experiment until a steady state potential reached.

EIS measurements were carried out with a frequency range of 100 KHz to 0.1 Hz with AC amplitude of 5 mV at OCP. The impedance data were analyzed using EC-Lab software. From the Nyquist plots, the charge transfer resistance (R_{ct}), constant phase element (CPE) and constant exponent (n) were obtained. The inhibition efficiencies (IE_i) were calculated using the formula

$$IE_i(\%) = \left[\frac{R'_{ct} - R_{ct}}{R'_{ct}}\right] \times 100 \quad (3)$$

where R_{ct} and R'_{ct} are the charge transfer resistance values in the presence and absence of the inhibitor.

The potentiodynamic polarization curves were recorded from cathodic to anodic (OCP ± 200 mV) potential with a scan rate of 1 mV/s. From the Tafel polarization curves, the corrosion current density values (I_{corr}) and corrosion potential (E_{corr}) were obtained. The inhibition efficiencies (IE_p) were calculated from I_{corr} values using the equation,

$$IE_P(\%) = \left[\frac{I_{corr} - I'_{corr}}{I_{corr}}\right] \times 100 \quad (4)$$

where I_{corr} and I'_{corr} are the corrosion current densities in case of uninhibited and inhibited solutions, respectively.

Surface examination studies: The carbon steel specimens were immersed in various test solutions for a period of 7 days. Then, they were taken out and dried. The protective film formed on the carbon steel surface was characterized by FTIR and SEM.

FTIR spectroscopy: FTIR spectra were taken out with a resolution of 4 cm^{-1} over the range of 4000-400 cm^{-1} wave number using a JASCO 460 PLUS Spectrophotometer. The spectra of pure TMA and the surface film formed on the carbon steel surface were done using KBr pellet method.

Scanning electron microscopy: SEM has been used to investigate the surface morphology. The surface features of carbon steel were examined after exposure to solution after 7 days with and without inhibitor. The SEM images of the surfaces of the carbon steel specimens were obtained using VEGA3 model.

Results and Discussion

Gravimetric method: The corrosion rate of carbon steel in control solution in the absence and presence of the inhibitor formulations containing various amounts of TMA and Zn^{2+} ions are given in table-1. Figure-1 shows the variation of inhibition efficiency with concentration of TMA. The CR of carbon steel in control solution was accelerated in the presence of TMA alone. Zinc ions are found to be corrosive. However, a combination of TMA and Zn^{2+} ions exhibited a higher corrosion inhibition capacity. Even at low concentrations of Zn^{2+} ions such as 10, 20 and 50 ppm in combination with TMA at 250 ppm, an inhibition efficiency of 94% was observed. Interestingly, the combination containing Zn^{2+} ions at 50 ppm and TMA at a low level such as 150 ppm gave an inhibition efficiency of 92%. But, with increasing concentration of Zn^{2+} ions from 50 ppm to 75 ppm, keeping TMA constant at 150 ppm, the maximum inhibition efficiency was obtained. The optimum concentration of each components is essential to protecting the carbon steel by forming an insoluble film. All these observations indicate that 150 ppm of TMA is necessary and also adequate to form a protective fim on the carbon steel surface. The decrease in inhibition efficiency at higher concentrations of TMA can be interpreted in terms of the formation of a soluble complex between Fe^{2+} and TMA. The formulation of 150 ppm TMA and 75 ppm Zn^{2+} ions afforded 97% corrosion inhibition efficiency. This is indicative of the strong synergistic effect of TMA and Zn^{2+} ions combination. A thin multicolored film was observed on the surface of the inhibited carbon steel after 7 days of immersion during the gravimetric method.

Effect of pH: The inhibitor system containing TMA (150 ppm) and Zn^{2+} (75 ppm) was selected for further studies at the pH range of 3-11 because of its good inhibiton efficiency. The effect of pH on the corrosion inhibition efficiency of 150 ppm TMA and 75 ppm Zn^{2+} ions is shown in figure-2. It is evident from the results that the corrosion inhibition efficiency of the inhibitor system decreases on increasing pH range from 7-11 and decreasing pH from 5-3. The synergistic inhibitor formulation is effective in the pH range 5-7 only.

Table-1
Values of inhibition efficiencies (%) obtained from TMA-Zn^{2+} system by gravimetric studies

TMA (ppm)	**Zn^{2+} (ppm)**													
	10		**20**		**50**		**75**		**100**		**125**		**150**	
	CR	**IE**	**CR**	**IE**	**CR**	**IE**	**CR**	**IE**	**CR**	**IE**	**CR**	**IE**	**CR**	**IE**
10	8.84	34	7.81	41	8.10	39	8.42	37	6.84	49	9.18	31	9.26	30
25	8.68	35	6.89	48	6.91	48	6.27	53	5.03	62	6.89	48	5.24	61
50	8.53	36	4.99	62	4.70	65	2.91	78	3.13	76	4.99	62	3.55	73
75	8.25	38	3.09	77	2.06	85	1.55	88	1.13	91	2.47	81	1.54	88
100	7.95	40	1.86	86	1.24	91	0.52	96	0.41	97	1.55	88	1.24	91
150	7.81	41	1.44	89	1.03	92	**0.41**	**97**	0.41	97	1.03	92	0.82	94
200	6.79	49	1.64	88	0.83	94	0.41	97	0.31	98	0.71	95	0.72	95
250	8.66	35	1.33	90	0.82	94	0.52	96	0.41	97	0.51	96	0.72	95

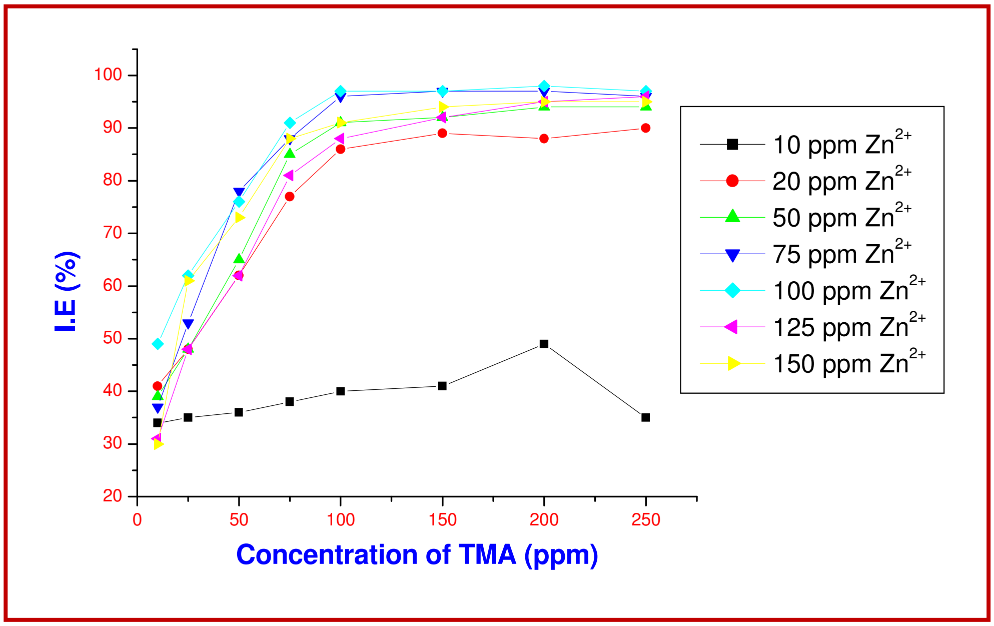

Figure-1
Variation of Inhibition efficiency with concentration of TMA

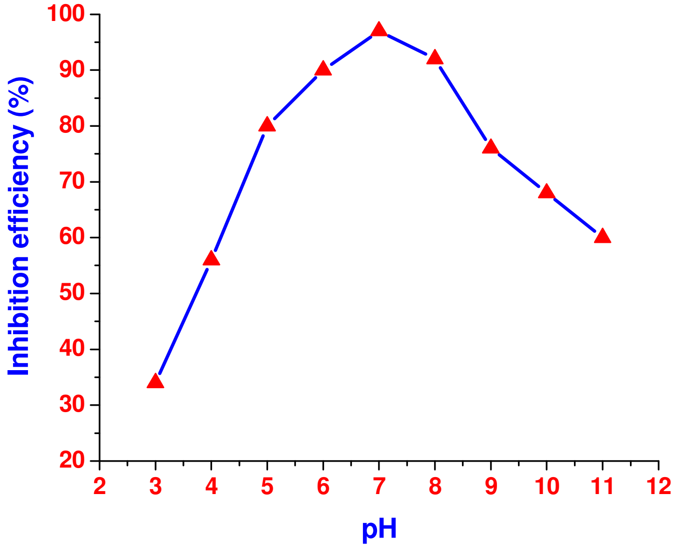

Figure-2
Effect of pH

EIS measurements: EIS is one of the simple and reliable techniques for corrosion measurements. EIS techniques can provide valuable kinetic parameters for electron transfer reactions at the iron/electrolyte interface[12]. The corrosion inhibition of carbon steel in control solution with and without inhibitor was also investigated by EIS measurements. The charge transfer resistance (R_{ct}), constant phase element (CPE) and constant exponent (n) obtained from the Nyquist plots and the calculated inhibition efficiency values (IE_I) are shown in table-2. Figure-3 shows the impedance behaviour of carbon steel corrosion in the form of Nyquist plots. From Nyquist plots in figure-3, it is found that the obtained Nyquist plots are not perfect semicircles due to frequency dispersion and this behaviour can be attributed to roughness and in-homogeneities of the electrode surface[13,14]. When there is non-ideal frequency response, it is common practice to use distributed circuit elements in an equivalent circuit. The most widely employed is the constant phase element (CPE). In general, a CPE is used in a model in place of a capacitor to compensate for inhomogeneity in the system. Therefore, a constant phase element (CPE) is used instead of a capacitive element to get a more accurate fit of experimental data sets using generally more complicated equivalent circuits[15].

The impendence of CPE is defined as

$$Z_{CPE} = Y_o^{-1}(j\omega)^{-n} \qquad (6)$$

Y_o is the modulus, j is the imaginary root; ω is the angular frequency and n is the surface irregularity[16]. Depending on the value of exponent n, Z_{CPE} represents a resistance with $R= Y^{-1}$; for n= -1, an inductance with C=Y[17]. The value range of a real electrode of n is often between 0 and 1. The smaller the value of n, the rougher the electrode surface and the more serious the corrosion of the electrode[18]. The electrical equivalent circuit model shown in figure-4 was used to analyze the obtained impedance data. The model consists of the solution resistance (R_s), the charge-transfer resistance of the interfacial corrosion reaction (R_{ct}) and the constant phase angle element (CPE). Excellent fit with this model was obtained with our experimental data. Such an equivalent circuit was also discussed by several researchers[19,20] who obtained similar depressed semicircles with single time constant.

In the present study, the R_{ct} of the surface film formed in the presence of the synergistic combination containing TMA (150 ppm) and Zn^{2+} ions (75 ppm) has an R_{ct} value of 12854 Ω, which is higher than the values of the surface films obtained in the presence of the individual constitutents, i.e., 1248 Ω for 150 ppm TMA and 790 Ω for 75 ppm Zn^{2+} ions. A larger value of R_{ct} implies the high inhibition efficiency. The corrosion inhibition efficiency of the synergistic combination obtained from impedance studies is 93%, which is in agreement with the efficiency obtained from the gravimetric studies. The CPE value of the metal/solution interface was 582 μFcm^{-2} in the absence of the inhibitor. A decrease in the CPE value (198 μFcm^{-2}) of the metal/solution interface is obtained in the persence of the inhibitor. The high CPE value is due to a large increase in the surface area caused by the presence of corrosion products on the carbon steel surface. Thus for the inhibitor solution a decrease in the CPE value can be explained by a decrease in the quantity of the corrosion products due to increase in the inhibition effect. They also concluded that the protective film consists of carboxylate-metal complexes. This is in concerdance with the synergistic inhibition offered by the combination.

Potentiodynamic polarization studies: The Potentiodynamic polarization curves of carbon steel immersed in aqueous solution in the absence and presence of various inhibitor formulations are given in figure-5. The Tafel parameters, i.e., corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and the inhibition efficiencies (IE_p) are obtained from polarization studies are shown in table-3. An examination of the Tafel slopes revealed that addition of Zn^{2+} ions (75 ppm) alone to the control solution shifted the carhodic Tafel slopes (39 mV/decade) to a larger extent than it did the anodic Tafel solpe (30 mV/decade). Addition of 150 ppm TMA alone to the control solution shifted predominantly the anodic Tafel slpoe (13 mV/decade) in comparison to the cathodic Tafel slpoe (9 mV/decade). The synergistic combination of 150 ppm TMA and 75 ppm Zn^{2+} ions also shifted the carhodic Tafel slopes (78 mV/decade) to a much greater extent when compared to the shifting of the anodic Tafel solpe (68 mV/decade). The corrosion potential (E_{corr}) is shifted to -556.42 mV/SCE and its corrosion current density (I_{corr}) is also reduced when compared to the control. The I_{corr} is significantly decreased from 22.68 $\mu A/cm^2$ to 1.41 $\mu A/cm^2$, corresponding to an inhibition efficiency of 94%. Thus, the synergistic mixture of 150 ppm TMA and 75 ppm Zn^{2+} is proved to be an effective corrosion inhibitor for carbon steel. These results indicate that the binary inhibitor formulation retards both the anodic dissolution of carbon steel and oxygen reduction at cathodic sites in the corrosion inhibition process. It can be inferred from the above results the inhibitor combination of TMA and Zn^{2+} ions acts as a mixed inhibitor. Similar carboxylate-based formulations were reported to be mixed inhibitors[10].

FTIR Studies: The FT-IR spectrum of pure TMA is shown in figure-6a. The C=O stretching frequency of carboxyl group appears at 1700.91 cm^{-1}. The C-S stretching vibration has been assigned to the region 700-600 cm^{-1} (14). The peak that appeared at 611.32 cm^{-1} is assigned to the C-S group and the other peak at 2564.86 cm^{-1} is assigned to the S–H group. The FTIR spectrum of the protective film formed on the carbon steel surface after immersion in control solution containing of TMA (150 ppm) and Zn^{2+} (75 ppm) is shown in figure-6b. The C=O stretching frequency has shifted from 1700.91 cm^{-1} to 1569.77 cm-1. This indicates that the TMA has coordinated with Fe^{2+} on the metal surface through oxygen atom of C=O group resulting in the formation of Fe^{2+}-TMA complex. The peak at 1392.35 cm^{-1} indicates the presence of $Zn(OH)_2$ on the carbon steel surface film[21]. The broad band of the OH stretching and bending modes of water or hydroxides within the protective film appeared at 3180.04 cm^{-1}. There are many weak bands in the region between 1,200 and 400 cm^{-1}. The peak at 464.75 cm^{-1} implies the presence of ferric and ferrous oxide and hydroxide in the protective film[22]. The FTIR spectra suggests that the protective film may consist of $[Fe^{2+}/Zn^{2+}–TMA]$, $Zn(OH)_2$ and small amounts of oxides and hydroxides of iron.

Table-2
Corrosion parameters obtained from potentiodynamic polarization studies for carbon steel immersed in the absence and in the presence of inhibitor

Inhibitior system		Tafel parameters				
TMA (ppm)	Zn^{2+} (ppm)	E_{corr} (mV/SCE)	I_{corr} ($\mu A/cm^2$)	β_a (mV/decade)	β_c (mV/decade)	IE_P (%)
-	-	-487.62	22.68	209	212	-
150	-	-477.23	17.30	196	203	24
-	75	-581.29	43.70	239	251	-
150	75	-556.42	1.41	277	290	94

Table-3
Corrosion parameters of carbon steel immersed in the presence and absence of inhibitor obtained by A.C. impedance spectra

Inhibitor system		R_{ct} (Ω)	CPE ($\mu F/cm^2$)	n	IE_i (%)
TMA (ppm)	Zn^{2+} (ppm)				
0	0	958	582	0.78	-
0	75	790	682	0.84	-
150	0	1248	370	0.92	23
150	75	12854	198	0.96	93

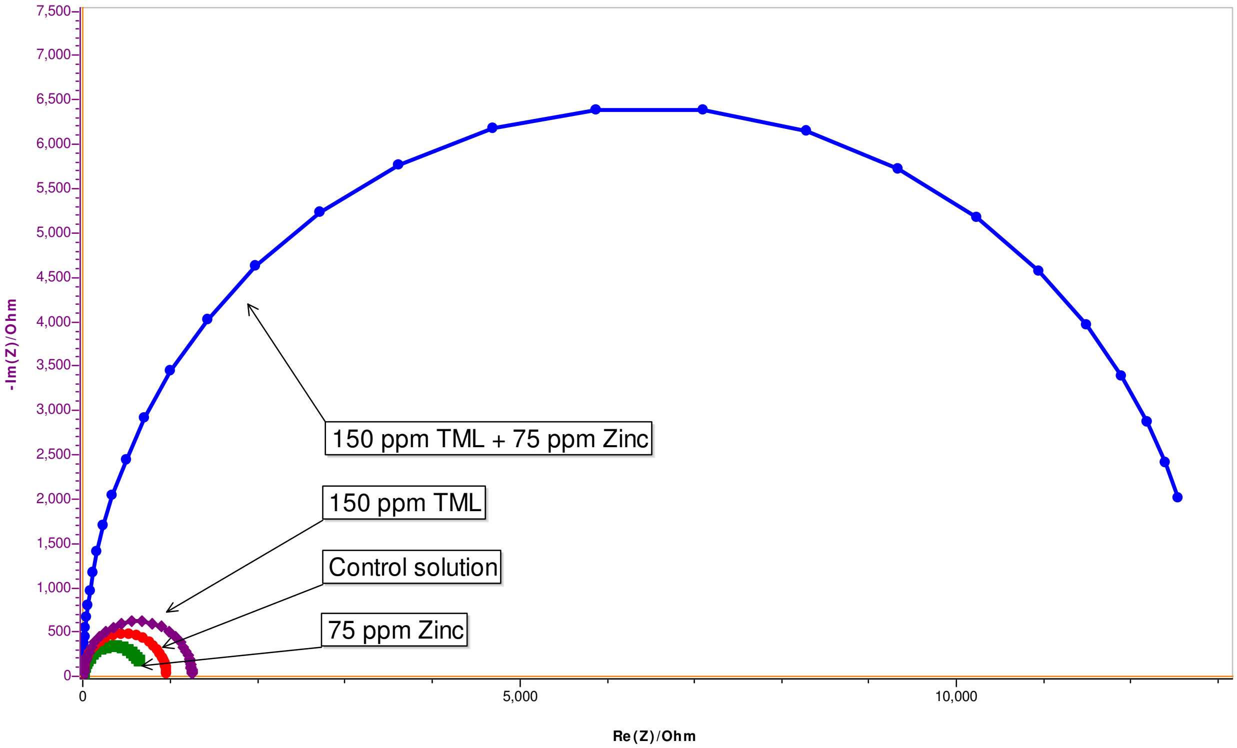

Figure-3
AC impedance spectra of carbon steel immersed in various test solutions

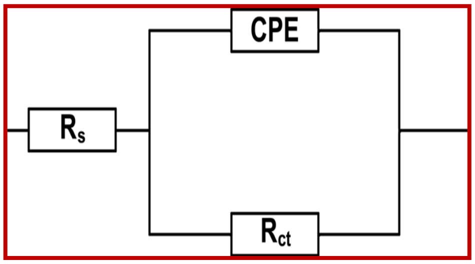

Figure-4
Equivalent electrical circuit fitted by the Nyquist plots

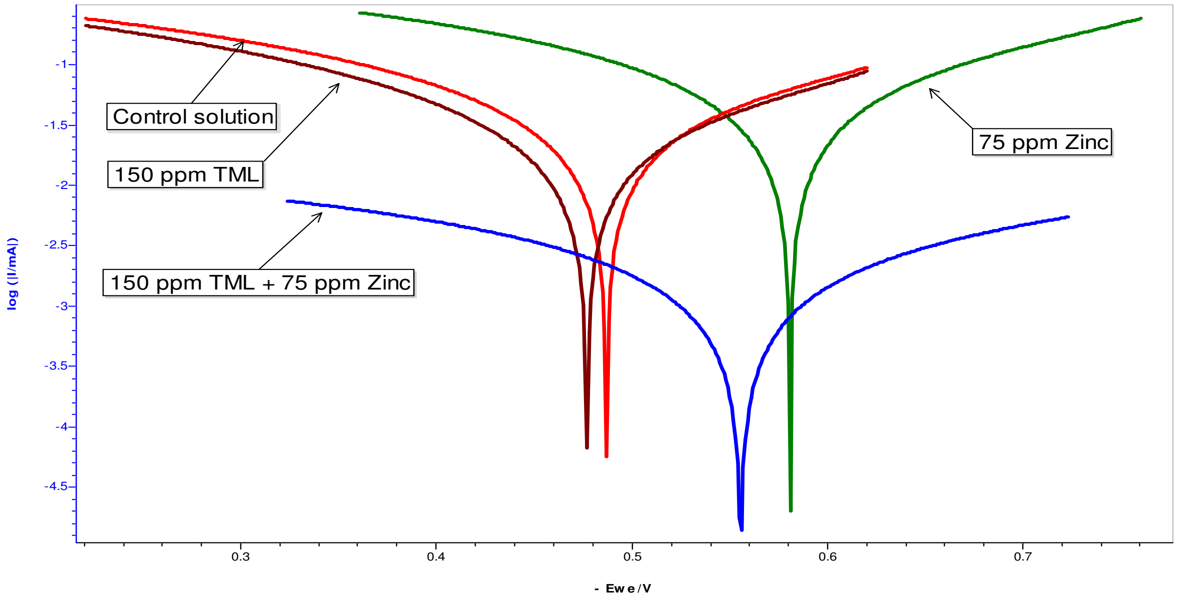

Figure-5
Tafel plots of carbon steel immersed in various test solutions

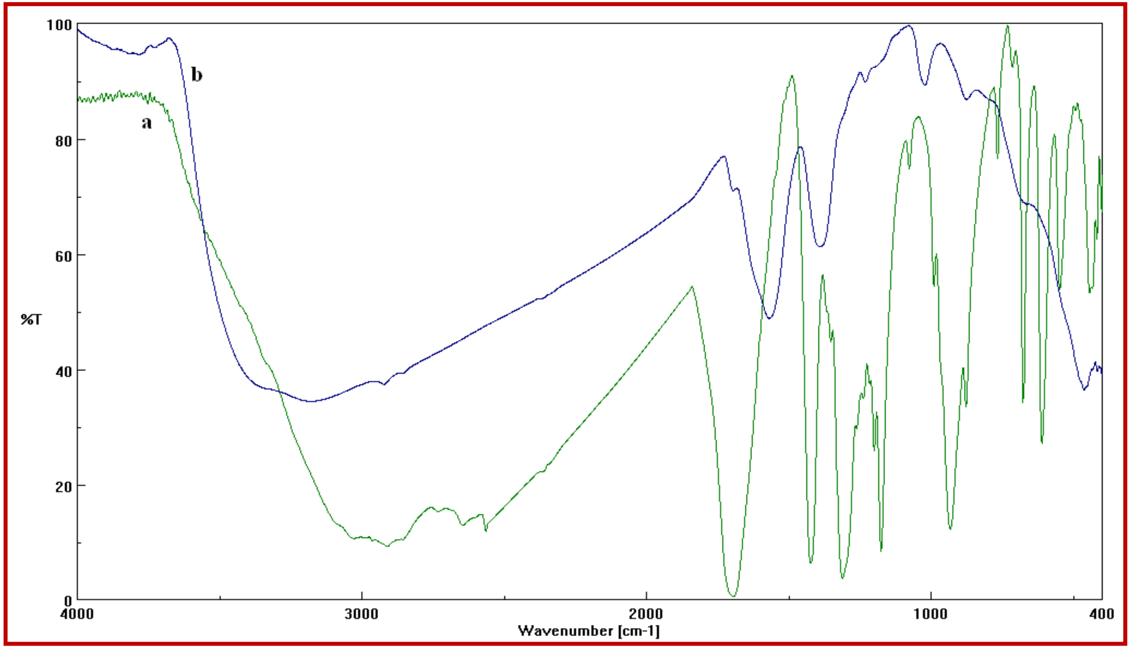

Figure-6
FTIR Spectra for (a) pure TMA (b) Surface film

Scanning electron microscopy: SEM analysis was carried out for characterizing the inhibitive film formed on the carbon steel surface. Figure-7(a, b) presents the micrograph obtained for the carbon steel sample after exposure to the corrosive environment, and figure-7(c, d) reveals the surface on the carbon steel after exposure to the control solution containing the inhibitor, 150 ppm TMA, 75 ppm and Zn^{2+} ions. It can be seen from figure-7(a, b) that in the absence of any inhibitor there is dendrite type of growth of porous and non-protective oxides and hydroxides of iron. Figure-7(c, d) shows SEM photograph of the surface film formed over the carbon steel surface, which suppresses the rate of corrosion[23]. The absence of any dendritic type of growth of iron oxides is clear. This is essentially because of the protective nature of the surface film and formation of insoluble complex on the carbon steel surface[24]. So, SEM analysis shows the protective nature of the surface film[25].

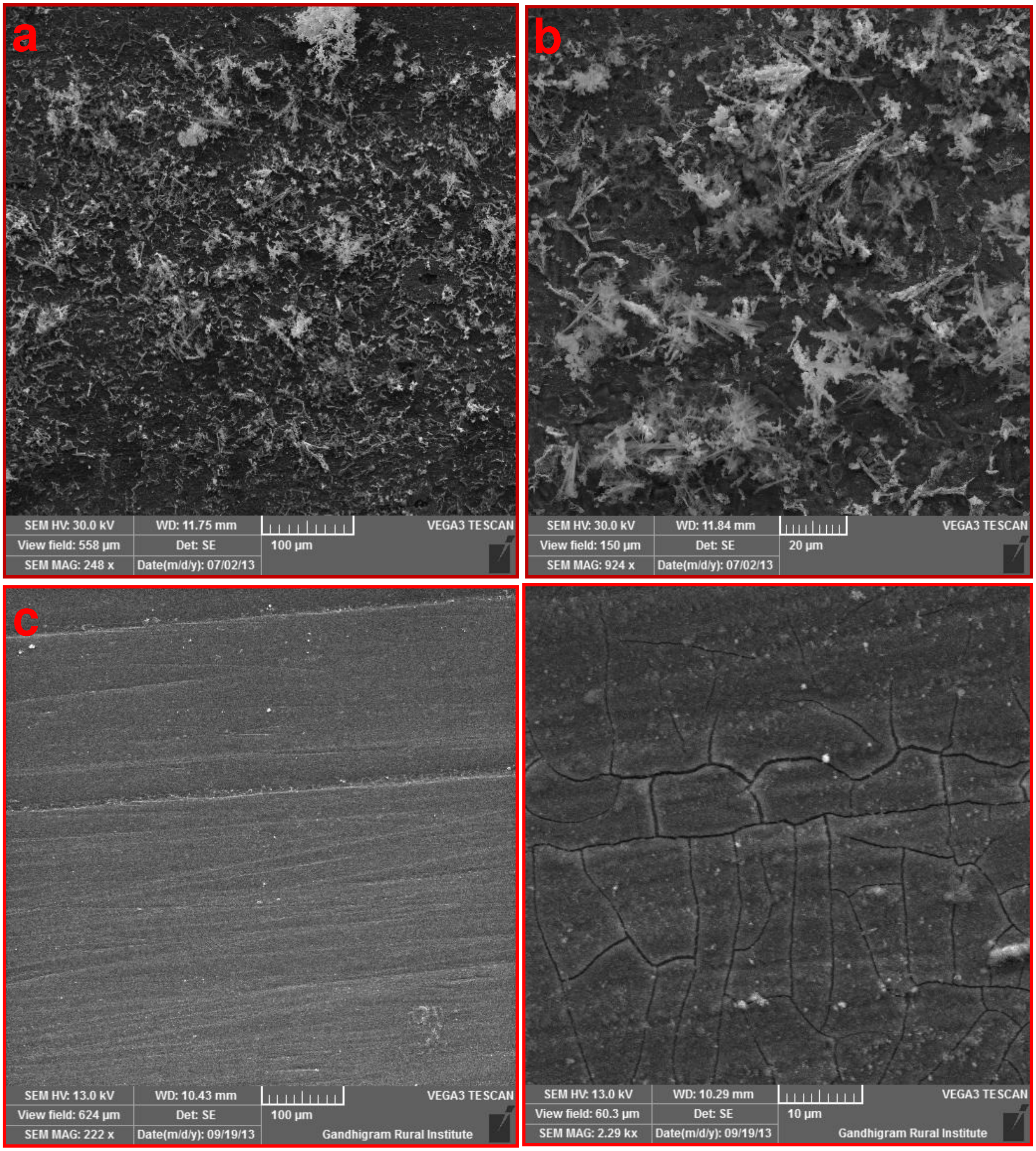

Figure-7

SEM images of (a) and (b) carbon steel immersed in control solution, (c) and (d) carbon steel immersed in TMA-Zn^{2+} ions

Mechanism of protection: In order to explain all the experimental results, the following mechanism of corrosion inhibition can be proposed:

When carbon steel is immersed in neutral aqueous environment the anodic reaction is

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (7)$$

Fe^{2+} further undergoes oxidation in the presence of oxygen available in the aqueous solution

$$Fe^{2+} \xrightarrow{[O_2]} Fe^{3+} + e^- \qquad (8)$$

and the cathodic reaction is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (9)$$

When the environment containing control solution (60 ppm Cl^- ions)/150 ppm TMA/75 ppm Zn^{2+} was prepared, a $[Zn^{2+}$-TMA] complex was formed in the solution. Besides this complex, there is presence of free TMA and Zn^{2+} ions.

When the metal was immersed in this environment, the $[Zn^{2+}$-TMA] complex diffused from the bulk of the solution onto the surface of the metal and further complexes with Fe^{2+}/Fe^{3+} ions available due to initial corrosion.

Free TMA molecule diffuse from bulk of the solution to the metal surface and form $[Fe^{2+}/Fe^{3+}$-TMA] complexes. These complexes fill the pores of the film formed on the surface and make it protective.

Free Zn^{2+} ions diffuse from the bulk of the solution to the metal surface and form $Zn(OH)_2$ at the local cathodic sites.

Thus, the corrosion is controlled by the protective film consisting of $Zn(OH)_2$ and metal-inhibitor complex, viz., $[Fe^{2+}/Fe^{3+}$-TMA].

Formation of $Zn(OH)_2$ controls the cathodic reaction and formation of (metal-inhibitor) complexes controls the anodic reaction. Hence, the inhibition is under mixed control. Similar reports of complex formation have been observed in the literature[11,23,24,26].

Conclusion

The present work shows an excellent inhibitive effect among TMA and Zn^{2+} in corrosion protection of carbon steel. The inhibitor system 150 ppm TMA and 75 ppm Zn^{2+} is effective and has 97% inhibition efficiency. The inhibitor system is effective in the pH range 5 to 7. The inhibitor formulation acts as a mixed inhibitor. EIS study reveal that the presence of a protective film on the carbon steel surface. FTIR spectral data appear to show that the protective film may consists of $[Fe^{3+}/Fe^{2+}/Zn^{2+}$-TMA] complex, $Zn(OH)_2$, hydroxides and oxides of iron. The protective film formation is also confirmed by SEM study. This inhibitor formulation consisting of TMA and Zn^{2+} can be used as a potential inhibitor to prevent the corrosion of carbon steel in aqueous solution.

Acknowledgement

M. Prabakaran is grateful to the UGC for the fellowship under Research Fellowship in Sciences for Meritorious Students. Authors thank the Co-ordinator, UGC-SAP, Gandhigram Rural Institute for his help and also thank the authorities of Gandhigram Rural Institute for the encouragement.

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