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Research Article

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Inhibitive properties of THAM-Zn^{2+} system and its synergism with ST

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ABSTRACT

The synergistic effect of THAM-Zn^{2+} and ST on the inhibition of corrosion of mild steel in aqueous solution containing 60 ppm Cl^- has been evaluated by the weight loss method. The mechanistic aspects of corrosion inhibition have been studied using potentiostatic polarization study, AC impedance spectra. The formulation consisting of 50 ppm of Tris (hrdroxy methyl) amino methane (THAM) and 50 ppm of Zn^{2+} and 250 ppm of sodiumtungstate (ST) has 73% corrosion inhibition efficiency. Synergism parameters have been calculated to evaluate the synergistic effect.

Keywords: Mild steel, Corrosion inhibition, Synergistic effect, THAM, Sodiumtungstate

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INTRODUCTION

Mild steel has many industrial applications because of its easy availability; low cost, uncomplicated fabrication of it into water pipe lines [1, 2], cooling water systems [3], boilers etc., Tungstate is more effective than molybdate in terms of its inhibition efficiency. Both tungstate and molybdate passivate iron only in the presence of air [4]. One of the most important methods in corrosion protection is to use inhibitors [5, 6]. First of all, this true for elements from group Vl b (Chromium, Molybdenum, and Tungsten) in the series, the ionization energy increases and the electron shells of atoms become more compact. However, due to close atomic and ionic radii, the affinity between molybdenum and tungsten is higher than between the indicated elements and chromium [7]. Thus in particular Mo(VI) and W(VI) frequently form polymeric oxyanions of complex structure [8]. The general principles of realization of intramolecular synergism in complex compounds of transition metals with organic ligands in the inner and outer spheres presented in[9-12] are true not only for corrosion but also for the corrosion mechanical fracture of steel. The protective action of MoO_4^{2-} and WO_4^{2-} in distilled water approximately identical and in the presence of corrosive ions. WO_4^{2-} was found to be more effective. So many researches concentrated to use some co-inhibitors [13-19]. Synergistic effect of certain phoshonic acids and Zn^{2+} in corrosion has been reported [20, 21]. Anodic inhibitors such as sodium tungstate are found to be the most effective and readily available but for its low oxidizing potential and high cost [22]. This is due to the fact that tungstate ions alone cannot shift the potential of the metal into the passive region substantially [23, 24]. Co-inhibitive effects have been investigated on molybdate and phosphate in synthetic tap water environments and on potassium permanganate with sodium tungstate for the protection of carbon steel [25, 26]. The present study evaluates the synergistic effect of THAM-Zn^{2+} system estimates the influence of ST on the inhibition efficiency (IE) of THAM-Zn^{2+} system. The mechanistic aspect of corrosion inhibition has been studied by electro chemical method.

EXPERIMENTAL SECTION

Preparations of the mild steel specimens were chosen from the same sheet of the following composition 0.1 percent C, 0.026 percent S, 0.06 percent P, 0.4 percent Mn and the balance Fe. Carbon steel specimen of the dimensions 1.0x4.0x0.2cm were polished to mirror finish, degreased with trichloroethylene and used for mass loss and electro chemical studies. The environment chosen is aqueous solution containing 60 ppm Cl^-

Determination of corrosion rate

The weighed specimen in triplicate were suspended by means of glass hooks in 100ml beakers containing 100ml of an aqueous solution containing 60ppm Cl^- and various concentrations of the inhibitors in the presence and absence of Zn^{2+} for 3 days of immersion. After 3days of immersion the specimens were taken out, washed in running water dried and weighed. From the change in weights of the specimen corrosion rates were calculated using the following relationship.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of immersion (days)}}$$

Corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100[1-W_2 / \ W_1]\ \%$$

Where W_1=corrosion rate in the absence of the inhibitors and W_2=corrosion rate in the presence of the inhibitors

Potentiodymanic polarization

Polarization studies carried out in a CHI electrochemical workstation with impedance, Model 660 A, a three electrode cell assembly was used. The working electrode was one of the three metals. A saturated calomel electrode (SCE 1 was the reference electrode and platinum was the counter electrode from the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and tafel slopes (anodic= b_a and cathodic = b_c) were calculated.

AC impedance measurements

EG and G electrochemical impedance analyser model 6310 was used to record AC impedance measurements. A three electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A rectangular platinum foil was used as the counter electrodes. A time interval of 5 to 10 minutes was given for the system circuit potential. There over this steady state potential an AC potential of 10mV was superimposed. The AC frequency was varied from 100MHz to 100KHz. the real part (Z') and imaginary part (Z'') of the cell impedance were measure in ohm for various frequencies. The R_t (Charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. C_{dl} values were calculated using the following relationship.

$$C_{dl} = \frac{1}{2\times3.14\times f_{max}\times R_t}$$

RESULTS AND DISCUSSION

The inhibition efficiencies (IE) and corrosion rates of Tris (Hydroxyl methyl) Amino methane (THAM) in controlling corrosion of mild steel immersed in an aqueous solution containing 60 ppm Cl^- for a period of three days in the presence and absence of Zn^{2+} by weight loss methods are given in Table (1-3). THAM alone has some IE and Zn^{2+} alone has some IE and Zn^{2+} alone found to corrosive. However the formulation consisting of 50 ppm of THAM and 50 ppm of Zn^{2+}, 250ppm of ST shows 73 percent IE. This suggests that THAM-Zn^{2+}-ST exhibit synergistic behaviour. The anodic reactions are retarded by the formation of Fe^{2+}-THAM and Fe^{2+}-ST complexes. In the presence of Zn^{2+}, the cathodic reaction is also retarded (by the formation of $Zn(OH)_2$ on the sites of the metal surface).

Table 1. Corrosion rates of (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- and the inhibition efficiencies (IE %) obtained by weight loss method. [Immersion period = 3days, pH=8.84]

Cl^- ppm	THAM ppm	Zn^{2+} ppm	CR mdd	IE %
60	0	0	23	-
60	0	50	17.48	24
60	50	50	8.74	62
60	100	50	11.04	52
60	150	50	13.34	42
60	200	50	13.57	41
60	250	50	13.80	40

Table 2. Corrosion rates of (CR mdd) carbon steel immersed in an aqueous solution containing 60ppm of Cl^- and the inhibition efficiencies (IE %) obtained by weight loss method. [Immersion period = 3days, pH=8.84]

Cl^- ppm	ST ppm	Zn^{2+} ppm	CR mdd	IE %
60	0	0	23	-
60	0	50	17.48	24
60	50	50	10.58	54
60	100	50	13.34	42
60	150	50	11.96	48
60	200	50	11.04	52
60	250	50	7.36	68

Table 3. Corrosion rates of (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- and the inhibition efficiencies (IE %) obtained by weight loss method. [Immersion period = 3days, pH=8.84]

Cl^- ppm	ST ppm	Zn^{2+} ppm	THAM ppm	CR mdd	IE %
60	0	0	0	23	-
60	0	50	0	17.48	24
60	0	50	50	8.74	62
60	50	50	50	8.28	64
60	100	50	50	8.74	62
60	150	50	50	13.8	40
60	200	50	50	8.05	65
60	250	50	50	6.21	73

It is observed for table 1-3 that THAM shows some inhibition efficiency.50 ppm of THAM has 52% inhibition efficiency. 50 ppm of Zn^{2+} has 24% IE. When ST is added inhibition efficiency of THAM increases. The increase in IE is more pronounced at 250 ppm of ST. Their combination THAM (50ppm) - Zn^{2+} (50 ppm)-ST (250ppm) has 73% IE. Synergistic effect exist between THAM-Zn^{2+} and ST.

Synergism parameters

Synergism parameters have been calculated to evaluate the synergistic effect existing between two inhibitors [27, 28]. When the value of synergism parameter is greater than 1 synergistic effect exists. Synergistic effect can be calculated using the following equation.

$$\text{Synergism parameters } (S_I) = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}}$$

Where

$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$

θ_1= Surface coverage for substance (ST)

θ_2= Surface coverage for substance (THAM - Zn^{2+})

θ'_{1+2} = Surface coverage for combined substance (THAM - Zn^{2+}-ST)

$$\text{When } \theta = \text{Surface coverage} = \frac{IE\%}{100}$$

Synergism parameter is given in table 4. It is observed that the value of synergism is greater that 1 [29]. This suggest that at synergistic effect exist between THAM and Zn^{2+} (50 ppm) and ST (250 ppm) [30, 31]. When the value of synergism parameters is less than one, it is an indication that the synergistic effect is not significant.

Table 4. Inhibition efficiencies and synergism parameters for 50 ppm of THAM –Zn^{2+}-ST system, when carbon steel immersed in an aqueous solution containing 60 ppm Cl^-
Immersion period: 3 Days

ST ppm	Zn^{2+} ppm	IE(%) of ST system θ_1	IE(%) of THAM 50 ppm -Zn^{2+} 50 ppm system θ_2	IE(%) of THAM - Zn^{2+} -ST system θ'_{1+2}	S_I
50	50	8	62	64	0.19
100	50	12	62	62	0.87
150	50	20	62	40	0.50
200	50	26	62	65	0.80
250	50	30	62	73	1.08

Analysis of potentio dynamic polarization curves

Polarization study has been used to study the formation of protective film on the metal surface.The potentio dynamic polarization curves of carbon steel immersed in an aqueous solution containing 60 ppm Cl^- in the absence and presence of inhibitors are shown Fig 1.

The corrosion parameters namely corrosion potential (E_{corr}) Tafel slopes, b_c and b_a, linear polarization resistance (LPR) and corrosion parameters (I_{corr}) are given in table 5. It is observed that when carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- .The corrosion potential is -578mV Vs SCE (Saturated calomel electrode). The LPR value is 1.46×10^3 ohm cm^2. The corrosion parameters value is 4.293×10^{-5} A/cm^2

When 50 ppm of THAM, 50 ppm of Zn^{2+} and 250 ppm of ST are added to the above environment, the corrosion potential is shifted to the anodic side (-531 mV Vs SCE). This indicates that the corrosion potential is shifted to the noble side to the formation of protective film formed on the metal surface. There is not much change in the value of cathodic tafel slopes (221 and 211 mV/decade).but there is slight change in the anodic tafel slope (415 and 381 mV/decades). This indicates that anodic reaction is controlled predominantly. The LPR value increases and the corrosion current value decreases. Theses observations suggest the formation if a protective film on the metal.

Table 5. Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- obtained from potentio dynamic polarization study

System	E_{corr} mV Vs SCE	b_a mV/decade	b_c mV/decade	LPR ohm cm^2	I_{Corr} A/cm^2
Aqueous solution containing 60 ppm Cl^-	-578	415	221	1.46×10^3	4.29×10^{-5}
Aqueous solution containing 60 ppm Cl^- + THAM (50 ppm) + Zn^{2+}+ST (250 ppm)	-531	381	211	1.76×10^3	3.361×10^{-5}

Analysis of the results of AC impedance spectra

The AC impedance spectra of carbon steel immersed in various solutions were recorded (Fig2). The AC impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in table 6. When carbon steel immersed in an aqueous solution containing 60ppm Cl^- , The R_t value is 428 ohm cm^2. The C_{dl} value is 1.19×10^{-8} F/cm^2. The impedance value [log (Z/ohm)] is 2.683

When inhibitors (50 ppm of THAM + 50 ppm of Zn^{2+}+ 250 ppm ST) are added the R_t value increases from 428 to 760 ohm cm^2. The C_{dl} value decreases from 1.19×10^{-8} to 0.67×10^{-8} F/cm^2. The impedance value increases from 2.683 to 2.962. This observation suggests that a protective film is formed on the metal surface.

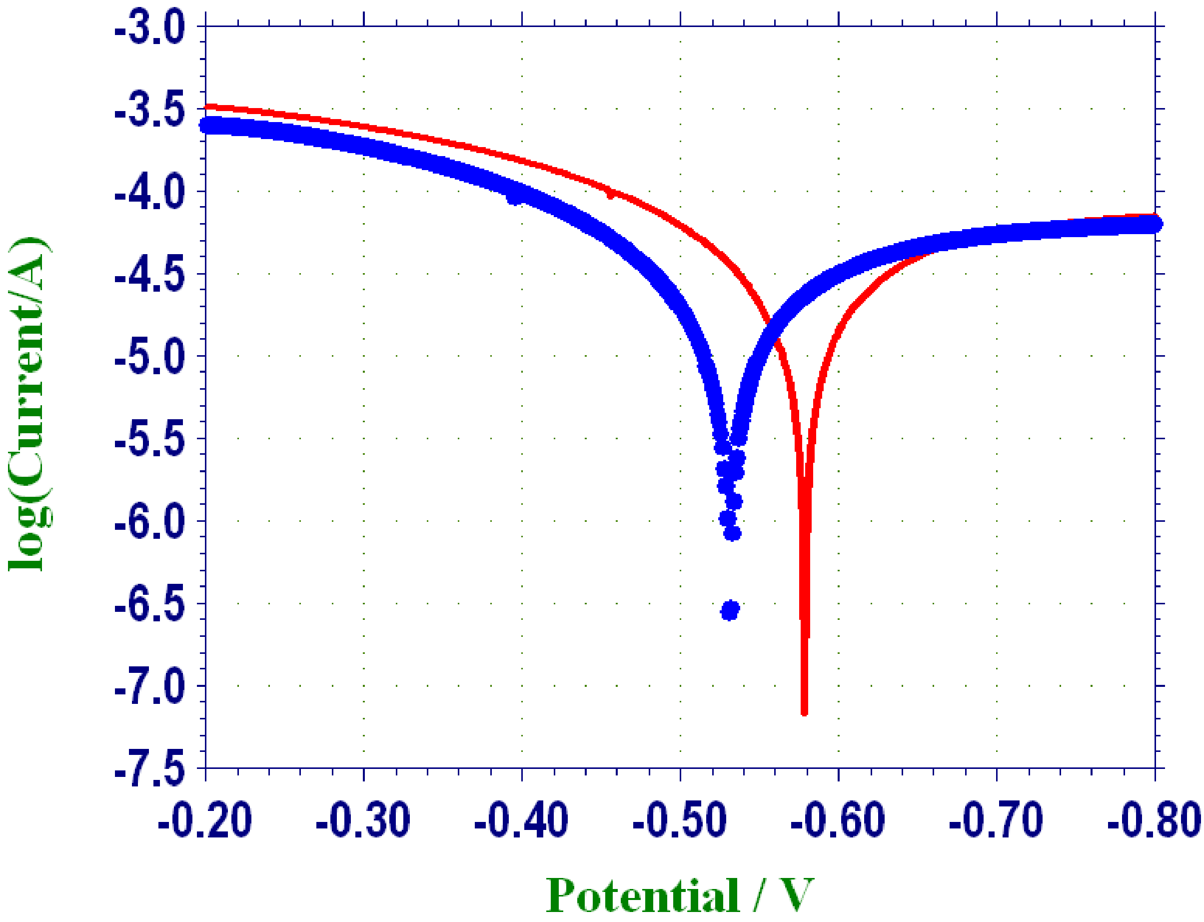


Fig.1. Polarization curves of carbon steel immersed in various test solutions
a) 60 ppm Cl^-(Blank) b) 60 ppm Cl^- + THAM (50 ppm) + Zn^{2+}(50 ppm) + ST (250 ppm)

Table 6. Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- obtained from AC impedance spectra.

System	R_t Ohm cm^2	C_{dl} F/cm^2	Impedance [log(Z/ohm)]
Aqueous solution containing 60 ppm Cl^-	428	1.19×10^{-8}	2.683
Aqueous solution containing 60 ppm Cl^- +THAM (50 ppm) + Zn^{2+}(50 ppm) +ST (250 ppm)	760.4	0.67×10^{-8}	2.962

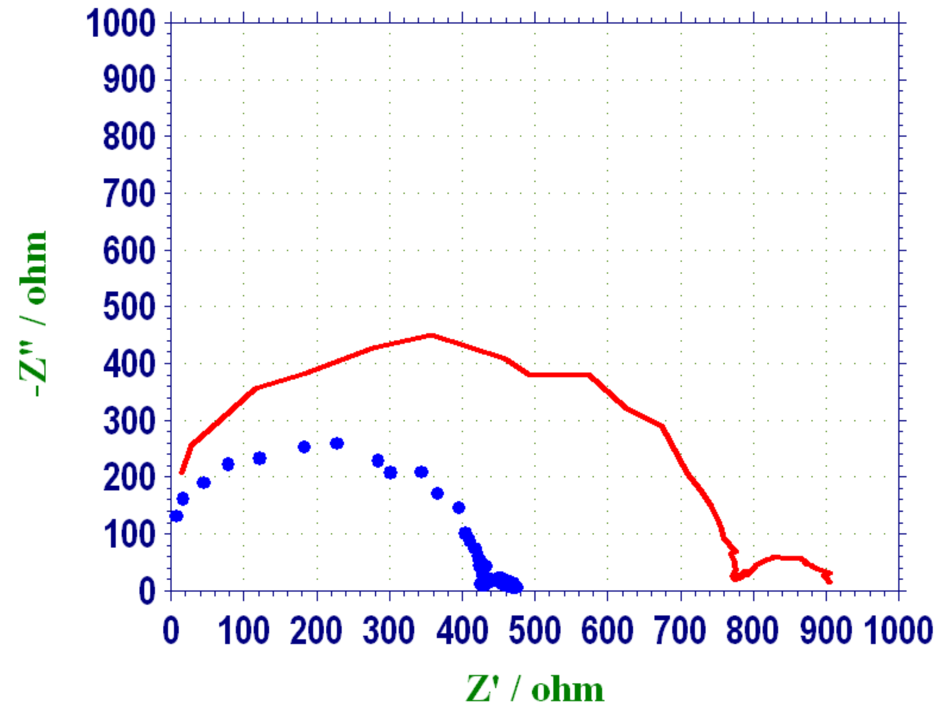
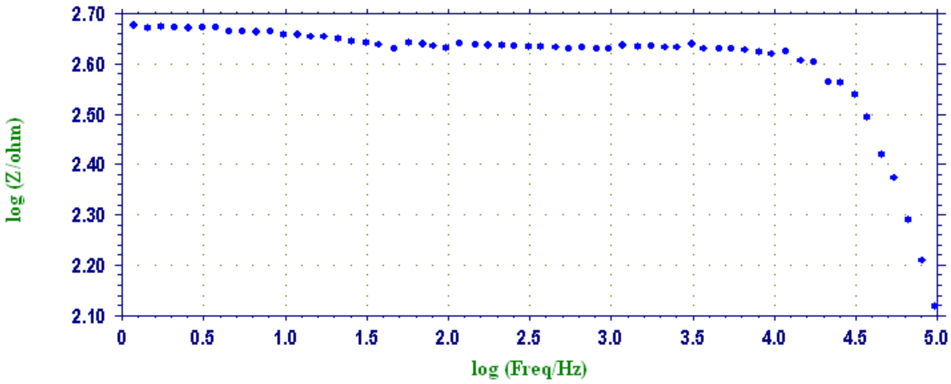


Fig.2. AC impedance spectra of carbon steel immersed in various test solutions (Nquist Plot)
a) 60 ppm Cl^- (Blank) b) 60 ppm Cl^- + THAM (50 ppm) + Zn^{2+} (50 ppm) + ST (250 ppm)



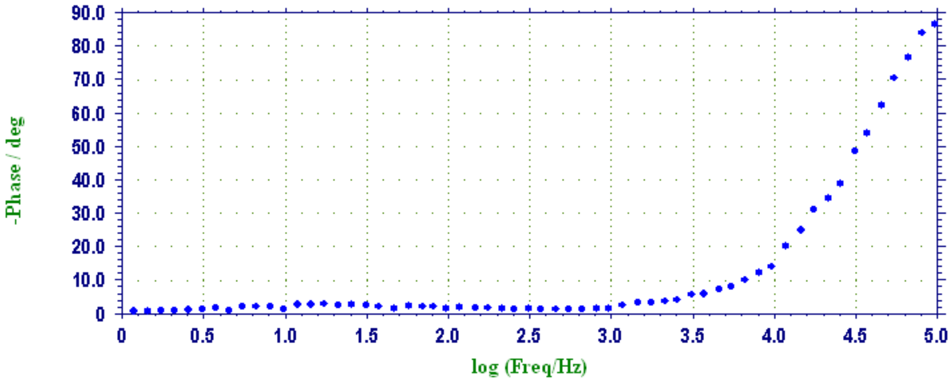


Fig.3a. AC impedance spectra of carbon steel immersed in various test solutions (Bode Plot)
a) 60 ppm Cl^- (Blank)

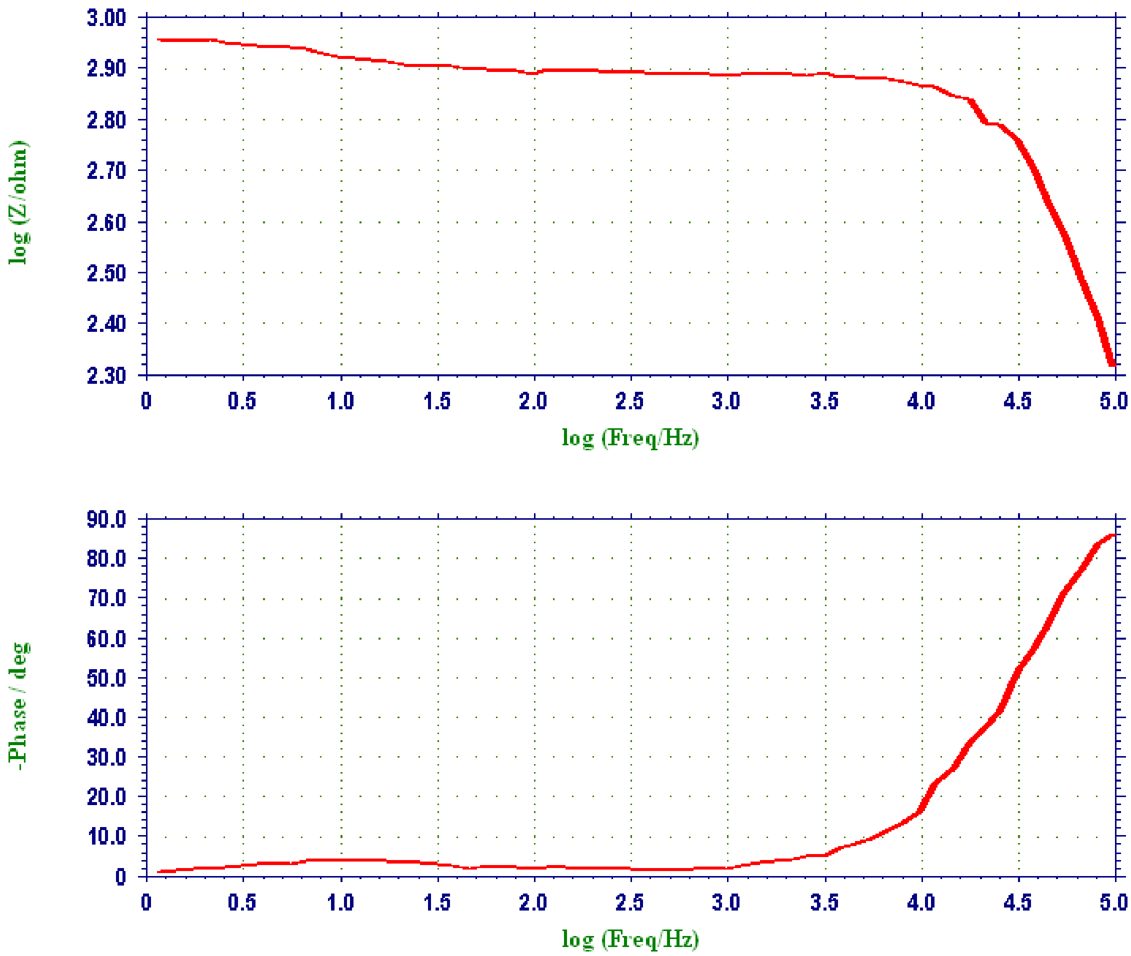


Fig.3b. AC impedance spectra of carbon steel immersed in various test solutions (Bode Plot)
a) 60 ppm Cl^- + THAM (50 ppm) + Zn^{2+} (50 ppm) + ST (250 ppm)

CONCLUSION

The results of the weight loss study shows that the formulation consisting of 50 ppm THAM and 50 ppm of Zn^{2+}, 250 ppm of ST has 73%. A synergistic effect exists between Zn^{2+} and THAM and ST. Polarization study reveals that this formulation function as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface.

- When the solution 60 ppm Cl^- 50 ppm Zn^{2+} and 50 ppm of THAM and 250 ppm of ST is prepared there is formulation of Zn^{2+}-THAM –Zn^{2+}-ST complex in solution.
- When carbon steel is immersed in this solution, the Zn^{2+}-THAM, Zn^{2+}-ST Complex diffuses from the bulk of the solution towards metal surface.
- On the metal surface Zn^{2+}-THAM, Zn^{2+}-ST complex is converted in to Fe^{2+}-THAM, Fe^{2+}-ST on the anodic sites. Zn^{2+} is released.

$$Zn^{2+}\text{-THAM, } Zn^{2+}\text{-ST} + Fe^{2+} \rightarrow Fe^{2+}\text{-THAM, } Fe^{2+}\text{-ST} + Zn^{2+}$$

- The releases Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites.

$$Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2\downarrow$$

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