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Synergistic Effect of Triisopropanolamine in Aqueous Solution by Sodium St–Zn^{2+} System

Brightson Arul Jacob Y.[1,*], Sayee Kannan R.[2] and Jeyasundari J.[1]
[1]Department of Chemistry, NMSSVN College, Madurai-625019, Tamilnadu, INDIA
[2]Department of Chemistry, Thiagarajar College, Madurai-625009, Tamilnadu, INDIA

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Abstract

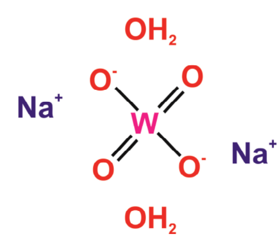
The aim of this present work is to study the corrosion behavior of mild steel in aqueous solution containing 60ppm Cl^- in the presence of TIPA (Triisopropanolamine)-Zn^{2+}-ST (Sodium Tungstate). Weight loss study has been employed to evaluate the inhibition efficiency of this system. It was found that the inhibition efficiency of TIPA-Zn^{2+} was improved from 63% to 97% by the addition of 150 ppm of ST. The corrosion rate was calculated in the presence and absence of inhibitor. The protective film consists of Fe^{2+}-Wo_4^{2-}, Fe^{2+} - TIPA complex on anodic site and Zn $(OH)_2$ complex at cathodic site. A mechanism for the inhibition of corrosion is proposed based on the above results. TIPA and Sodium tungstate (Na_2WO_4) as a corrosion inhibitors of mild steel in aqueous solution containing 60 ppm Cl^- was investigated by potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). The surface of the specimen has been examined using, scanning electron microscope

Keywords: Mild steel, corrosion inhibition, impedance spectra, scanning electron microscope.

Introduction

The principles and practice of corrosion inhibition in recent years have begun taking into account health and safety considerations. The use of hazardous chemicals has been restricted with no contact with the environment. Hence, there is a search for non-toxic, eco-friendly corrosion inhibitors. Several inhibitors have been used for cooling water systems. When studying inhibiting phenomena, the investigators have discovered that some oxyanions can be used as corrosion inhibitors because, through their functional groups, they form complexes with metal ions and on the metal surfaces. These complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents present in the solution[1].

The inhibitor protection with inorganic compounds in neutral media is most often based on the principle of formation of passive films of oxide or salt types. These films decrease the rate of transfer of oxygen to the metal surface[2]. The good chemical stability and solubility in water make possible their use in oil production, in the formulation of detergents, and in the inhibition of corrosion and scale formation[3]. Amines that are reported as good organic inhibitor for aqueous acid solution have been used as inhibitor in this chemical[4]. Oxyanions, such as tungstate[5,6], molybdate[7,8], and chromates have been used as corrosion inhibitors. Tungstate is more effective than molybdate in terms of its inhibition efficiency. Both tungstate and molybdate passivate iron only in the presence of air[6]. The protective action of MoO_4^{2-} and WO_4^{2-} in distilled water and in the presence of corrosive ions is approximately identical. MoO_4^{2-} was found to be more effective[7]. Tungstate proved to be an effective corrosion inhibitor for Al[9-11] and with zinc[12] in neutral, acidic, and basic solutions. Protection of corrosion of carbon steel by inhibitors in chloride containing solutions has been reported[13]. Tungstate and Molybdate were found to be effective inhibitors for cold rolling steel in hydrochloric acid solution[14]. In spite of the advantage of combining zinc salts with certain inhibitors, they have been found to adversely affect the water released during the cooling process. Therefore, the permissible limit of zinc in water/wastewater has been restricted to a maximum value of 2 mg/l[15]. Molecular structure of sodium tungstate is shown in scheme 1.



Scheme-1
Sodium tungstate

The present study evaluates the synergistic effect of TIPA-Zn^{2+} system estimates the influence of ST on the IE of TIPA-Zn^{2+} system studies mechanistic aspects of corrosion inhibition by electro chemical studies.

Material and Methods

Preparation of the specimen: In our experiments, mild steel samples having composition of C, 0.1 %; Mn, 0.4%; P, 0.06; S, 0.026 were used. For weight loss experiments, coupons were cut in the form 1.0cm x 4.0cm x 0.2cm. The surface of the specimen was polished using successive grades of emery paper, from 1/0 to 4/0, washed with soap solution and then by running tap water followed by double distilled water, finally degreased with acetone, dried in air and kept in a desiccator. Later, the samples were weighed and immersed in 300 mL of test solution in a glass beaker for a fixed interval of time. The samples were kept in the beaker in such a way that both the surfaces were in contact with the solution.

Weight loss method: Mild steel specimens were immersed in aqueous solution containing 60 ppm Cl^- and concentrations of the inhibitor (TIPA, ST) in the absence and presence of Zn^{2+}. The weights of the specimens before and after immersion were determined using a Digital Balance (Model A x 62 SHIMADZU). The corrosion products were cleaned with Clark's Solution.

The corrosion IE was been calculated using the equation.
$IE = 100[1- W_2 / W_1]$ %

Where, W_1 is the weight loss value in the absence of inhibitor and W_2 is the weight loss value in the presence of the inhibitor.

Electrochemical Tests: Electrochemical tests to investigate the effect of TIPA in aqueous solution by ST–Zn^{2+} system on the corrosion behavior of mild steel electrochemical tests of potentiodynamic polarization measurements were carried out. The tests were carried out in aqueous solution containing 60 ppm Cl^- at room temperature.

Potentiodynamic polarization Study: The potentiodynamic polarization measurements were conducted on EG and G potentiostat/galvanostat Model 263A. The experiments were carried out using a corrosion cell, with Ag/AgCl electrodes (saturated KCl) as reference and Pt as counter electrode. The potentiodynamic polarization measurements were carried out using a scan rate of 0.166mV commencing at a potential above 250mV more active than stable open circuit potential. However, before starting the scanning at each concentration, the specimen was stabilized for about 30mts for attaining a steady state which was shown by a stable potential.

The real part (Z') and imaginary part (Z") of the cell impedance were measured in Ohms for 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.

$$C_{dl} = \frac{1}{2\pi R_t f_{max}}$$

SEM Analysis: SEM provides a pictorial representation in the surface to understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of carbon steel. The surface morphology of the samples after performing the weight loss experiments was observed carefully and analyzed by a JEOL JSM-840A scanning electron microscope at an operating voltage of 10 kV.

Results and Discussion

Weight- loss study: Corrosion inhibition of the binary inhibitor system TIPA- Zn^{2+}- ST is shown in table 1 to 3. TIPA alone has some inhibition efficiency of 46%. 100ppm of TIPA and 50 ppm of Zn^{2+} shows 63% inhibition efficiency. After the addition of sodium tungstate (150 ppm) the inhibition efficiency increases from 63% to 97%. Interestingly, addition of 150 ppm of ST to this binary inhibitors system increases the IE from 63% to 77%. The improvement in the protection efficiency is attributed to a synergistic effect with results from the combination of the binary inhibitors. As a result of this complex formation, the inhibitor molecules are readily transported from the bulk to the metal surface.

Table- 1
Corrosion rates of (CR mdd) mild steel immersed in an aqueous solution containing 60 ppm of Cl^- and the inhibition efficiencies obtained by weight loss method

Cl^- ppm	TIPA ppm	IE %	CR mdd
60	50	28	8.12
60	100	47	13.34
60	150	31	8.99
60	200	31	8.99
60	250	25	7.25

Table-2
Corrosion rates (CR mdd) mild steel immersed in an aqueous solution containing 60 ppm Cl^- and the inhibition efficiencies (IE%) obtained by weight loss method

Cl^- ppm	TIPA ppm	Zn^{2+} ppm	IE %	CR mdd
60	0	0	-	29
60	0	50	23	6.67
60	50	50	18	5.04
60	100	5	63	18.13
60	150	50	38	10.8
60	200	50	34	10
60	250	50	18	5.22

Table-3
Corrosion rates (CR mdd) mild steel immersed in an aqueous solution containing 60 ppm Cl^- and the inhibition efficiencies obtained by weight loss method

Cl^- ppm	TIPA ppm	Zn^{2+} ppm	ST ppm	IE %	CR mdd
60	100	50	50	90.62	2.72
60	100	50	100	87.5	3.63
60	100	50	150	96.87	0.91
60	100	50	200	93.75	1.81
60	100	50	250	81.25	5.45

Potentio dynamic Polarization study: The Polarization curves of carbon steel immersed in an aqueous solution containing 60 ppm Cl^- are shown in figure-1.

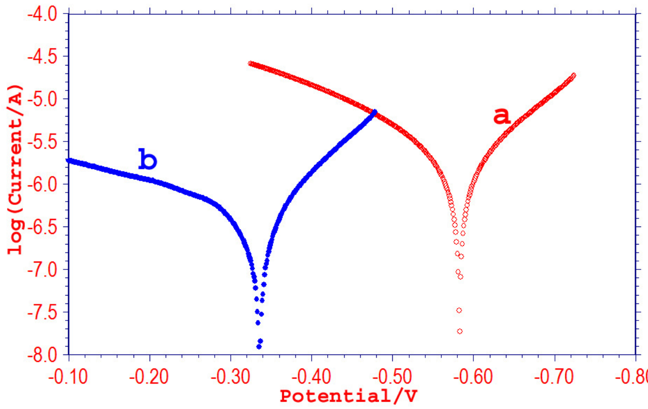


Figure-1
Polarization curves of mild steel immersed in various test solutions a) 60 ppm Cl^- (Blank) b) TIPA (100 ppm) + Zn^{2+} (50 ppm)+ ST (150 ppm)

The corrosion parameters namely, corrosion potential (E_{corr}) anodic tafel slope (b_a), cathodic tafel slope (b_c) linear. Polarization resistance (LPR) and corrosion current (I_{corr}) are give in table 3. When carbon steel is immersed in 60 ppm Cl^-, the corrosion potential is -583 mv Vs SCE. When the addition of inhibitions 100 ppm of TIPA, 50 ppm of Zn^{2+} and 250 ppm of ST, the corrosion potential in -336 mV Vs SCE. The LPR increases from 1.693 x 10^4 to 7.8 x 10^4 ohm cm^2 and corrosion current decreases from 1.873 x 10^{-6} A/cm^2 to 4.47 x 10^{-7} A/cm^2. These observations indicate that when carbon steel surface is protective film formed on the metal surface. The corrosion current for the formulation of TIPA-Zn^{2+}-ST has decreased to 8.90x10^{-10} A/cm^2.

AC impedance spectroscopy: The AC impedance spectra of mild steel immersed in aqueous solutions containing 60 ppm Cl^- in the absence and presence of inhibitors are shown in figure 2 (Nyquist plots) and figure 3 (Bode plots). The AC impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance C_{dl} and log Z/ohm are calculated. The impedance values derived from Bode plots are also given in table 5. It is observed that when carbon steel immersed in aqueous solution containing 60 ppm Cl^- the R_t value is 1834 ohm cm^2. The C_{dl} value is 5.07 x 10^{-7} F/cm^2. The impedance value (log Z/ohm) is 3.411. When inhibitors (100 ppm TIPA + 50 ppm Zn^{2+} + 150 ppm ST) added the R_t values increases from 1834 to 2556 ohm cm^2. The C_{dl} value decreases from 5.07 x 10^{-7} to 8.90 x 10^{-10} F/cm^2. The impedance value increases from 3.4110 to 3.4820. These observations suggest that a protective film formed on the metal surface[16-18].

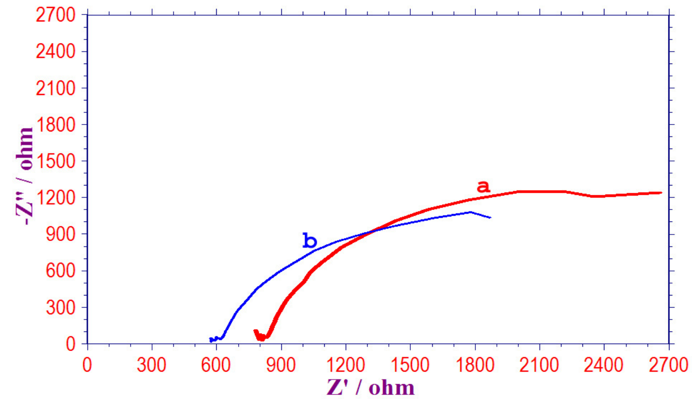


Figure-2
AC impedance spectra of mild steel immersed in various test solutions (Nyquist Plot) a) 60 ppm Cl^- (Blank) b) TIPA (100 ppm) + Zn^{2+} (50 ppm) + ST (150 ppm)

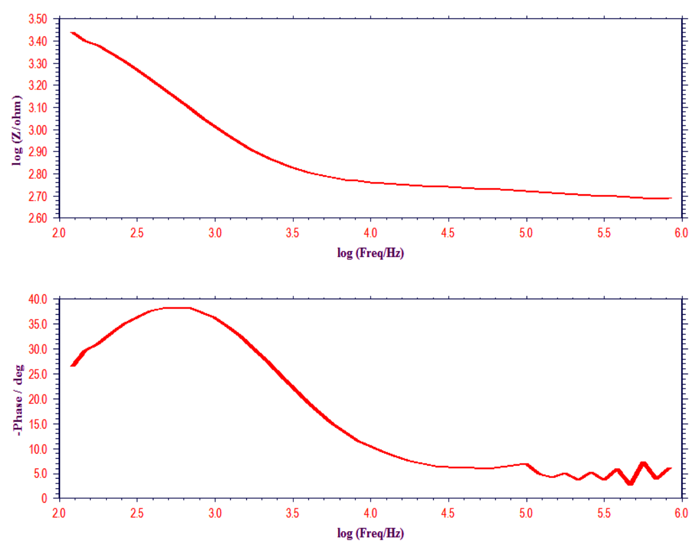


Figure-3
AC impedance spectra of mild steel immersed in various test solutions (Bode Plot) a) 60 ppm Cl^-(Blank)

Table-4
Corrosion parameters of mild steel immersed in an aqueous solution containing 60 ppm of Cl^- obtained from potentiodynamic 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^-	-583	170	127	1.693 x 10^4	1.873 x 10^{-6}
Aqueous solution containing 60 ppm Cl^- +TIPA (100 ppm) + Zn^{2+} (50 ppm) + ST (150 ppm)	-336	290	112	7.80 x 10^4	4.47 x 10^{-7}

Table-5
Corrosion parameters of mild steel immersed in aqueous solution containing 60 ppm Cl^- obtained by AC impedance spectra

System	R_t Ω cm^2	C_{dl} F/cm^2	Impedance [log(Z/ohm)]
Aqueous solution containing 60 ppm Cl^-	1834	5.07×10^{-7}	3.4110
Aqueous solution containing 60 ppm Cl^- +TIPA (100 ppm) + Zn^{2+} (50 ppm) + ST (150 ppm)	2556	8.90×10^{-10}	3.4820

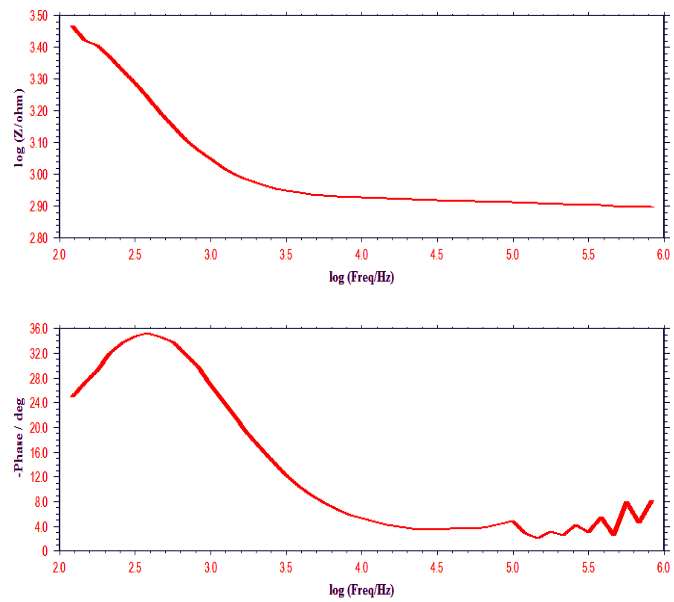


Figure-4
AC impedance spectra of carbon steel immersed in various test solutions (Bode Plot) a) 60 ppm Cl^- + TIPA (100 ppm) + Zn^{2+} (50 ppm) + ST (150 ppm)

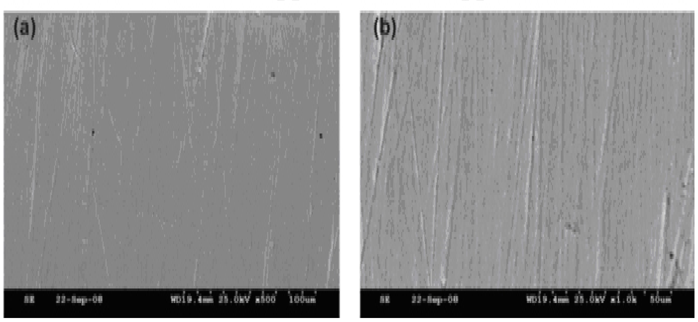


Figure-5.1
SEM micrographs of a) Mild steel (Control); Magnification-X 500 b) Mild Steel (Control); Magnification-X 1000

SEM analysis of metal surface: The SEM images of different magnification (X500, X1000) of mild steel specimen immersed in aqueous solution contain 60 ppm of Cl^- for 1 day in the absence and presence of inhibitor system are shown in figure 5.1(a,b) respectively.

The SEM micrographs of mild steel surface was immersed in an aqueous solution containing 60 ppm Cl^-. Figure 5.2(c,d) shown the roughness of the metal surface. figure 5.2(e,f) indicates that in the presence of 100 ppm TIPA + 50 ppm Zn^{2+} + 150 ppm ST in an aqueous solution containing 60 ppm Cl^- , the surface coverage increased with in turn results in the formation of insoluble complex on the surface of the metal. In the presence of TIPA, Zn^{2+} and ST system, the surface is covered by a thin layer of inhibitor which effectively control the dissolution of mild steel[19-22].

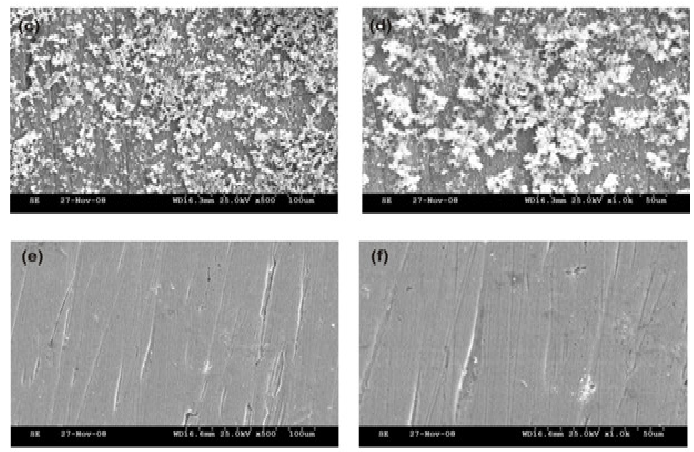


Figure-5.2
SEM micrographs of a) 60 ppm Cl^- Magnification-X 500 b) 60 ppm Cl^- Magnification-X 1000, c) 60 ppm Cl^- + TIPA (100 ppm) + Zn^{2+} (50 ppm) + ST (150 ppm) Magnification –X500, d) 60 ppm Cl^- + TIPA (100 ppm) + Zn^{2+} (50 ppm) + ST (150 ppm) Magnification –X1000

Conclusion

The results of the weight loss study shows that the formulation consisting of 100 ppm TIPA, 50 ppm of Zn^{2+} and 150 ppm ST has 96.87% IE i. A synergistic effect exists between Zn^{2+} and TIPA and ST system. ii. Ac impedance spectra reveal that the protective film formed on the metal surface. iii. When the solution containing 60 ppm of Cl^-, 50 ppm of Zn^{2+} and 100 ppm of TIPA and 150 ppm of ST, there is a formulation of Zn^{2+}-TIPA complex and Zn^{2+} -ST complex in solution. iv. When mild steel is immersed in this solution, the Zn^{2+}-TIPA, Zn^{2+}-ST complex diffuses from the bulk of the solution towards metal surface. v. On the metal surface Zn^{2+}-TIPA-ST complex is converted in to Fe^{2+}-TIPA, Fe^{2+}-ST complex on the anodic sites. Zn^{2+} is released. vi. Zn^{2+}-TIPA, Zn^{2+}-ST+$Fe^{2+}$$\rightarrow$ Fe^{2+}-ST, Fe^{2+}-TIPA+$Zn^{2+,}$ vii. The released Zn^{2+} combines with OH^- to form Zn $(OH)_2$ on the cathodic sites. viii. Zn^{2+} + $2OH^-$ $\rightarrow$ $Zn(OH)_2$.

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