Investigation of Corrosion Inhibition of Stainless steel by Sodium tungstate

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Abstract

The corrosion inhibition of sodium tungstate (ST) in controlling corrosion of stainless steel 410 in sea water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consists of 250 ppm of ST and 50 ppm of Zn^{2+} has 98% IE. AC impedance spectra reveals that the formation of protective film on the metal surface. The nature of the protective film has been characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Keywords: sodium tungstate, sea water, SEM, AFM

Introduction

Corrosion can be defined as the destruction of metals and alloys by electrochemical reaction with its surroundings. The corrosion occurs because of the normal trend of metals to come back to their thermodynamically stable native state. It cannot be avoided, but it can be controlled and prevented by using suitable protective procedures like cathodic protection, anodic protection, coating, alloying and using inhibitors, etc. Of these the application of inhibitors reduces the aggressiveness of the corrosive and unsafe aqueous surroundings and preventing the metal and alloy from corrosion by forming a protective layer over the metal surface. Especially inhibitors find applications in cooling water system, shipboard condensers, nuclear power plant condensers and heat exchangers, etc[1,2]. The corrosion behaviour of stainless steel and other metals in sea water has been studied by many researchers[3-5]. The corrosion inhibition of various metals in different aqueous surrounding using sodium tungstate has been studied[6-8]. The objective of the present investigation is to study corrosion inhibition of stainless steel 410 in sea water in the presence and absence of ST and Zn^{2+} combination. The physicochemical parameters of sea water are given in table 1 and which is collected from Bay of Bengal at Cuddalore Port, Cuddalore, Tamil Nadu, India. The corrosion inhibition was calculated using AC impedance spectra. The protective film formed on the metal surface has been characterized using surface morphological studies such as scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Material and Methods

Preparation of specimens: Stainless steel 410 specimens (0.095 % C, 0.001 % P, 6.03.4 % Mn, 0.340 % Si, 0.001 % P, 13 % Cr, 0.710 % Ni and the rest Fe) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Table -1
Physicochemical Parameters of Sea water

Parameter	Value
Total Dissolved Solid	36441 ppm
Electrical conductivity	53590 micro-mho/cm
pH	6.91
Total Hardness (CaCO$_3$ equivalent)	84 ppm
Mg	11 ppm
Na	8900 ppm
Chlorides	16900 ppm
Sulphate	4239 ppm

Weight-loss method: Stain stainless steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for seven days at $25 \pm 0.1^{o}C$. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution[9]. The IE was then calculated using the equation (1).

$$IE = 100 \, [1 - (W_2 / W_1)] \% \qquad (1)$$

where W_1 and W_2 are corrosion rate in the absence and presence of the inhibitor respectively.

The corrosion rate (CR) was calculated using the equation (2).

$$CR = \text{Weight loss in mg} / (0.11 \, dm^3 \times \text{Immersion period}) \quad (2)$$

AC Impedance Spectra: AC Impedance Spectra were carried out in an H and CH electrochemical workstation impedance analyzer, model CHI 660A. A three-electrode cell assembly was used. The working electrode was stainless steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular Pt foil was used as the counter electrode. The real

part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The corrosion parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) and impedance log (Z/ohm) values were calculated.

Surface examination study: The stainless steel specimens were immersed in various test solutions for a period of seven days. After seven days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was characterized by surface analytical techniques such as SEM and AFM.

Scanning Electron Microscopy (SEM): The stainless steel specimens immersed in various test solutions were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the stainless steel were carried out by SEM using HITACHI S – 3000 H SEM.

Atomic Force Microscopy (AFM): Atomic Force Microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before. The microscope used for the present study was PicoSPM I Molecular Imaging, USA make. Polished specimens prior to the initiation of all corrosion experiments were examined through an optical microscope to find out any surface defects such as pits or noticeable irregularities like cracks, etc. Only those specimens with a smooth pit-free surface were subjected for AFM examination. The protective films formed on the stainless steel specimens after immersion in the inhibitor systems for different time durations were examined for a scanned area of 30 x 30 μm^2 and 15 x 15 μm^2. The two-dimensional topography of surface films gives average roughness parameters of the film.

Results and Discussion

Analysis of results of weight loss study: The corrosion rates (CR) of stainless steel 410 immersed in sea water in the absence and presence of inhibitor is given in table 2. It is observed that as the concentration of ST increases, the IE increases. This is due to the fact that as the concentration of ST increases the protective film formed on the surface controls the anodic reaction and protects the metal. Thus a synergistic effect exists between ST and Zn^{2+}. The combination of 250 ppm of ST and 50 ppm of Zn^{2+} has a high IE, namely 98 percent. In the presence of Zn^{2+} more amount of ST is transported towards the metal surface. On the metal surface Fe^{2+} - ST complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH ¯, which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn^{2+} and ST [10,11].

Table-2
Inhibition efficiencies (IE) and Corrosion rates (CR) obtained from ST – Zn^{2+} systems, when stainless steel immersed in sea water

Na$_2$WO$_4$ ppm	Zn^{2+} ppm	IE%	CR (mdd)
0	0	-	6.75
0	50	25	5.06
50	50	59	2.77
100	50	64	2.43
150	50	73	1.82
200	50	81	1.28
250	50	98	0.14

Analysis of AC impedance spectra: AC impedance spectra have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases and the impedance log(Z/ohm) value increases. The AC impedance spectra of stainless steel immersed in sea water in the absence and presence of inhibitors are shown in figure 1 to 3. The AC impedance parameters such as R_t, C_{dl} and log(Z/ohm) are given in table 3. It is observed that in the presence of ST (250 ppm) - Zn^{2+} (50 ppm) formulation, R_t value increases from 12.315 ohm cm^2 to 39.363 ohm cm^2 and C_{dl} value decreases from 4.141x10^{-7} F /cm^2 to 1.296 x10^{-7} F /cm^2. Moreover, the impedance value [log (Z/ohm)] increases from 1.1630 to 1.223. These observations suggest that the formation of protective film on the metal surface [10,11].

Table – 3
Corrosion parameters of stainless steel immersed in sea water in the absence and presence of inhibitor system obtained from AC impedance spectra

System	R$_t$ Ohm cm^2	C$_{dl}$ F/cm^2	log (Z/ohm)
Sea water	12.315	4.141 x 10^{-7}	1.1630
Sea water + ST (250 ppm) + Zn $^{2+}$ (50 ppm)	39.363	1.296 x10^{-7}	1.223

Figure – 1
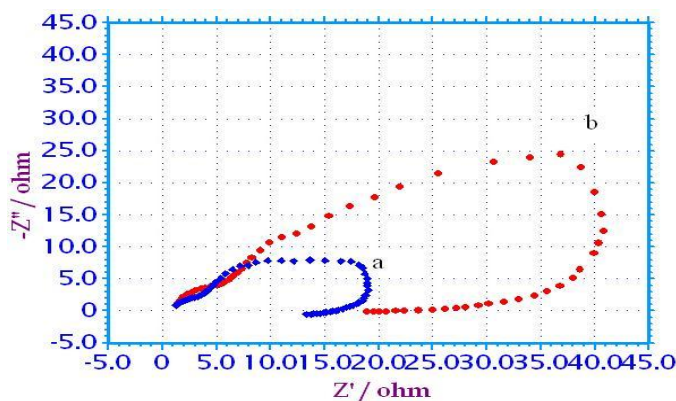**AC Impedance spectra (Nquist plot) (a) Sea water (b) Sea water + ST (250 ppm) + Zn^{2+} (50 ppm)**
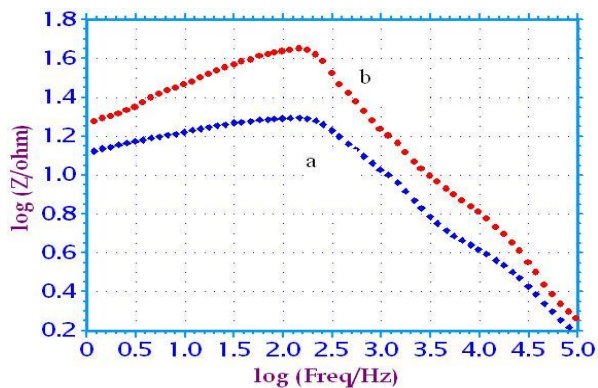
Figure – 2
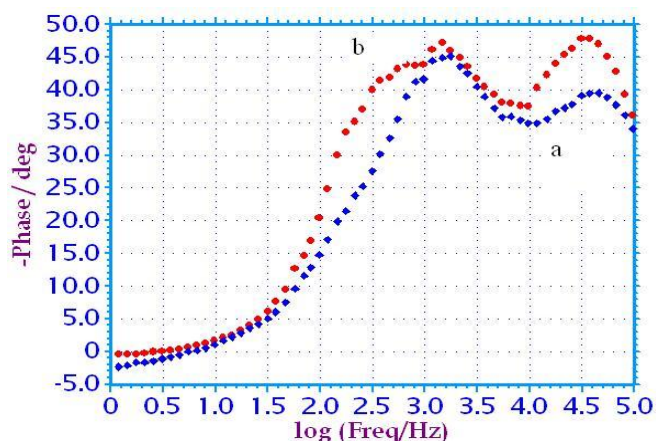**AC Impedance spectra (Bode plot) (a) Sea water (b) Sea water + ST (250 ppm) + Zn^{2+} (50 ppm)**

Figure - 3
AC Impedance spectra (Phase Bode plot) (a) Sea water (b) Sea water + ST (250 ppm) + Zn^{2+} (50 ppm)

SEM analysis of metal surface: SEM provides pictorial representation of the metal surface. To understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of stainless steel, the SEM micrographs of the surface are examined. The SEM images of different magnification (x 3000) of stainless steel specimen immersed in sea water for 7 days in the absence and presence of inhibitor system are shown in figure 4. The SEM micrographs of polished carbon steel surface (control) in figure 4(a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrographs of carbon steel surface immersed in sea water figure 4(b) shows the roughness of the metal surface which indicates the corroded area of stainless steel in sea water. However figure 4(c) indicates the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The metal surface is almost free from corrosion due to the formation of insoluble complex on the surface of the metal. In the presence of ST and Zn^{2+}, the surface is covered by thin layer of inhibitors, which effectively controls the dissolution of stainless steel [12,13].
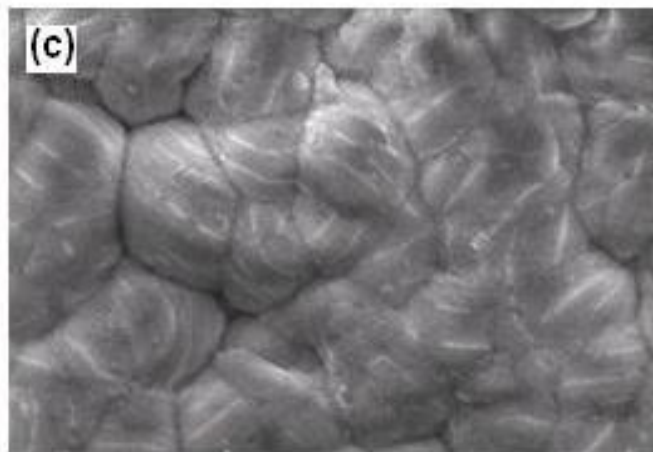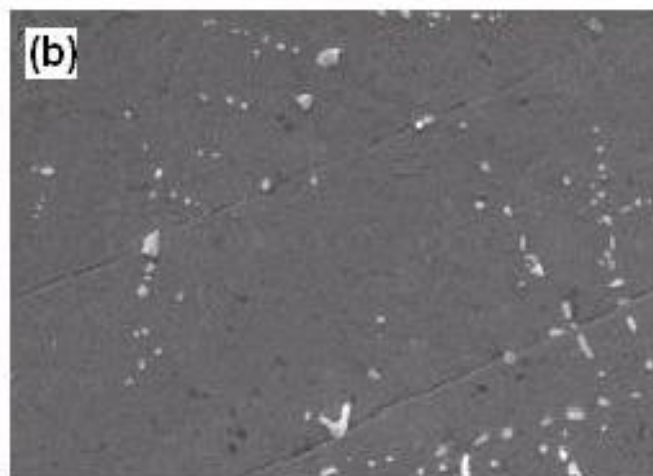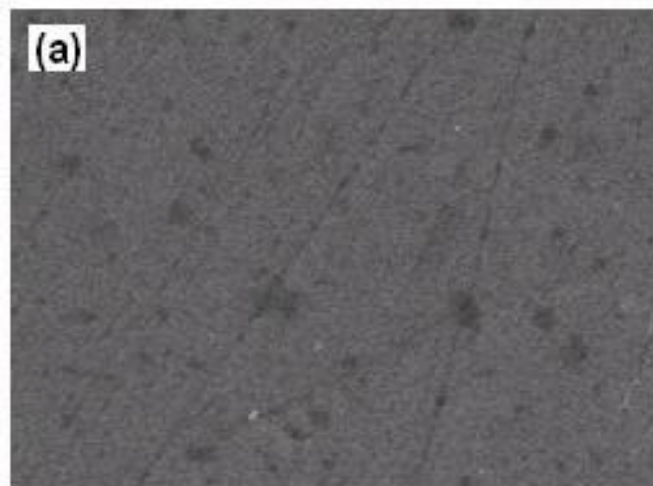

Figure – 4
SEM micrographs of stainless steel (Magnification – X 3000) (a) Polished stainless steel (Control), (b) Stainless steel immersed in sea water, (c) Stainless steel immersed in sea water consists of ST (250 ppm)+Zn^{2+}(50 ppm)

Atomic Force Microscopy (AFM) analysis of metal surface: AFM is a powerful technique for the gathering of roughness statistics from a variety of surfaces [14]. AFM is becoming an accepted method of roughness investigation[15-17]. All atomic force microscopy images were obtained in a VECCO lab incorporation AFM instrument operating in typing mode in air. The scan size of all the AFM images are 5 µm x 5 µm areas at a scan rate of 6.685 µm/sec. The two dimensional (2D) AFM morphologies for polished stainless steel surface (reference sample), stainless steel immersed in sea water (blank), and stainless steel surface immersed in sea water consists of ST 250 ppm and 50 ppm of Zn^{2+} are shown in the figure 5 (a), (b) and (c) respectively. AFM image analysis was performed to obtain average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length)[18]. Table 4 is a summary of the average roughness (R_a) value for stainless steel surface immersed in different environments. The values of R_a for the polished stainless steel surface (control) are 3.3 nm. This shows that the surface is more homogenous, with some places where the height is lower than the average depth [19]. Figure 5(a) displays the non-corroded metal surface. The slight roughness observed on the polished stainless steel surface is due to atmospheric corrosion. Figure 5(b) displays the corroded metal surface in sea water. The average roughness value for the stainless steel surface immersed in sea water is 24 nm. This value suggest that stainless steel surface immersed in sea water has a greater surface roughness than the polished metal surface, indicating that the unprotected stainless steel surface is rougher and were due to the corrosion of stainless steel in sea water environment. Figure 5(c) displays corroded metal surface with few pits. The formulation consists of 250 ppm ST and 50 ppm of Zn^{2+} in sea water shows R_a value of 10.9 nm reduced from 24 nm confirms that the surface appears smoother. The smoothness of the surface is due to the formation of a protective film of Fe^{2+}- ST complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of stainless steel. The above parameters are also somewhat greater than the AFM data of polished metal surface, which confirms the formation of film on the metal surface, which is protective in nature.

Table – 4
AFM data for stainless steel surface

Samples	Average Roughness (nm)
Polished stainless steel (Control)	3.3
Stainless steel immersed in sea water (blank)	24
Stainless steel immersed in sea water consists of 250 ppm ST and 50 ppm Zn^{2+}.	10.9

Mechanism of corrosion inhibition: With these discussions, a mechanism is proposed for the inhibition of corrosion of stainless steel immersed in sea water consists of 250 ppm ST and 50 ppm Zn^{2+} formulation. When the formulation consists of 250 ppm ST and 50 ppm Zn^{2+} in sea water there is a formation of ST – Zn^{2+} complex in solution. When stainless steel is immersed in this solution ST – Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface. ST – Zn^{2+} complex is converted into ST – Fe^{2+} complex on the anodic sites of the metal surface with release of Zn^{2+} ion.
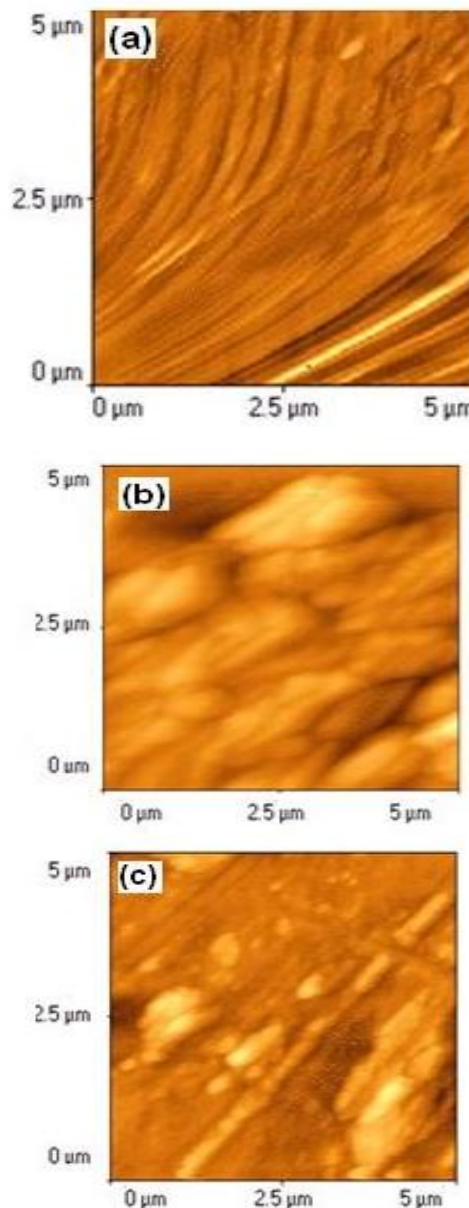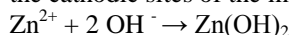

Figure – 5
2D AFM images of stainless steel surface (a) Polished stainless steel (control), (b) Stainless steel immersed in sea water (blank), (c) Stainless steel immersed in sea water consists of ST (250 ppm) + Zn^{2+} (50 ppm)

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

The released Zn^{2+} combines with hydroxide to form $Zn(OH)_2$ on the cathodic sites of the metal surface.
$$Zn^{2+} + 2 OH^- \rightarrow Zn(OH)_2$$

Thus the protective film consists of ST – Fe^{2+} complex and $Zn(OH)_2$. In near neutral aqueous solution the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of ST – Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of hydroxide. It is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2\ e^-$
Cathodic reaction: $H_2O + \frac{1}{2}O_2 + 2\ e^- \rightarrow 2\ OH^-$
$Fe^{2+} + ST \rightarrow ST – Fe^{2+}$ complex, $Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2$

This accounts for the synergistic effect of ST – Zn^{2+} system.

Conclusion

The corrosion inhibition of ST in controlling corrosion of stainless steel in sea water has been evaluated by weight loss method. The combination of ST (250 ppm) – Zn^{2+} (50 ppm) shows IE of 98%. AC impedance spectra reveal that the system controls the cathodic reaction predominantly due to the formation of a protective film on the metal surface. The SEM micrographs and AFM images confirm the formation of protective film on the metal surface.

Acknowledgement

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