Asian Journal of Chemistry; Vol. 29, No. 12 (2017), 2755-2760

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20875

Evaluation of Synergism in Sodium Tungstate/Sodium Silicate - (PA-Zn^{2+}) System for Mitigating Mild Steel Corrosion in Industrial Cooling Water System

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Received: 19 June 2017; *Accepted*: 19 August 2017; *Published online*: 30 October 2017; AJC-18628

Mild steel was extensively used in many industrial applications for the last few decades. Industries depend water particularly for cooling machines and other equipments to a temperature that allow manufacturing process to keep going, washing machineries *etc*. The dissolved oxygen present in water accelerates corrosion of steel equipments. Therefore it was absolutely needed to develop eco-friendly inhibitors having low cost and high efficiency in cooling water system that work even under accelerated conditions. Here we took PA-Zn^{2+} solution as the basic inhibitive system and then evaluated the role of different concentrations of sodium tungstate (ST) and sodium silicate (SS) in the optimum PA-Zn^{2+} combinations in neutral aqueous environment at normal as well as stimulated environment. Synergistic action of sodium tungstate and sodium silicate along with PA-Zn^{2+} system in the corrosion inhibition of mild steel was carried out by physico chemical and electro-chemical methods such as weight loss measurement, potentiodynamic polarization, open circuit potential measurement, electrochemical impedance spectroscopy *etc*. Based on the results of analysis we proposed a mechanism of passivation. 200 ppm sodium tungstate and 500 ppm sodium silicate exhibited optimum inhibitive action with 50 ppm phthalic acid - 60 ppm Zn^{2+} system and the values of efficiencies were found to be 99.04 and 96.1 % respectively. The composition of protective film was identified by IR spectroscopy and its homogenous nature was confirmed by the bode plots. The study confirmed that optimum combinations possessed excellent inhibitive power even under vigorous conditions and thereby proved the importance of PA+Zn^{2+}-ST/SS as corrosion inhibitor and suitability to use in industrial cooling water system.

Keywords: Corrosion inhibitors, Phthalic acid-Zn^{2+}, Sodium tungstate, Sodium silicates, Passive film.

INTRODUCTION

Mild steel was the lowest carbon containing steel (0.05-0.25 %) and was the widely used form of steel because of its low cost, ease of availability *etc*. Since it was hard as well as malleable it was an ideal choice for the construction of pipelines, construction materials, boilers, cooling water system *etc*. [1,2]. The main disadvantage associated with the usage of mild steel was that it was easily susceptible to corrosion. There were different methods available for corrosion prevention. Application of inhibitor was one of the best methods in corrosion control. It was reported that many organic acids were used as effective inhibitors. Organic compounds contain functional group such as N, O, S *etc*. could acted like an adsorption type indicator and thereby reducing metal dissolution. Several studies reported the formation of a donor-acceptor complex between free electrons or π-electrons of the inhibitor and vacant *d* orbital of a metal [3]. There were evidences of using succinic acid, benzoic acid, salicylic acid, anthranilic acid, different amino acids *etc*. as corrosion inhibitors in aqueous as well as acidic medium [4-8]. Studies also reported that the addition of Zn^{2+} to the inhibitors brought a positive effect in the inhibition efficiency [9]. Literature supported the use of phthalic acid as a corrosion inhibitor in acidic as well as aqueous environment [10]. Studies were reported on the inhibitive action of PA-Zn^{2+} system in distilled water [11]. Sodium tungstate and sodium silicates were widely used inhibitors due to its characteristics such as low cost, eco friendliness and wide availability *etc*. Shibli and Saji [12] reported the synergistic inhibitive action of sodium tungstate and potassium iodate on mild steel corrosion. There were reports of synergistic inhibition of corrosion of mild steel by sodium tungstate and sodium silicate [13]. Kanimozhi and Rajendran [14] reported the inhibitive properties of sodium tungstate-Zn^{2+} system and its synergism with HEDP. There were studies on sodium tungstate-Zn^{2+}-N-(phosphenomethyl)iminodiacetic acid system in well water. The present work involved the study of effect of sodium tungstate (ST) and sodium silicate (SS) in PA-Zn^{2+} system in neutral aqueous medium.

EXPERIMENTAL

Preparation of the specimen: A mild steel sheet C1018 with composition (W %) Fe-98.704 %, C-0.18 %, Mn-0.79 %, Si-0.21 %, P-0.022 %, S-0.024 %, Cr- 0.02 %, Mo- 0.001 % and Ni – 0.02 % was used for the present study. The specimen were polished using different grades of sand papers, degreased with trichloro ethylene and washed with distilled water before immersed in to the test solutions for physico-chemical and electrochemical analysis.

Inhibitor selected: The present work evaluated the synergistic inhibitive action of different concentrations of sodium tungstate/sodium silicate solutions with 50 ppm phthalic acid + 60 ppm Zn^{2+} combination on the corrosion of mild steel specimen in neutral aqueous medium. Here varied concentration of sodium tungstate and sodium silicate from 100 ppm to 1000 ppm for the study.

Weight loss method: The pre-treated steel coupons were immersed in different concentrations of inhibitor solutions for a period of 30 days. Corrosion products were cleaned by ammonium per chlorate solution. Coupons were weighed using an electronic balance (Shimadzu AY62) before and after immersion. Inhibition efficiency can be calculated using the equation [15]:

$$\text{Inhibition efficiency } (\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

W_1 and W_2 are the weight loss of the specimen after immersing in solution with and without inhibitor. Corrosion rate of the inhibitor was given by Manivannan *et al.* [16]:

$$\text{Corrosion rate (CR)} = [W \times 5.34 \times 10^5]/DAT \quad (2)$$

A is the area of the specimen and t is the period of immersion in hours. The surface coverage of the inhibitor can be determined by the equation:

$$\text{Surface coverage } (\theta) = \frac{W_2 - W_1}{W_2} \quad (3)$$

The influence of immersion period on the inhibitive action of the test solutions was also evaluated.

Calculation of synergism parameter: The synergistic interaction existing between the inhibitors were evaluated in terms of synergism parameter, S_I [17].

$$S_I = 1\text{-}I_{1+2}/1\text{-}I'_{1+2} \quad (4)$$

I_1 = Inhibition efficiency of (PA+ Zn^{2+}); I_2 = Inhibition efficiency of ST/SS.

$$I_{1+2} = (I_1+I_2) - I_1I_2$$

I'_{1+2} = Combined efficiency of the inhibitors.

Electrochemical measurements

Open circuit potential analysis: Analysis of open circuit voltage of the steel coupons immersed in various test solutions were evaluated using an Abbe digital multimeter using a saturated calomel electrode as reference for a period of 30 days.

Potentio dynamic polarization: The study was carried out using an SP200 model AC impedance analyzer consist of a three electrode cell assembly was used. A rectangular mild steel coupon with 1 cm^2 area exposed on one of its face was used as the working electrode. A platinum mesh was used as the counter electrode. A saturated calomel electrode was used as the reference electrode. Both cathodic and anodic polarization curves were recorded with potential (V) as a function of log I (A/cm^2). From polarization curve E_{corr}, I_{corr}, corrosion rate, tafel slope, *etc*. can be calculated [18]. Inhibition efficiency can be calculated as:

$$\text{Inhibition efficiency } (\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \quad (5)$$

AC impedance analysis: Corrosion behaviour of the mild steel in experimental solutions was explained by AC impedance parameters. Impedance spectra were recorded in the same instrument as that of polarization study, a three electrode cell assembly containing a working electrode, reference electrode and a counter electrode. Nyquist plots were recorded for different frequencies. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated. R_{ct} and C_{dl} were related as [19-21]:

$$R_{ct} = (R_s + R_{ct}) - R_s \quad (6)$$

where R_s is the solution resistance.

$$C_{dl} = 1/2\pi R_t \gamma_{max} \quad (7)$$

γ_{max} is the maximum frequency.

FTIR: FTIR spectra of corrosion product (with and without inhibitor) were taken to analyze the layer formed on the metal surface to confirm the interaction between the inhibitor solution and metal surface. The film formed on the mild steel coupon immersed in optimum concentration of inhibitor solution were collected, washed, dried, mixed with KBr and its IR spectrum was recorded using a Nicolet model759 spectrophotometer. IR spectrum of aqueous solutions of phthalic acid - Zn^{2+}, sodium tungstate and sodium silicate were also recorded for comparison.

Corrosion evaluation under extreme conditions: The inhibition efficiency of the optimum inhibitor combinations was evaluated under high temperature and also under stirring condition in order to explore its ability to prevent corrosion under vigorous environment. In order to provide high temperature, the inhibitor solutions were placed on a hot plate. Stirring was provided by a magnetic stirrer rotated at a speed of 100 rpm.

RESULTS AND DISCUSSION

Influence of sodium tungstate and sodium silicate on the inhibitive action of PA-Zn^{2+} system on the corrosion of mild steel in aqueous medium was evaluated by immersing the steel coupons in various test solutions for a period of 30 days. As per the results of weight loss method summarized in Table-1, 200 ppm sodium tungstate exhibited an excellent synergistic action with PA-Zn^{2+} system, with an inhibition efficiency of 99.04 %. All higher concentrations gave efficiency lower than solution containing 200 ppm. Sodium silicate also exhibited synergistic action with PA-Zn^{2+} system. It exhibited a gradual increase in inhibition efficiency with increase in concentration till 500 ppm. 500 ppm sodium silicate solution gave optimum efficiency of 96.1 % whereas 1000 ppm solution had efficiency lower than this value. Corrosion rate decreased from 0.269

TABLE-1
CORROSION RATES OF MILD STEEL IMMERSED IN INHIBITOR SOLUTIONS OBTAINED BY WEIGHT LOSS METHOD

Combination	Weight loss (%)	Corrosion rate (mpy)	Inhibition efficiency (%)
50 PA	0.0258	0.3308	75.4
60 Zn^{2+}	0.0413	0.5269	60.6
50PA+60 Zn^{2+}	0.0210	0.2690	80.0
50PA+60 Zn^{2+}+100ST	0.0041	0.0525	96.1
50PA+60 Zn^{2+}+200ST	0.0010	0.0128	99.1
50PA+60 Zn^{2+}+300ST	0.0020	0.0256	98.1
50PA+60 Zn^{2+}+500ST	0.0043	0.0551	95.9
50PA+60 Zn^{2+}+1000ST	0.0098	0.1256	90.6
50PA+60 Zn^{2+}+100SS	0.0120	0.1538	88.5
50PA+60 Zn^{2+}+200SS	0.0061	0.0769	94.3
50PA+60 Zn^{2+}+300SS	0.0058	0.0743	94.4
50PA+60 Zn^{2+}+500SS	0.0042	0.0530	96.1
50PA+60 Zn^{2+}+1000SS	0.0063	0.0807	94.0

mpy to 0.013 mpy with optimum sodium tungstate solution and to 0.053 mpy with optimum sodium silicate solution. In presence of sodium tungstate and sodium silicate rate of transport of inhibitor ions to steel surface increased. Protection was due to complex formation with Fe^{2+}/Fe^{3+}. When the complex cover the entire specimen surface further increase in concentration does not enhance efficiency of inhibition [22]. As the immersion time increased migration of components of inhibition also increased led to increased efficiency of inhibition and attained a steady value after three or four days of immersion revealed that protective film formation was completed as well as the film was stable. Variation of efficiency with immersion time was plotted in Fig. 1. Synergism parameters of optimum inhibitor solutions of sodium tungstate and sodium silicate were calculated and presented in Table-2. If the value of S_I tends to zero indicated that there was no interaction between the inhibitor substances. If S_I greater than 1 suggested synergistic interaction. S_I less than zero imply interaction result in negative effect, *i.e.*, rate of corrosion increases. Here we got positive values for S_I confirmed the synergistic interaction between ST/SS with PA-Zn^{2+} system. The consistency of action of inhibitor solution was evaluated by OCP analysis. Although initially there were variations in potential, it came to a steady state after two or three days and maintained the potential over the experimental duration. Variations in OCP for all experimental solution under all test conditions were represented in Fig. 2. During OCP analysis, with all test solutions potential shifted to anodic region and remained almost steady for 30 days. Initial variation in potential was due to the dissolution of air formed oxide and due to the adsorption of inhibitor on the steel surface for the formation

TABLE-2
SYNERGISM PARAMETERS OF MILD STEEL COUPONS IN THE PRESENCE OF OPTIMUM COMBINATIONS

50 ppm PA + 60 ppm Zn^{2+}	ST/SS		PA + Zn^{2+} + ST/SS		S_I
(I_1) IE (%)	(I_2) IE (%)		(I_{1+2}) IE (%)		
	ST (200 ppm)	SS (500 ppm)	ST (200 ppm)	SS (500 ppm)	
80	8	–	99.04	–	4.153
80	–	10	–	96.1	7.476

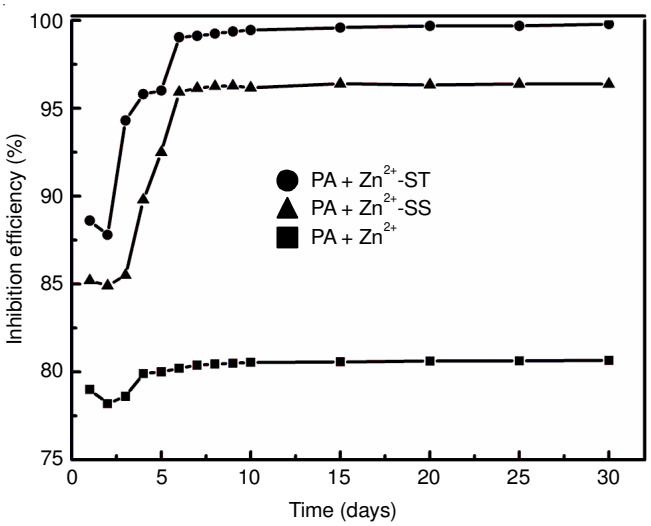

Fig. 1. Variation of inhibition efficiency with immersion period

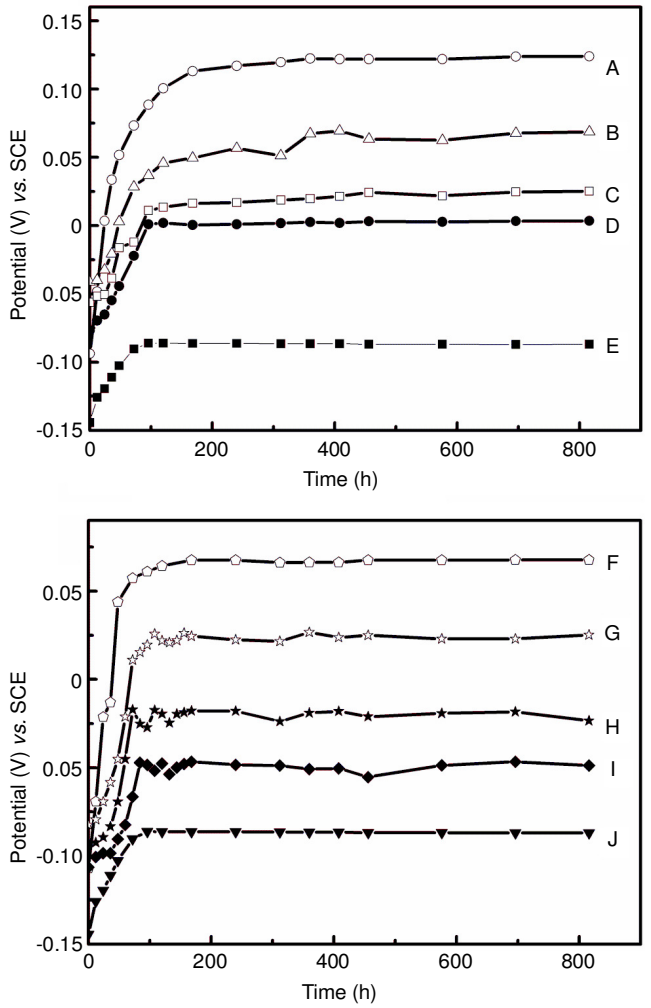

Fig. 2. Variation of open circuit voltage with time. (A) PA+Zn^{2+}- 200 ppm ST (stagnant at RT) (B) PA-Zn^{2+}-200 ppm ST(Stirring at RT) (C) PA+Zn^{2+}- 200 ppm ST (Stagnant at 80 °C) (D) PA+Zn^{2+}- 200 ppm ST (Stirring at 80 °C) (E,J) PA+Zn^{2+} (Stagnant at RT) (F) PA+Zn^{2+}-500 ppm SS (Stagnant at RT) (G) PA+Zn^{2+}-500 ppm SS (Stirring at RT) ((H) PA+Zn^{2+}-500 ppm SS (Stagnant at 80 °C) (I) PA-Zn^{2+}-500 ppm SS (Stirring at 80 °C)

of a protective film [22,23]. After three or four days potential remains steady, indicated completeness of film formation. The

TABLE-3
CORROSION PARAMETERS OF STEEL SPECIMENS IN PRESENCE AND ABSENCE OF INHIBITOR COMBINATIONS OBTAINED BY POTENTIODYNAMIC POLARIZATION STUDY

System	E_{corr} (V)	I_{corr} (A/cm^2)	IE (%)	b_a (mV)	b_c (mV)
Water	-0.725	6.542×10^{-5}	–	152	327
PA + Zn^{2+}	-0.631	1.689×10^{-5}	74.1	145	280
50 ppm PA + 60 ppm Zn^{2+} + 200ST	-0.442	1.361×10^{-6}	98.0	129	131
50 ppm PA + 60 ppm Zn^{2+} + 500SS	-0.523	1.997×10^{-6}	96.9	303	402

constant potential over the study period revealed that even under stimulated condition the protective film firmly adsorbed on the surface of the steel specimen. Corrosion parameters of mild steel immersed in different experimental solutions evaluated by the efficient, precise and versatile electrochemical method, potentiodynamic polarization and the observations were listed in Table-3. The Tafel polarization curves of steel coupons immersed in various test solutions were plotted in Fig. 3. On potentiodynamic polarization, the I_{corr} value obtained for PA-Zn^{2+} system was 6.542×10^{-5} A cm^{-2}, on adding optimum sodium tungstate and sodium silicate solution to the system I_{corr} decreased to 1.3618×10^{-6} A cm^{-2} and 1.9976×10^{-6} A cm^{-2}, respectively. This significant reduction in the value of corrosion current lighted on the efficiency of inhibitor combination. The E_{corr} value shifted to positive region on adding ST/SS. The anodic shift in E_{corr} value indicated that the optimum combination act as an anodic inhibitor that prevented corrosion by forming a protective film. Inhibition efficiency of the optimum combinations were calculated from I_{corr} value was in close agreement with those obtained from weight loss method [24]. The observation suggested an excellent efficiency for PA + Zn^{2+} system containing 200 ppm sodium tungstate and 500 ppm sodium silicate in terms of its lowest corrosion current. I_{corr} value of system containing sodium tungstate was smaller than sodium silicate. Surface analysis of mild steel coupons in inhibitor combinations were done by impedance analysis. The Nyquist plots of mild steel immersed in the ternary solutions were represented in Fig. 4. The steel coupon immersed in water possessed a charge transfer resistance of 175 Ω/cm^2 and a double layer capacitance of 4.67×10^{-8} F/cm^2. While PA - Zn^{2+} + 200 ppm sodium tungstate solution had an R_{ct} value of 2280 Ω/cm^2 and C_{dl} of 4.67×10^{-8} F/cm^2. The R_{ct} and C_{dl} value of PA-Zn^{2+} + 500 ppm sodium silicate solution was 1660 Ω/cm^2 and 1.67×10^{-8} F/cm^2. The higher value of charge transfer resistance and lower value of double layer capacitance obtained in presence of inhibitor combinations confirmed the formation of a protective inhibitive layer over the mild steel coupon. Thus explained the excellent inhibitive action [11,25-27]. The data obtained from impedance analysis were given in Table-4. Impedance values of steel specimens immersed in optimum combinations were identified from the Bode plots. The homogeneous character of the film formed over the steel specimen was identified from the nature of the Bode plot obtained in presence of the inhibitor. Impedance of the steel specimen was increased in presence of the optimum combinations [27]. The composition of scale developed on steel in optimum combinations were analyzed by Fourier transform spectroscopy. The band positions from Fig. 6 helped to identify the chemical constituents of the film. FTIR spectrum of pure sodium tungstate contains a band at 1682 cm^{-1} corresponds to

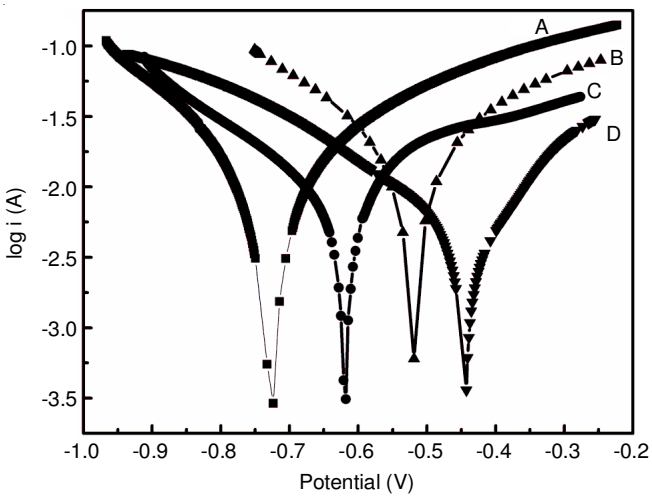

Fig. 3. Potentiodynamic polarization analysis of mild steel coupons in presence and absence of inhibitors. (A) Water B) PA-Zn^{2+} C) PA+Zn^{2+}-500 ppm SS D) PA+Zn^{2+}-200 ppm ST

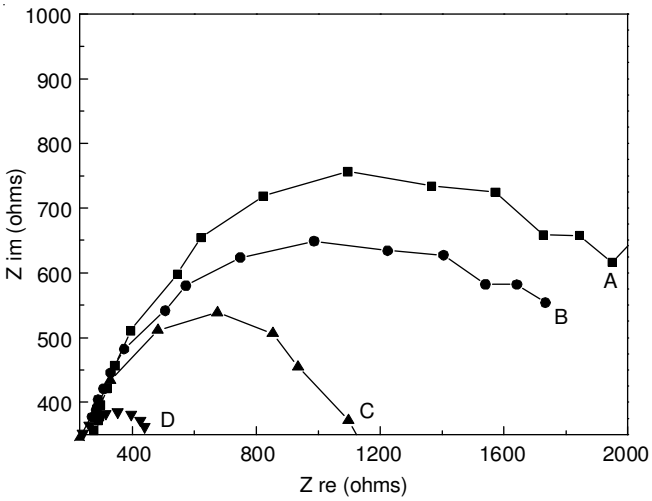

Fig. 4. AC impedance analysis of mild steel coupons immersed in PA-Zn^{2+} system contains optimum concentrations of sodium tungstate and sodium silicate. A) PA + Zn^{2+}+ 200 ppm ST B) PA + Zn^{2+} + 500 ppm SS C) PA+Zn^{2+} D) Water

TABLE-4
AC IMPEDANCE PARAMETERS OF MILD STEEL IMMERSED IN NEUTRAL AQUEOUS MEDIUM IN PRESENCE AND ABSENCE OF OPTIMUM INHIBITOR COMBINATIONS

System	R_{ct} (Ω/cm^2)	C_{dl} (F/cm^2)	log Z/Ω
Water	175	4.674×10^{-8}	2.89
PA + Zn^{2+}	845	3.80×10^{-8}	2.92
PA + Zn^{2+} + 200 ST	1660	1.67×10^{-8}	3.44
PA + Zn^{2+} + 500 SS	2280	2.56×10^{-8}	3.09

WO_4^{2-} stretching frequency. Peak at 941.58 cm^{-1} in the FTIR spectrum of pure sodium silicate corresponds to SiO_4^{2-} stretching frequency. Spectrum of pure phthalic acid contains a

TABLE-5
EVALUATION OF CORROSION PARAMETERS UNDER STIMULATED CONDITIONS

Concentration of inhibitors	Condition	OCP (V)	Corrosion rate (mpy)	IE (%)
50 PA + 60Zn^{2+}	Stagnant at room temperature	-0.086	0.269	80.0
50 PA + 60Zn^{2+} + 200ST	Stagnant at room temperature	0.160	0.013	99.1
50 PA + 60Zn^{2+} + 500SS	Stagnant at room temperature	0.066	0.053	96.1
50 PA + 60Zn^{2+}	Stirring at room temperature	-0.096	0.286	78.7
50 PA + 60Zn^{2+} + 200ST	Stirring at room temperature	0.096	0.019	98.5
50 PA + 60Zn^{2+} + 500SS	Stirring at room temperature	0.022	0.061	95.4
50 PA + 60Zn^{2+}	Stagnant at 80 °C	-0.113	0.242	74.3
50 PA + 60Zn^{2+} + 200ST	Stagnant at 80 °C	0.046	0.339	94.5
50 PA + 60Zn^{2+} + 500SS	Stagnant at 80 °C	-0.019	0.083	93.9
50 PA + 60Zn^{2+}	Stirring at 80 °C	-0.217	0.681	49.1
50 PA + 60Zn^{2+} + 200ST	Stirring at 80 °C	0.23	0.206	84.6
50 PA + 60Zn^{2+} + 500SS	Stirring at 80 °C	-0.048	0.235	82.4

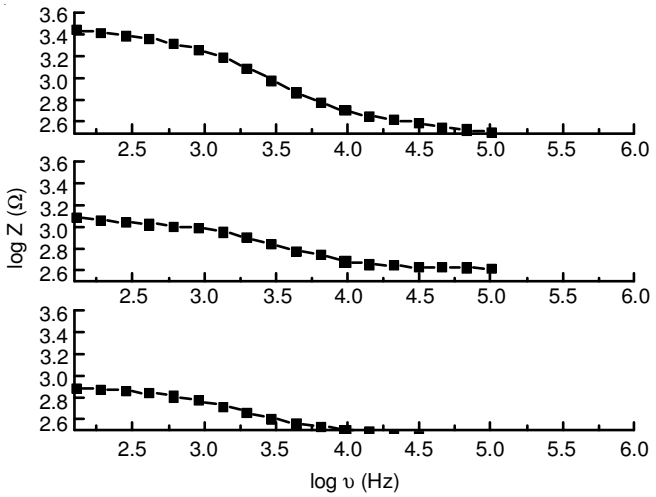

Fig. 5. Bode plots of steel coupon in presence and absence of inhibitor

band at 1740 cm^{-1} corresponds to C=O stretching frequency and O-H stretching vibration was indicated by the band located at 3396.49 cm^{-1}. FTIR spectrum of corrosion product formed over the mild steel immersed in optimum sodium tungstate and sodium silicate solution was represented in Fig. 6. On analyzing the spectrum of corrosion product obtained from the steel specimen immersed in optimum sodium tungstate it is clear that WO_4^{2-} stretching frequency decreased from 1682 to 1643.26 cm^{-1}. This proposes that tungstate ion react with metal ion present in the anodic site result in the formation of Fe^{2+}-sodium tungstate complex. C=O stretching frequency of phthalic acid decreased from 1740 to1710 cm^{-1}, indicated the formation of Fe^{2+}-PA complex by the reaction between oxygen atom of C=O group and Fe^{2+} ion. Band at 1352 cm^{-1} was due to the formation of $Zn(OH)_2$ on the cathodic site of the metal surface. Similarly spectrum of corrosion product obtained from PA-Zn^{2+}-sodium silicate contain a peak at 934.62 cm^{-1} corresponds to silicate stretching frequency. The decreased stretching frequency compared to silicate stretching frequency of pure sodium silicate solution was due to the formation of Fe^{2+}-sodium silicate complex on the surface. The band at 1632.80 cm^{-1} indicated C=O stretching frequency. The decreased stretching frequency shows Fe^{2+}-PA complex on the anodic site of the metal surface. $Zn(OH)_2$ formed on the cathodic surface was confirmed by the peak at 1385 cm^{-1}. The results suggested that both sodium tungstate and sodium silicate exhibit good corrosion resistance with PA-Zn^{2+} system even under stimulated conditions.

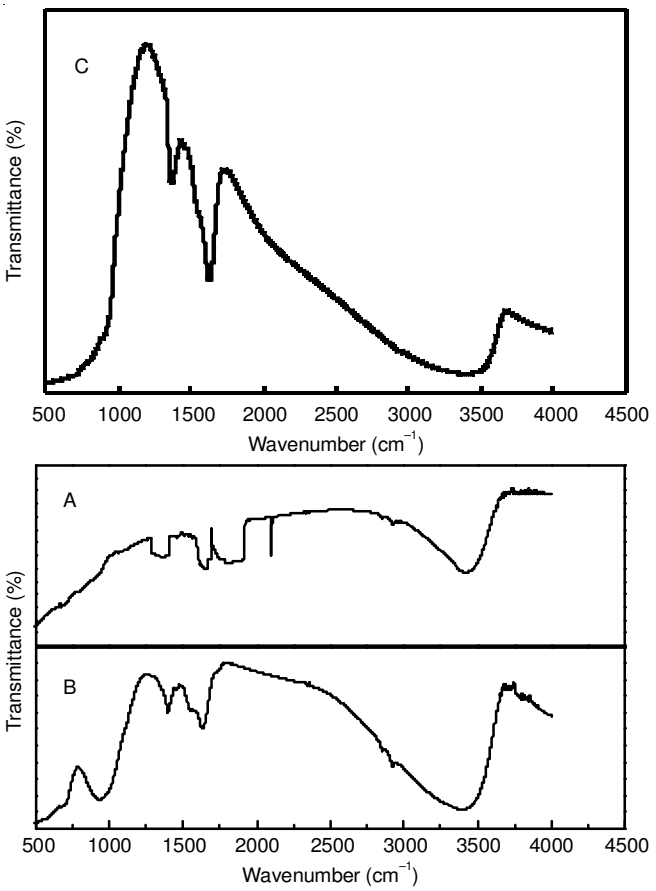

Fig. 6. IR spectrum of corrosion product obtained from mild steel coupons immersed in inhibitor solutions. A) PA-Zn^{2+} B) PA+Zn^{2+}- 200 ppm ST C) PA+Zn^{2+} - 500 ppm SS

A slight decrease in inhibition efficiency under stimulated condition was due to the delay involved in surface film formation.

Explanation for the synergistic effect: The test solutions initially contained ST/SS, Zn^{2+} and phthalic acid. They formed complexes such as ST/SS - Zn^{2+}, PA - Zn^{2+}, ST/SS - Zn^{2+} - PA, were in equilibrium with free ions. When the mild steel specimen was immersed in the inhibitor solutions the complexes migrated from the bulk of the solution to the metal surface, where the Fe^{2+}/Fe^{3+} ions combined with ST/SS to form Fe^{2+}-ST/SS complex and with phthalic acid form Fe^{2+}- PA complex in the anodic region, They were more stable. The released Zn^{2+} ions precipitated as $Zn(OH)_2$ in the cathodic region of the metal strip, thereby decreased metal dissolution.

Conclusions

• Sodium tungstate and sodium silicate exhibited better inhibition efficiency when used along with PA-Zn^{2+} system in aqueous medium. 200 ppm sodium tungstate and 500 ppm sodium silicate are found to be the optimum combination and the efficiencies are given by 99.04 and 96.1 % respectively. Increased inhibition efficiency of PA-Zn^{2+} system in presence of sodium tungstate and sodium silicate suggested a synergistic interaction between these two inhibitors, again supported by synergism parameter.

• The increased E_{corr} value obtained in presence of inhibitor combinations during potentiodynamic polarization studies confirmed PA-Zn^{2+}-sodium tungstate and PA-Zn^{2+}-sodium silicate as anodic inhibitors.

• The higher R_{ct} and lower C_{dl} values obtained for mild steel immersed in optimum combinations of sodium tungstate and sodium silicate during AC impedance analysis confirmed the formation of protective layer over the steel surface in presence of ternary combinations containing optimum concentrations of sodium tungstate and sodium silicate. The constituents of protective layer were identified by IR spectroscopy confirmed the presence of components of inhibitor solution on the specimen surface and its homogeneous character was understood from the nature of Bode plots.

• Evaluation of immersion period on inhibition efficiency explored that as immersion period increased inhibition efficiency also increased up to a certain period and then remained constant. The OCP decay also agreed with this observation indicated the stability of the adsorbed film formed over the steel specimen.

• This work presented PA-Zn^{2+} - 200 ppm sodium tungstate and PA-Zn^{2+} - 500 ppm sodium silicate as an efficient, economical and nature friendly inhibitor for the corrosion of mild steel in neutral aqueous medium even under accelerated conditions. The efficiency of preventing corrosion of PA-Zn^{2+} system containing sodium tungstate was superior to sodium silicate for mild steel in industrial cooling water system.

ACKNOWLEDGEMENTS

The authors thank Prof & Head of Department of Chemistry, University of Kerala for providing the technical facilities in support of the present work.

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