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Inhibitive Properties of Sodium tungstate-Zn^{2+} System and its Synergism with HEDP

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Sodium tungstate in the presence of Zn^{2+} ions is used to function as the corrosion inhibitors in the corrosion of mild steel. However, in view of the toxicity of Zn^{2+}, focus is now shifted to low- Zn^{2+} or no- Zn^{2+} formulations. In order to reduce the concentration of Zn^{2+} in Sodium tungstate- Zn^{2+} formulations, a second substance, which is environmentally friendly, is desired. 1-hyroxyethane-1,1-diphosphonicacid (HEDP) is environment-friendly, forms complexes with metal ions, and possesses passivating properties. The ternary system containing 50 ppm of ST, 10 ppm of Zn^{2+} and 200 ppm of HEDP is quite effective. AC impedance studies indicate that surface films formed on mild steel exhibit high charge transfer resistance and low double layer capacitance, which suggests that the film is non-porous and hence protective. Potentiodynamic polarization studies show that this system works as an anodic inhibitor. From the results of reflection absorption spectral studies on the surface film, a mechanism for the inhibition of corrosion is proposed.

Keywords: Corrosion inhibition, mild steel, oxyanions, sodium tungstate, F-test

1. 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., However, they are susceptible to different forms of corrosion inducted by chloride and so on. One of the most important methods in corrosion protection is to use inhibitors [4-5]. Inhibitors should be of low toxicity and easily biodegradable in order to meet environmental protection requirements. Tungstate is an environmentally friendly inhibitor and has been extensively studied for its application in the protection of iron, Zinc and Aluminium substrates in neutral, acidic and alkaline solutions. Normally it is not feasible to use tungstate alone as a corrosion inhibitor due to its low inhibition ability at low concentrations of tungstate and high cast. In most causes, the combinations of tungstate with co-inhibitors were described in the literature [6-10]. However, previous literature has not reported the use of tungstate as the corrosion inhibitor for mild steel with more than one co inhibitors. Phosphates in the form of poly phosphates control the corrosion of ferrous metals [11]. They act as cathodic inhibitors [12,13]. Phosphonic acid is used as a corrosion inhibitor for the corrosion control in industrial boiler water and municipal water treatment [3]. Saha et al [15] studied the mechanism of phosphate based cooling system corrosion inhibitors in a mild steel plant. Their inhibition properties were increased by the addition of metallic ions [16]. Their metallic ions form insoluble complexes with phosphonic acids and repair the porous oxide and prevent for the corrosion. Predominantly Zn^{2+} ions are used for elevating the corrosion inhibiting properties of phosphonic acids [17,18]. The Zn-Phosphonate complexes showed excellent corrosion inhibition as compound to other metal cations. For this present work, the first synergist is Zn^{2+} and second synergist is HEDP with sodium tungstate (ST). Kalman et al [19] have discussed impedance spectra of mild steel in neutral solutions in the presence of HEDP. Results of their investigations increasing HEDP concentration beyond the optimal value decreases its inhibition efficiency due to the dissolution of the oxide layer. The synergistic effect of HEDP with metal ions, co-inhibitors and some phosphonic acid are reported often in the literature [20-25]. The present study evaluates the synergistic effect of sodium tungstate-Zn^{2+}system; estimates the influence of HEDP on the IE of ST-Zn^{2+} system; a studies mechanistic aspects of corrosion inhibition by electrochemical studies and analysis protective film by FTIR spectroscopy.

2. EXPERIMENTAL PART

2.1. Preparation of the specimens

Mild steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and rest iron) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish, degreased with trichloroethylene, and used for the weight-loss method and surface examination studies.

2.2. Weight – loss method

Mild steel specimens in triplicate were immersed in 100 ml of the well water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for seven days. The parameter of well water is shown in Table 1. The corrosion product cleaned with Clark's solution [26]. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The inhibition efficiency (IE) was then calculated using the equation

$$IE = 100\ [1-(w_2/w_1)]\ \%$$

where

w_1 = Corrosion rate (mmy) in absence of inhibitor
w_2 = Corrosion rate (mmy) in presence of inhibitor

Table 1. Physico – chemical parameters of well water

Parameters	Value
pH	8.38
Conductivity	3110 μmhos/cm
Chloride	665 ppm
Sulphate	14 ppm
TDS	2013 ppm
Total hardness	1100 ppm

3. SURFACE EXAMINATION STUDY

3.1. FTIR spectra

In a Perkin – Elmer 1600 spectrophotometer the film formed on mild steel specimen were taken out and dried and was carefully removed, mixed thoroughly with KBr and made into pellets and the FTIR spectra were recorded.

3.2. Potentiodynamic polarization study

This study was carried out using CHI 660A electrochemical impedance analyzer model a three – electrode cell assembly was used. The working electrode was used as a rectangular specimen of mild steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing *i*R compensation. The results such as Tafel slopes, I_{corr} and E_{corr} values were calculated. During the Polarization study, the scan rate (v/s) was 0.01; Hold time at Ef (s) was zero and quiet time (s) was 2.

3.3. AC impedance measurements

CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. AC Impedance spectra were recorded with initial E(v) = 0; High frequency (Hz) = $1x10^5$,Low frequency (Hz) = 1;Amplitude (v)= 0.05 and Quiet time (s) =2.

3.4. Determination of the biocidal efficiency

The biocidal efficiency of the system was determined using Zobell medium and calculating the numbers of colony forming units per ml using a bacterial colony counter. ST-Zn^{2+}-HEDP system was selected. The biocidal efficiency of sodium dodecyl sulphate (SDS) was determined. Various concentrations of SDS namely 50 ppm, 100 ppm, 150 ppm, 200 ppm and 250 ppm were added to the formulation consisting of the inhibitor system. Polished and degreased mild steel specimens in triplicate were immersed in these environments for a period of seven days. After seven days, one ml each of test solutions from environments was pipetted out into sterile petri dishes each containing about 20 ml of the sterilized Zobell medium. The petri dishes were then kept in a sterilized environment inside the laminar flow system fabricated and supplied by CEERI-pilani, for 48 hours. The total viable heterotropic bacterial colonies were counted using a bacterial colony counter. The corrosion inhibition efficiencies of the formulation consisting of the inhibitor in the presence of various concentrations of SDS were also determined.

3.5. Synergism parameter (S_I)

Synergism parameters are indications of synergistic effect existing between the inhibitors [27-29]. S_I value is found to be greater then one suggesting that the synergistic effect between the inhibitors.

$$S_I=1-I_{1+2} /1-I'_{1+2}$$

where

I_1 = Inhibition efficiency of substance 1
I_2 = Inhibition efficiency of substance 2
I'_{1+2} = Combined Inhibition efficiency of substance 1& 2.
I'_{1+2} = Combined Inhibition efficiency of substance 1& 2.

3.6. Analysis of variance (F-test)

F-test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant [30]. If F-value is above 5.32 for 1,8 degrees of freedom, it was proved to be at statically significant. If it is below the value of 5.32 for 1,8 degrees of freedom, it was statically insignificant at 0.05 level of significance confirmed.

4. RESULTS AND DISCUSSION

4.1. Weight loss method

4.1.1. Evaluation of improvement of IE of Zn^{2+} with tungstate

The inhibition efficiency (IE) of sodium tungstate (ST) in controlling corrosion of mild steel immersed in well water for a period of seven days in the absence and the presence of Zn^{2+} is given in Table 2. It can be seen from the data that ST alone shows some IE whereas Zn^{2+} alone is found to be corrosive. In the absence of ST, the rate of transport of Zn^{2+} from the bulk of solution towards the metal surface is slower than the rate of corrosion process on the metal surface. Hence, acceleration of corrosion (negative IE) takes place in the absence of ST. Similar observations has already been reported [31,32]. When ST is combined with Zn^{2+} ions it is found that the IE increase with concentration of Zn^{2+} ions. For example, 250 ppm ST has only 12% IE and 50 ppm of Zn^{2+} has only –12 % IE. Interestingly their combination shows 98% IE. This suggests a synergistic effect between the binary inhibitor formulation ST and Zn^{2+} ions; ST is able to transport Zn^{2+} towards the metal surface.

Table 2. Corrosion rates (CR) of mild steel in well water, in the absence and the presence of inhibitors and inhibition efficiencies (IE) obtained by weight loss method.

ST (ppm)	Zn^{2+} (ppm)					
	0	5	10	25	50	75
	CR (mmy)					
0	0.0868	0.0911	0.0972	0.1015	0.1041	0.1102
50	0.0850	0.0798	0.0738	0.0382	0.0243	0.0026
100	0.0824	0.0781	0.0677	0.0286	0.0174	0.0026
150	0.0798	0.0755	0.0625	0.0234	0.0148	0.0026
200	0.0781	0.0738	0.0555	0.0165	0.0104	0.0002
250	0.0764	0.0712	0.0477	0.0130	0.0002	0.0002
	IE (%)					
0	-	-5	-12	-17	-20	-27
50	2	8	8	56	72	97
100	5	10	22	67	80	97
150	8	13	28	73	83	97
200	10	15	36	81	88	98
250	12	18	45	85	98	98

4.1.2. Evaluation of synergistic effect of HEDP with tungstate-Zn^{2+} system

In order to examine the role of HEDP in the ternary inhibitor formulation, experiments were conducted with HEDP alone, ST and with Zn^{2+}+ HEDP in a wide concentration range. The highest inhibition efficiencies with these systems are shown in Table 3. The synergistic effect in the ST- Zn^{2+}-HEDP system is evident from the data in Table 3. The Zn^{2+} ion acts as one synergist and HEDP acts as the other. From the Table 3, it is seen that at relatively higher concentrations of both ST and Zn^{2+} 98% IE was obtained. However, such an efficiency is not obtained with combinations if ST and HEDP, even at relatively high concentrations. Thus, it may be concluded that Zn^{2+} is the primary synergistic and HEDP is the secondary synergist and both play a significant synergistic role. Hence, the highest IE is obtained at such low concentrations of each of the components in the ternary inhibition formulation.

Table 3. Corrosion rates (CR) and Inhibition Efficiencies (IE) of mild steel in well water, in the absence and the presence of inhibitors and IE obtained by weight loss method.

ST ppm	Zn^{2+} ppm	HEDP ppm	IE %	CR mmy
0	0	0	-	0.0868
50	0	0	2	0.0850
0	10	0	-12	0.0972
0	0	200	33	0.0581
50	10	0	8	0.0798
50	10	50	75	0.0022
50	10	100	79	0.0018
50	10	150	83	0.0015
50	**10**	**200**	**98**	**0.0002**
50	10	250	91	0.0008
50	0	200	47	0.0459
0	10	200	59	0.0356

4.1.3. Influence of immersion period on the ST-Zn^{2+}-HEDP system

The influence of immersion period on IE of ST (50 ppm)-Zn^{2+}(10 ppm)-HEDP (200 ppm) is given in Table 4. It is found that as the immersion period increases, the inhibition efficiency decreases [33]. This is due to the fact as the immersion period increases the protective film is ruptured by the continuous attack of the Cl^-, present in the solution. There is competition between two processes, namely, formation of iron-ST and iron-HEDP complex and iron chloride. It appears that the formation of iron chloride is more favoured than the formation of iron complexes. Moreover, the iron complexes of ST and HEDP film formed on metal surface is converted into iron chloride which goes into solution and hence, the IE decreases as the immersion period increases.

Table 4. Influence of immersion period on the IE of ST(50ppm)-Zn^{2+} (10ppm) –HEDP (200ppm) system. Inhibitor system: ST-Zn^{2+}-HEDP

System	Immersion period (Days)			
	1	3	5	7
Well water (WW) CR (mmy)	0.0093	0.0637	0.0833	0.0868
WW+ST(50ppm)-Zn^{2+}(10 ppm)-HEDP (200 ppm) CR (mmy)	0.0019	0.0013	0.0017	0.0017
IE (%)	98	98	98	98

5. SYNERGISM PARAMETERS

The values of synergism parameters are shown in the Table 5. Here values of S_I are greater than one, suggesting a synergistic effect. S_I approaches 1 when no interaction exists between the inhibitor compounds. When $S > 1$, this points to synergistic effects. In the case of <1, the negative interaction of inhibitors prevails (i.e., corrosion rate increases) [27-29].

Table 5. Synergism parameters of mild steel immersed in well water in the presence and absence of inhibitor.

ST+Zn^{2+} (I_2) IE(%)	HEDP (I_1) IE(%)	ST-Zn^{2+}-HEDP (I'_{1+2}) IE(%)	S_I
8	42	75	3.87
8	50	79	4.39
8	34	83	2.81
8	33	98	2.30
8	21	91	1.55

5.1. Analysis of Variance (ANOVA)

To investigate whether the influence of Zn^{2+} on the inhibition efficiencies of ST combined with HEDP is statistically significant, F-test was carried out [30]. The results are given Tables 6 and 7. In Table 6, the influence of 50 ppm of ST and 10 ppm of Zn^{2+} on the inhibition efficiencies of 50,100,150,200,250 ppm of HEDP is investigated. The obtained F-value is 33.36 statistically significant, since it is greater than the critical F-value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it is concluded that the influence of 50 ppm of ST, 10 ppm of Zn^{2+} on the inhibition efficiencies of concentrations of ST, Zn^{2+} and 150 ppm of HEDP is statistically significant. In Table 7, the influence of inhibition efficiencies of 50 ppm of ST-10 ppm of Zn^{2+} and 50 ppm of ST-10 ppm of Zn^{2+} with 50,100,150,200,250 ppm of HEDP is investigated. The obtained F – value 345.69 is statistically significant, since it is greater than the critical F–value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it is concluded that the influence of 50 ppm Zn^{2+} on the inhibition efficiencies of various concentrations of HEDP is statistically significant.

Table 6. Distribution of F Value Between the Inhibition Efficiencies of the Influence of ST-Zn^{2+} and HEDP

Source of variance	Sum of squares	Degrees of freedom	Mean square	*F*	Level of significance of F
Between	1960	1	1960	33.36	p>0.05
Within	470	8	58.75		

Table 7. Distribution of F Value Between the Inhibition Efficiencies of the Influence of ST-Zn^{2+} and ST-Zn^{2+}-HEDP

Source of variance	Sum of squares	Degrees of freedom	Mean square	*F*	Level of significance of F
Between	14899.6	1	14899.6	345.69	p>0.05
Within	344.8	8	43.1		

5.2. Effect of sodium dodecyl sulphate (SDS) on the inhibition efficiency of ST-Zn^{2+}-HEDP.

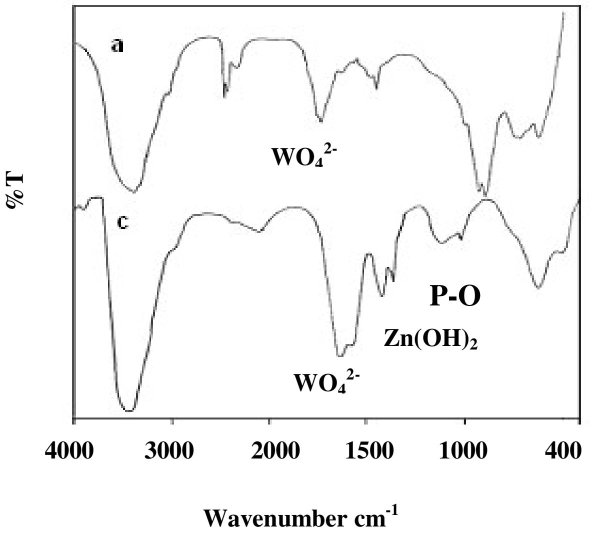
The influence of various concentrations of SDS on the IE of ST-Zn^{2+}-HEDP system is given in the Table 8. It is observed that IE of ST-Zn^{2+}-HEDP with 100 ppm of SDS system has 98 percent. It is interesting to note that sodium tungstate-Zn^{2+} system has some biocidal efficiency (BE) in Table 8. When HEDP is added, the BE increases from 25% to 75%. When 100 ppm of SDS is added, 100% BE is noticed. The formulation consisting of 50 ppm ST, 10 ppm Zn^{2+}, 200 ppm HEDP and 100 ppm SDS has 100% BE and 98% of corrosion inhibition efficiency. This formulation may find application, if the investigation is carried out at high temperature and under flow condition. In corrosion inhibition with surfactant inhibitors, the critical micelle concentration (CMC) is the most important parameter. When the concentration of surfactant adsorbed on the solid surface is high enough, organized structures (hemi-micelles such as bi or multilayer) are formed, which decrease the corrosion reaction by blocking the metallic surface. A large number of papers concerning this corrosion system in the presence of SDS have been published [34,35]. This formulation may find application, if the investigation is carried out at high temperature and under flow condition.

Table 8. Corrosion rates of mild steel in well water in the presence and absence of inhibitors and the corrosion inhibition efficiencies, biocidal efficiencies of various environments obtained by the weight – loss method.
Inhibitor: ST+Zn^{2+}+HEDP+SDS Immersion period: 7 days

ST ppm	Zn^{2+} ppm	HEDP ppm	SDS ppm	CR mmy	IE %	Colony forming units/mL	Biocidal Efficiency (%)
0	0	0	0	0.0868	-	$8x10^8$	-
50	10	0	0	0.0798	8	$6 x10^8$	25
50	10	200	0	0.0002	98	$2x10^8$	75
50	10	200	50	0.0005	94	$1x10^8$	88
50	10	200	100	0.0002	98	Nil	100
50	10	200	150	0.0003	97	Nil	100
50	10	200	200	0.0035	60	Nil	100
50	10	200	250	0.0019	78	Nil	100

5.3. FTIR spectra

The FTIR spectrum of pure ST is shown in Fig 1a. The WO_4^{2-} stretching frequency of the sodium tungstate appears at 1680 cm^{-1}. The FTIR spectrum of pure HEDP is shown in Fig 1b. The P-O stretching frequency appeared at 1119 cm^{-1}. The FTIR spectrum (KBr Pellet) of the film formed on mild steel surface after immersion in the solution containing 50 ppm of ST, 10 ppm of Zn^{2+} and 200 ppm of HEDP is shown in Fig 1c. The WO_4^{2-} stretching frequency of ST decreased from 1680 cm^{-1} to 1634 cm^{-1}. This suggests that WO_4^{2-} of ST is coordinated with Fe^{2+} on the anodic sites of the metal surface also resulting in the formation of Fe^{2+}-WO_4^{2-} complex. The P-O stretching frequency decreased from 1119 cm^{-1} to 1110 cm^{-1}, which suggests that oxygen atom of HEDP is coordinated with Fe^{2+} on the anodic sites of the metal surface, resulting in the formation of Fe^{2+}-HEDP complex [36-39]. The band at 1345 cm^{-1} is due to $Zn(OH)_2$ is shifted to 1323 cm^{-1} formed on the cathodic sites of the metal surface.



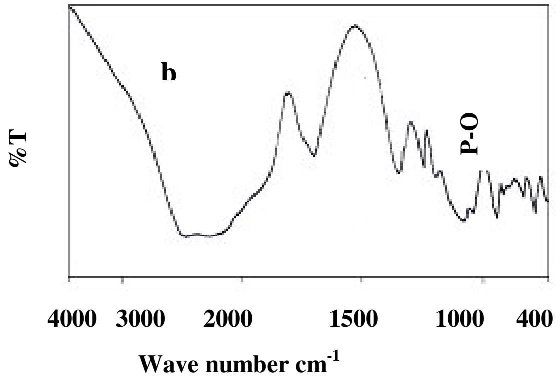


Figure 1-FTIR spectra: a) Pure ST b) Pure HEDP c) Film formed on the carbon steel surface after immersion in the well water containing ST (50 ppm)+ HEDP (200 ppm)+Zn^{2+}(10 ppm)

5.4. Analysis of potentiodynamic polarization curves

The potentiodynamic polarization curves of mild steel immersed in well water medium are shown in Fig 2. The corrosion parameters of mild steel immersed in various test solutions obtained by polarization study are given in Table 9. When mild steel is immersed in well water the corrosion current I_{corr} is $9.642x10^{-5}$A /cm^2. When ST (50 ppm) and Zn^{2+}(10 ppm) are added, it decreases to $8.891x10^{-5}$ A /cm^2. When ST (50 ppm), Zn^{2+}(10 ppm) and HEDP (200 ppm) are added, it decreases to it decreases to $5.402x10^{-5}$ A /cm^2. This significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of the inhibitor. The corrosion potential is shifted to the cathodic side (from -522 to 517 mV vs SCE). Hence the cathodic reaction prominently and reduces the corrosion rate [40,41]. Linear polarization resistance (LPR) value increases in the presence of the inhibitors.

Table 9. Corrosion parameters of mild steel in well water in the presence of inhibitors, obtained by polarization study

System	E_{corr} mVvs SCE	b_a mV	b_c mV	LPR Ω cm^2	I_{corr} A /cm^2
Well water (WW)	-522	148	332	$4.623x10^2$	$9.642x10^{-5}$
WW+ST (50ppm)+Zn^{2+}(10ppm)	-531	178	231	$4.927X10^2$	$8.891x10^{-5}$
WW+ST(50ppm)+Zn^{2+} (10ppm)+ HEDP(200ppm)	-517	129	407	$7.868x10^2$	$5.402x10^{-5}$

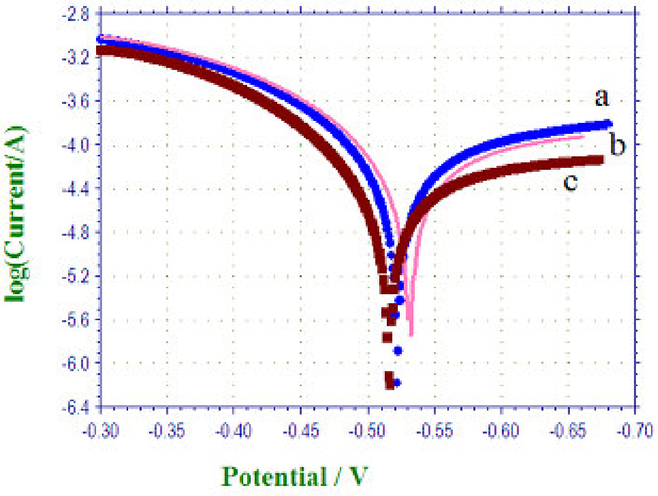


Figure 2. Polarization curves of Mild steel immersed in various test solutions a) Well Water b) Well Water+50 ppm of ST+10 ppm of Zn^{2+} c) Well Water+50 ppm of ST+10 ppm of Zn^{2+}+200 ppm of HEDP

5.5. Analysis of AC impedance spectra

The AC impedance spectra of mild steel immersed in various test solution are shown Fig 3a and 3b. The AC impedance parameters namely, charge transfer resistance (R_t) and double later capacitance (C_{dl}) are given in Table 10. In the presence of well water, the R_t value is 100.136 Ωcm^2

and C_{dl} value is 5.0886x10^{-8} μFcm^{-2}. When ST and Zn^{2+} are added to this solution, R_t value increases to 121.119 Ωcm^2 and the C_{dl} value decreases to 4.4271x10^{-8} μFcm^{-2}. For the formulation consisting of 50 ppm of ST+ 10 ppm of Zn^{2+}+ 200 ppm of HEDP, the R_t value increases to 145.001Ωcm^2 and C_{dl} value decreases 3.5142x10^{-8} μFcm^{-2}. This confirms that the formation of a protective film on the metal surface. This accounts for the very high IE of ST-Zn^{2+}-HEDP system. Fig 4 represents the Bode plots obtained in the absence and the presence of ternary inhibitor formulation. The plot obtained in the presence of inhibitor is characterized by a single time constant. This indicates the formation of a homogeneous film on the metal surface [42,43]. The impedance values increase in presence of inhibitors.

Table 10. Impedance parameters of mild steel immersed in well water the presence and absence of inhibitor obtained by AC impedance spectra

Systems	R_t Ω cm^2	C_{dl} μFcm^{-2}	Impedance Log(z/ohm)
Well water (GW)	100.196	5.0886x10^{-8}	2.03
WW+ST (50ppm)+Zn^{2+}(10ppm)	110.296	4.6198x10^{-8}	2.09
WW+ST(50ppm)+Zn^{2+}(10ppm)+ HEDP(200ppm)	145.001	3.5142x10^{-8}	2.18

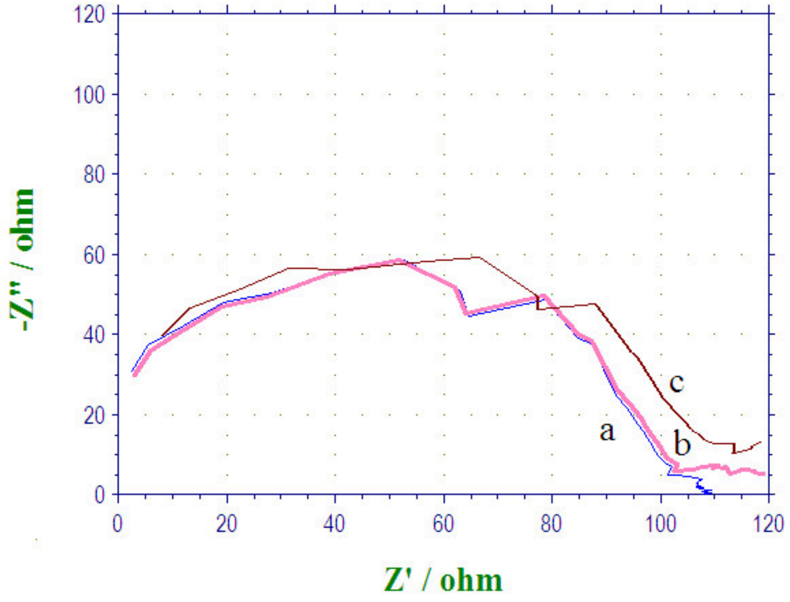


Figure 3. Nyquist plots of Mild steel immersed in various test solutions a) Well Water b) Well Water+50 ppm of ST+10 ppm of Zn^{2+} c) Well Water+50 ppm of ST+10 ppm of Zn^{2+}+200 ppm of HEDP

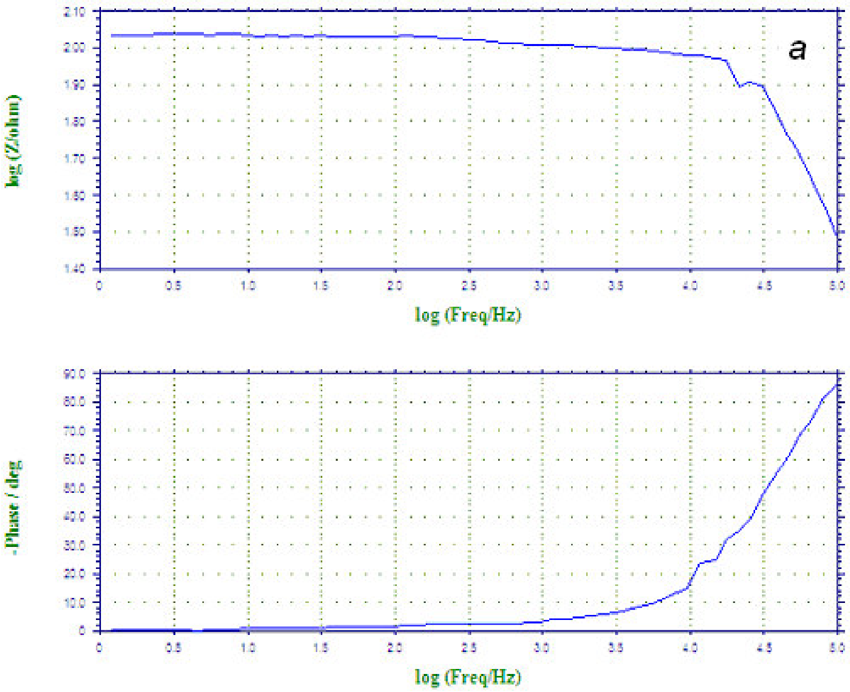


Figure 4a. Bode plots of Mild steel immersed in Well water

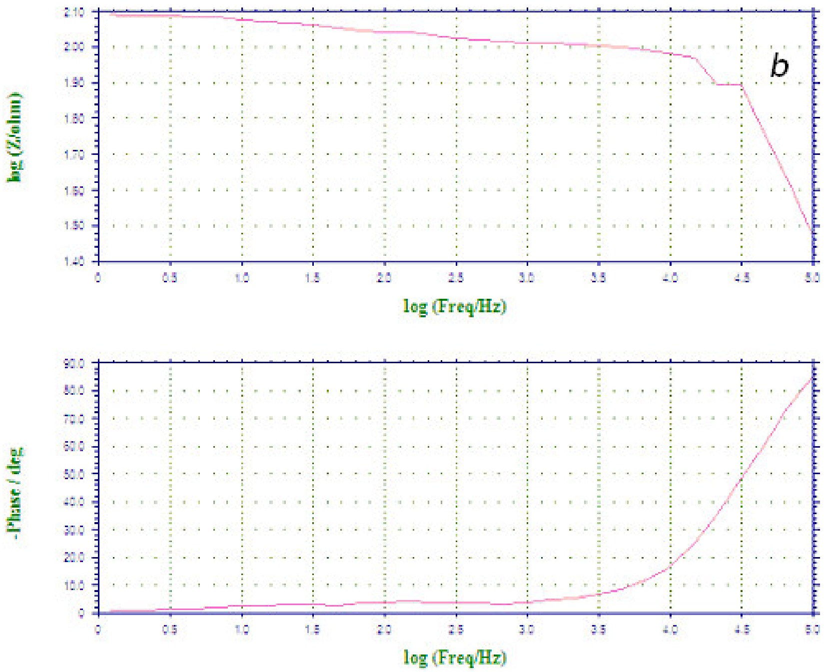


Figure 4b. Bode plots of Mild steel immersed in well water +50 ppm of ST+10 ppm of Zn^{2+}

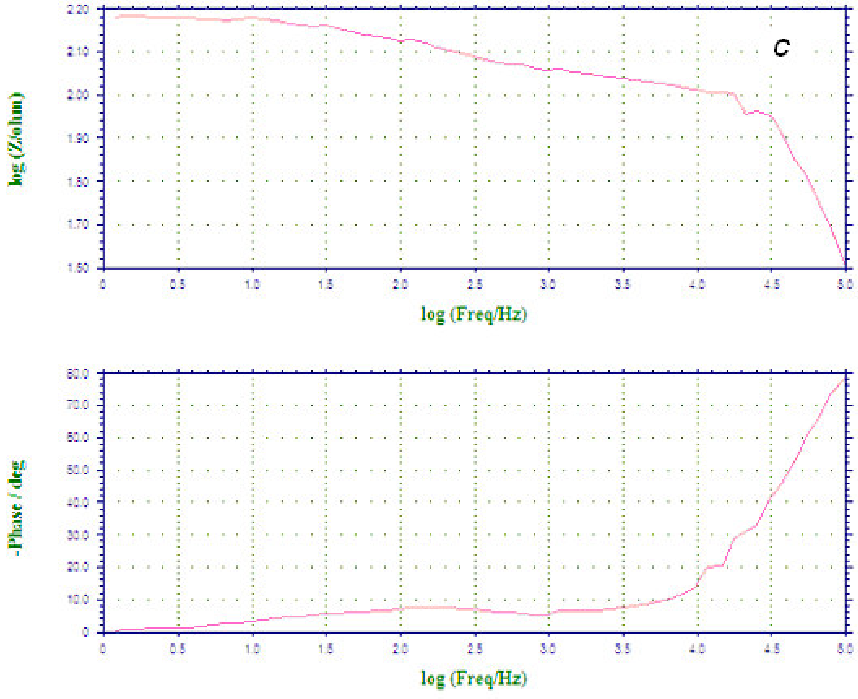


Figure 4c. Bode plots of Mild steel immersed in well water +50 ppm of ST+10 ppm of Zn^{2+}+200 ppm of HEDP

6. MECHANISM

In order to explain the experimental results, the following mechanism of corrosion inhibition is proposed. The mechanistic aspect of the inhibition of mild steel in well water by ST-Zn^{2+} and HEDP can be explained in terms of complexation.

i. Before immersion of mild steel in well water environment, ST, Zn^{2+} and HEDP, zinc ions form complexes, viz., Zn^{2+}-ST, Zn^{2+}-HEDP and Zn^{2+}-ST-HEDP. These complexes are in equilibrium in the solution with free Zn^{2+}, ST and HEDP ions.
ii. During the dissolution of iron, the pH increases at the metal/electrolyte interface due to oxygen reduction. Thus $Zn(OH)_2$ precipitate may take place at cathodic sites [44,45] thus decreasing the rate of further oxygen reduction.
iii. Addition of phosphonic acids (PA) reduces metal dissolution; this may be due to adsorption and complex formation at the surface [44-48, 49,50] with the combined application of $Zn^{2+}$and HEDP, the corresponding anodic and cathodic reactions of the metal can be generalized as follows. Zn^{2+} inhibited the local cathodic region and the local anodic region was inhibited by HEDP.
iv. The Zn-PA complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe-PA complex, which is more stable than Zn-PA [45]. The released

Zn^{2+} causes $Zn(OH)_2$ precipitation at the local cathodic sites. Thus the protective film consists of an Fe-PA complex and $Zn(OH)_2$.

v. The film formed on the metal surface of the mild steel consists of oxides/hydroxides of iron and zinc. It is also likely to comprise of complexes of Fe^{2+}/Fe^{3+} and Zn^{2+} with ST as well as with HEDP.

vi. The FTIR spectrum of the surface film suggests. The formation of these complexes and the presence of $Zn(OH)_2$ in the surface.

7. CONCLUSION

A formulation consisting of Zn^{2+}, ST and HEDP can be used as a potent inhibitor to prevent the corrosion attack of mild steel in well water media. HEDP plays an excellent synergistic role in the ST-Zn^{2+}-HEDP system. The ternary system ST (50 ppm)-Zn^{2+}(10 ppm)-HEDP (200 ppm) is effective and has 98% IE. Significant synergism was attained by the combined application of ST- Zn^{2+}-HEDP. The concentrations of both ST and Zn^{2+} are reduced and HEDP, which is environmentally friendly, is required only at low concentrations. Thus, this new inhibitor formulation is more environment-friendly. The inhibitor formulation acts as an anodic inhibitor. In presence of the inhibitor, the charge transfer resistance is significantly increased. Also, the double layer capacitance of surface film reduced markedly. Both ST and HEDP form stable complexes with metal ions in the metal surface. The protective film consists of $Zn(OH_2)$ and complexes of Fe^{2+}/Fe^{3+} and Zn^{2+} with HEDP and ST.

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