

Realization of Synergism in Sodium Tungstate-Zn²⁺-N-(Phosphenomethyl) Iminodiaceticacid System in Well Water

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Abstract: The aim of this present work is to study, the corrosion behavior of carbon steel in well water in the presence of sodium tungstate (ST)-Zn²⁺-N-(phosphenomethyl) iminodiaceticacid (NPMIDA) solutions. Electrochemical studies and FTIR spectral studies and weight loss study have been employed. It was found that the inhibition efficiency (IE) of ST (50 ppm)-Zn²⁺ (10 ppm) was improved from 8% to 82% by the addition of 150 ppm of NPMIDA. The protective film consists of Fe²⁺-WO₄²⁻, Fe²⁺-NPMIDA complex on anodic site and Zn(OH)₂ complex at cathodic site. The NPMIDA-ST-Zn²⁺ system increases linear polarization resistance value, decreases corrosion current, increases charge transfer resistance and decreases double layer capacitance value. Based on the above results a mechanism of corrosion inhibition is proposed.

Keywords: Carbon steel, corrosion inhibition, N-(phosphenomethyl) iminodiaceticacid oxyanions, F-Test, sodium tungstate, synergistic effect.

1. INTRODUCTION

Corrosion is a natural phenomenon that cannot be avoided completely, but it can be controlled and prevented. It means corrosion mitigation and control methods shall be properly selected to meet the specific environment and operational condition. Depending upon the metal / environment combinations, different types of inhibitors are used in suitable concentrations. Inhibitors for carbon steel in near neutral, aqueous solutions are soluble chromates, dichromates, nitrites, phosphates, borates, benzoates and salts of other carboxylic acids. As passivating inhibitors of iron and its alloys, we can mention the oxyanions of transition elements containing *d*-electrons and vacant *d*-orbitals [1, 2]. First of all, this is true for elements from Group VI b (chromium, molybdenum, and tungsten). In the series Cr-Mo-W, 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 [3]. Thus, in particular, Mo (VI) and W (VI) frequently form polymeric oxyanions of complex structure [4], which is not typical of chromium. Note that, in the presence of inhibitors with common MeO₄⁻ⁿ anion, the surface is passivated only partially. This means that the role played by the nature of cations should also be important. 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 [5-8] are true not only for corrosion but also for the corrosion-mechanical fracture of steel. The protective action of MoO₄²⁻ and WO₄²⁻ in distilled water is approximately identical and in the presence of corrosive ions. WO₄²⁻ was found to be more effective. Also, it is not feasible to use tungstate alone as a corrosion inhibitor in

industrial cooling water systems due to its low oxidizing ability and high cost. So many researches concentrated to use some co-inhibitors [9-15]. Phosphonic acids have been widely used as corrosion inhibitor in neutral medium because of their high corrosion inhibition efficiency and scale-resistance activity, greater stability for hydrolysis and at the same time low toxicity. Synergistic effect of certain phosphonic acids and Zn²⁺ in corrosion inhibition has been reported [16-17]. Organic compounds for protection against corrosion—mainly amino carboxylic acids and their *N*-phosphenomethyl derivatives -with or without additives (zinc or metavanadate ion) have been studied in neutral solution by three different methods *via* impedance spectroscopy, weight loss and potentiostatic polarization in order to show the significance of CH₂-PO₃H₂ substitution and to detect a synergism in the presence of metals. For understanding the synergistic effect the stability of the zinc ion complex with organic acids was determined pH-metrically [18]. The present study evaluates the synergistic effect of sodium tungstate-Zn²⁺ system; estimates the influence of NPMIDA on the IE of ST-Zn²⁺ system; and studies mechanistic aspects of corrosion inhibition by electrochemical studies and analysis protective film by FTIR spectroscopy.

2. EXPERIMENTAL

2.1. Preparation of the Specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, and 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

Carbon 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 Zn²⁺ for seven days. The corrosion product cleaned with Clark's solution [19]. The parameter of the well water is given in Table 1.

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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 $\mu\text{mhos cm}^{-1}$
Chloride	665 ppm
Sulphate	14 ppm
TDS	2013 ppm
Total hardness	1100 ppm

2.3. Surface Examination Study

The carbon 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 metal specimens was analyzed by surface analysis technique, FTIR spectra.

FTIR Spectra

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

2.4. 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 carbon steel with one face of the electrode of constant 1 cm² 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 *iR* 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 E_f (s) was zero and quiet time (s) was 2.

2.5. 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) = 1×10^5 , Low frequency (Hz) = 1; Amplitude (v) = 0.05 and Quiet time (s) = 2.

2.6. 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-Zn²⁺-NPMIDA 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 carbon 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 hydrotropic 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.

2.7. Synergism Parameter (S_1)

Synergism parameters are indications of synergistic effect existing between the inhibitors [20, 21]. S_1 value is found to be greater than one suggesting that the synergistic effect between the inhibitors.

$$S_1 = 1 - I_{1+2} / 1 - I'_{1+2}$$

where I_1 = Inhibition efficiency of substance 1

I_2 = inhibition efficiency of substance 2

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

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

2.8. Analysis of Variance (F-test)

F-test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant [22]. If F-value is above 5.32 for 1,8 degrees of freedom, it was proved to be statistically significant. If it is below the value of 5.32 for 1,8 degrees of freedom, it was statistically insignificant at 0.05 level of significance confirmed.

3. RESULTS AND DISCUSSION

3.1. Weight loss Method

Evaluation of Improvement of IE of Zn²⁺ with Tungstate

The inhibition efficiency (IE) of sodium tungstate (ST) in controlling corrosion of carbon steel immersed in well water for a period of seven days in the absence and the presence of Zn²⁺ is given in Table 2. It can be seen from the data that ST alone shows some IE whereas Zn²⁺ alone is found to be corrosive. In the absence of ST, the rate of transport of Zn²⁺ 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 have already been reported [23, 24]. When ST is combined with Zn²⁺ ions it is

found that the IE increase with concentration of Zn²⁺ ions. For example, 250 ppm ST has only 12% IE and 50 ppm of Zn²⁺ has only -12 % IE. Interestingly their combination shows 98% IE. This suggests a synergistic effect between the binary inhibitor formulation ST and Zn²⁺ ions; ST is able to transport Zn²⁺ towards the metal surface.

Table 2. Corrosion Rates (CR) of Carbon 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

3.2. Evaluation of Synergistic Effect of NPMIDA with Tungstate-Zn²⁺ System

In order to examine the role of NPMIDA in the ternary inhibitor formulation, experiments were conducted with NPMIDA alone, ST and with Zn²⁺+NPMIDA in a wide concentration range. The highest inhibition efficiencies with these systems are shown in Table 3. The synergistic effect in the ST-Zn²⁺-NPMIDA system is evident from the data in Table 3. The Zn²⁺ ion acts as one synergist and NPMIDA acts as the other. From the Table 3, it is seen that at relatively higher concentrations of both ST and Zn²⁺ 98% IE was obtained. However, such an efficiency is not obtained with combinations if ST and NPMIDA, even at relatively high concentrations. Thus, it may be concluded that Zn²⁺ is the primary synergistic and NPMIDA 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.

3.3. Influence of Immersion Period on the ST-Zn²⁺-NPMIDA System

The influence of immersion period on IE of ST (50 ppm)-Zn²⁺(10 ppm)-NPMIDA (150 ppm) is given in Table 4. It is found that as the immersion period increases, the

inhibition efficiency decreases [25]. 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-NPMIDA 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 NPMIDA 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 3. Corrosion Rates (CR) and Inhibition Efficiencies (IE) of Carbon 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	NPMIDA ppm	IE %	CR mmy
0	0	0	-	0.0868
50	0	0	2	0.0850
0	10	0	-12	0.0972
0	0	150	10	0.0781
0	10	150	14	0.0746
50	10	0	8	0.0798
50	10	50	41	0.0512
50	10	100	56	0.0382
50	10	150	92	0.0069
50	10	200	73	0.0234
50	10	250	50	0.0434
50	0	150	59	0.0356

Table 4. Influence of Immersion Period on the IE of ST (50 ppm)-Zn²⁺ (10 ppm)-NPMIDA (150 ppm) System

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⁺ (10ppm)- NPMIDA (150 ppm) CR (mmy)	0.0003	0.0006	0.0042	0.0069
IE (%)	98	98	95	92

3.4. Synergism Parameter (S₁)

The values of synergism parameters are shown in Table 5. Here values of S₁ are greater than one, suggesting a synergistic effect. S₁ 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).

Table 5. Synergism Parameter of Carbon Steel Immersed in Well Water in the Presence and Absence of Inhibitor

ST+Zn ²⁺ (I ₂) IE (%)	NPMIDA (I ₁) IE (%)	ST-Zn ²⁺ -NPMIDA (I ₁₊₂) IE (%)	S _i
8	40	41	6.8
8	13	56	1.52
8	10	92	0.69
8	3	73	12.8
8	-9	50	1.14

3.5. Analysis of Variance (ANOVA)

To investigate whether the influence of Zn²⁺ on the inhibition efficiencies of ST combined with NPMIDA is statistically significant, F-test was carried out [22]. The results are given Tables 6 and 7. In Table 6, the influence of 50 ppm of ST and 10 ppm of Zn²⁺ on the inhibition efficiencies of 50,100,150,200,150 ppm of NPMIDA is investigated. The obtained F-value is 0.176. It is not statistically significant, since it is less 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 Zn²⁺ on the inhibition efficiencies of concentrations of ST, Zn²⁺ and 150 ppm of NPMIDA is statistically significant. In Table 7, the influence of 50 ppm of Zn²⁺ on the inhibition efficiencies of 50,100,150,200,150 ppm of NPMIDA is investigated. The obtained F - value 9.77 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 Zn²⁺ on the inhibition efficiencies of various concentrations of NPMIDA is statistically significant.

Table 6. Distribution of F Value Between the Inhibition Efficiencies of the Influence of ST-Zn²⁺ and NPMIDA

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	Level of Significance of F
Between	28.9	1	28.9	0.176	p<0.05
Within	1309.2	8	163.65		

Table 8. Corrosion Rates of Carbon 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

ST ppm	Zn ²⁺ ppm	NPMIDA 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	150	0	0.0512	41	7x10 ⁸	13
50	10	150	50	0.0382	56	5x10 ⁸	38
50	10	150	100	0.0069	92	Nil	100
50	10	150	150	0.0234	73	Nil	100
50	10	150	200	0.0434	50	Nil	100
50	10	150	250	0.0356	59	Nil	100

Table 7. Distribution of F Value Between the Inhibition Efficiencies of the Influence of ST-Zn²⁺ and ST-Zn²⁺-NPMIDA Systems

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	Level of Significance of F
Between	6864.4	1	6864.4	9.77	p>0.05
Within	5617.40	8	702.18		

3.6. Effect of Sodium Dodecyl Sulphate (SDS) on the Inhibition Efficiency of ST-Zn²⁺-NPMIDA

The influence of various concentrations of SDS on the IE of ST-Zn²⁺-NPMIDA system is given in Table 8. It is observed that IE of ST-Zn²⁺-NPMIDA with 100 ppm of SDS system has 98 percent. It is interesting to note that sodium tungstate-Zn²⁺ system has some biocidal efficiency (BE) in Table 8. When NPMIDA is added, the BE increases from 25% to 38%. When 100 ppm of SDS is added, 100% BE is noticed. The formulation consisting of 50 ppm ST, 10 ppm Zn²⁺, 150 ppm NPMIDA and 100 ppm SDS has 100% BE and 98% of corrosion inhibition efficiency. 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 [26, 27]. This formulation may find application, if the investigation is carried out at high temperature and under flow condition.

3.7. FTIR Spectra

The FTIR spectrum of pure ST is shown in Fig (1A). The WO₄²⁻ stretching frequency of the sodium tungstate appears at 1680 cm⁻¹. The FTIR spectrum of pure NPMIDA is shown in Fig (1B). The P-O stretching frequency appeared at 1085 cm⁻¹ and C-N stretching frequency appeared at 1134 cm⁻¹. The FTIR spectrum (KBr Pellet) of the film formed on carbon steel surface after immersion in the solution containing 50 ppm of ST, 10 ppm of Zn²⁺ and 150 ppm of NPMIDA is

shown in Fig (1C). The WO_4^{2-} stretching frequency of ST decreased from 1680 cm^{-1} to 1630 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 C-N stretching frequency of NPMIDA shifted from 1134 cm^{-1} to 1106 cm^{-1} and the P-O stretching frequency decreased from 1085 cm^{-1} to 1027 cm^{-1} . This suggests that nitrogen and oxygen atom of NPMIDA are coordinated with Fe^{2+} on the anodic sites of the metal surface, resulting in the formation of Fe^{2+} -NPMIDA complex [28-31]. The band at 1324 cm^{-1} is due to $\text{Zn}(\text{OH})_2$ formed on the cathodic sites of the metal surface.

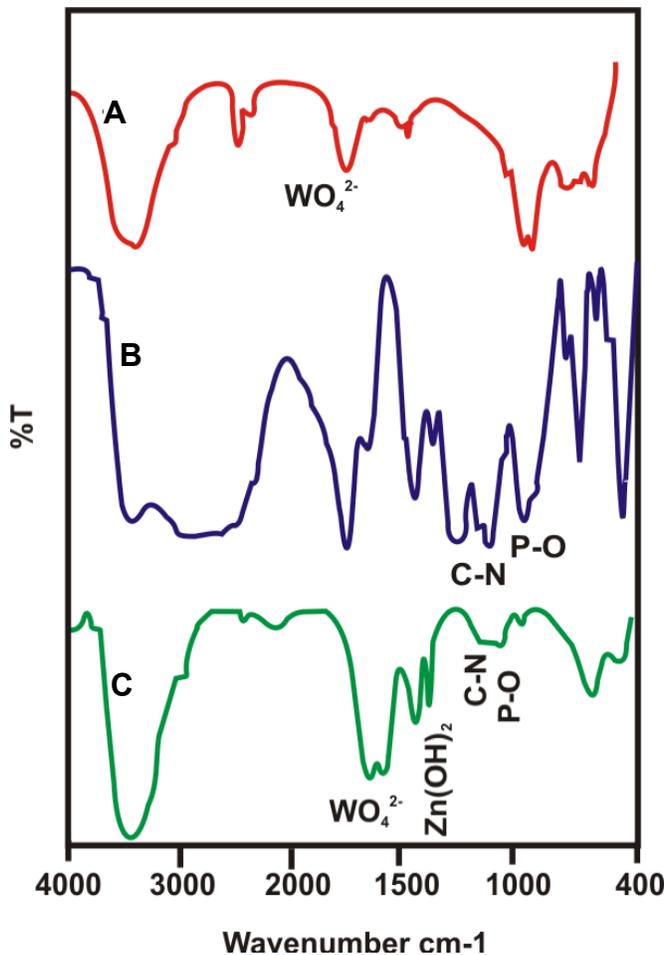


Fig. (1). FTIR spectra. A. Pure ST, B. Pure NPMIDA, C. Film formed on the carbon steel surface after immersion in the well water containing ST (50 ppm)+ NPMIDA (150 ppm)+ Zn^{2+} (10 ppm).

3.8. Analysis of Potentiodynamic Polarization Curves

The potentiodynamic polarization curves of carbon steel immersed in well water medium are shown in Fig (2). The

corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 9. When carbon steel is immersed in well water the corrosion current I_{corr} is $9.642 \times 10^{-5}\text{ A/cm}^2$. When ST (50 ppm) and Zn^{2+} (10 ppm) are added, it decreases to $8.891 \times 10^{-5}\text{ A/cm}^2$. When ST (50 ppm), Zn^{2+} (10 ppm) and NPMIDA (150 ppm) are added, it decreases to $5.228 \times 10^{-5}\text{ A/cm}^2$. This significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of the inhibitor. This significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of the inhibitors. The corrosion potential is shifted to the cathodic side (from -522 to -534 mV vs SCE). Hence the cathodic reaction prominently and reduces the corrosion rate [32, 33]. Linear polarization resistance (LPR) value increases in the presence of the inhibitors.

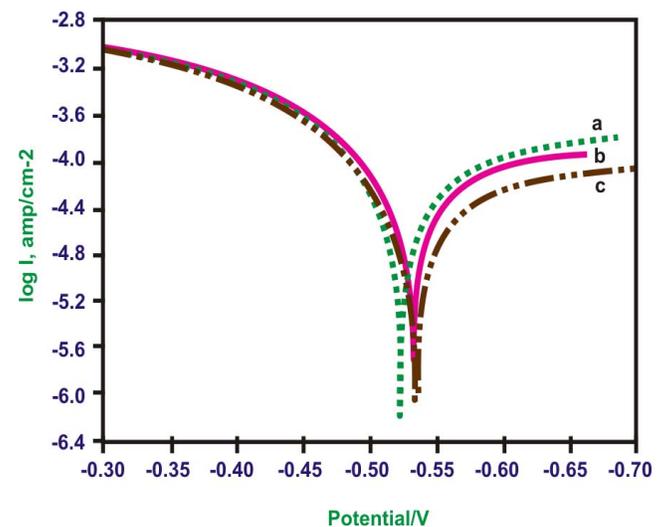


Fig. (2). Polarization curves of carbon steel immersed in various test solutions. (a) Well Water, (b) Well Water+50 ppm of ST+10 ppm of Zn^{2+} , (c) Well Water+50 ppm of ST+10 ppm of Zn^{2+} +150 ppm of NPMIDA.

3.9. Analysis of AC Impedance Spectra

The AC impedance spectra of carbon steel immersed in various test solution are shown in Fig. (3a, b, c). The AC impedance parameters namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 10. In the presence of well water, the R_t value is $100.136\text{ }\Omega\text{cm}^2$ and C_{dl} value is $5.0886 \times 10^{-8}\text{ }\mu\text{Fcm}^2$. When ST and Zn^{2+} are added to this solution, R_t value increases to $121.119\text{ }\Omega\text{cm}^2$ and the C_{dl} value decreases to $4.4271 \times 10^{-8}\text{ }\mu\text{Fcm}^2$. For the formulation consisting of 50 ppm of ST+ 10 ppm of Zn^{2+} + 150 ppm of NPMIDA, the R_t value increases to $121.119\text{ }\Omega\text{cm}^2$ and C_{dl} value decreases $4.4271 \times 10^{-8}\text{ }\mu\text{Fcm}^2$. This con-

Table 9. Corrosion Parameters of Carbon Steel in Well Water in the Presence of Inhibitors, Obtained by Polarization Study

Systems	E_{corr} mV vs SCE	b_a mV	b_c mV	LPR $\Omega\text{ cm}^2$	I_{corr} A cm^{-2}
Well water (WW)	-522	148	332	4.623×10^2	9.642×10^{-5}
WW+ST(50 ppm)+ Zn^{2+} (10 ppm)	-531	178	231	4.927×10^2	8.891×10^{-5}
WW+ST(50 ppm)+ Zn^{2+} (10 ppm)+ NPMIDA(150 ppm)	-534	128	351	7.624×10^2	5.228×10^{-5}

Table 10. Impedance Parameters of Carbon Steel Immersed in Well Water Obtained by AC Impedance Spectra

Systems	R _t , Ω cm ²	C _{dl} , μF cm ⁻²	Impedance log (z/ohm)
Well water (WW)	100.196	5.0886x10 ⁻⁸	2.03
WW+ST (50 ppm)+Zn ²⁺ (10 ppm)	110.296	4.6198x10 ⁻⁸	2.06
WW+ST(50ppm)+Zn ²⁺ (10 ppm)+NPMIDA (150 ppm)	121.119	4.4271x10 ⁻⁸	2.09

firmly that the formation of a protective film on the metal surface. This accounts for the very high IE of ST-Zn²⁺-NPMIDA 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 [34, 35]. The impedance values increase in the presence of inhibitors.

MECHANISM

In order to explain the experimental results, the following mechanism of corrosion inhibition is proposed. The mechanistic aspect of the inhibition of carbon steel in well water by ST-Zn²⁺ and NPMIDA can be explained in terms of complexation and adsorption.

- i. Before immersion of carbon steel in well water environment, ST, Zn²⁺ and NPMIDA, Zinc ions form complexes, viz., Zn²⁺-ST, Zn²⁺-NPMIDA and Zn²⁺-ST-NPMIDA. These complexes are in equilibrium in the solution with free Zn²⁺, ST and NPMIDA ions.

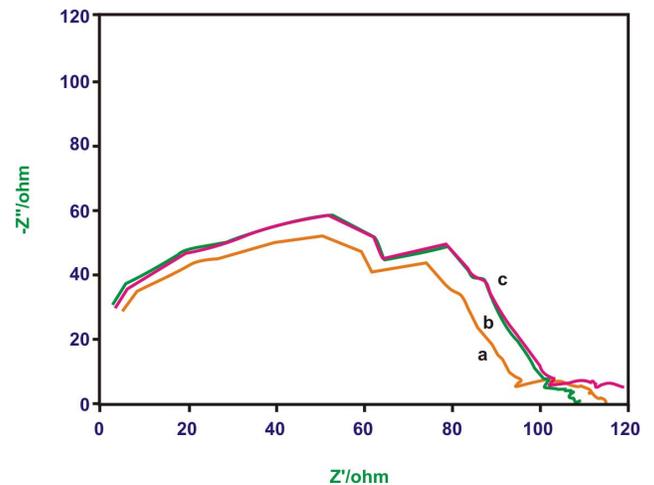


Fig. (3). Nyquist plots of carbon steel immersed in various test solutions. (a) Well water, (b) Well water+50 ppm of ST+10 ppm of Zn²⁺, (c) Well water+50 ppm of ST+10 ppm of Zn²⁺+150 ppm of NPMIDA.

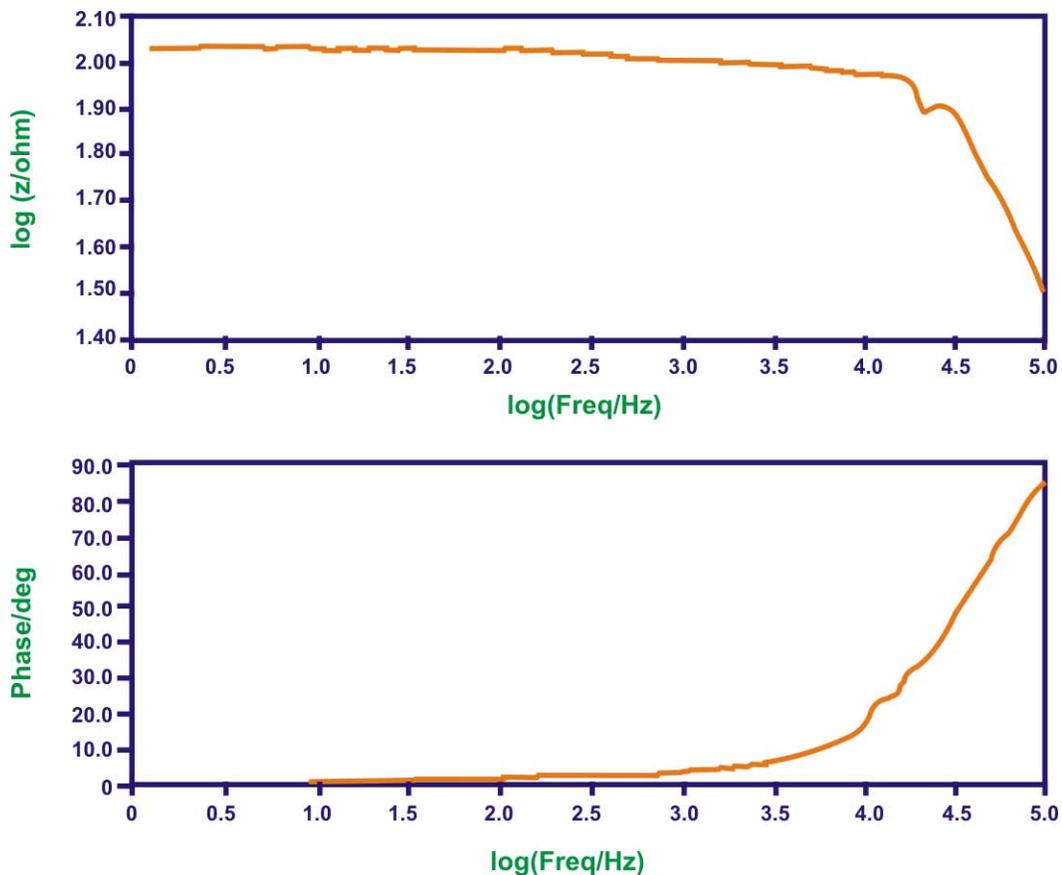


Fig. (4a). Bode plots of carbon steel immersed in well water.

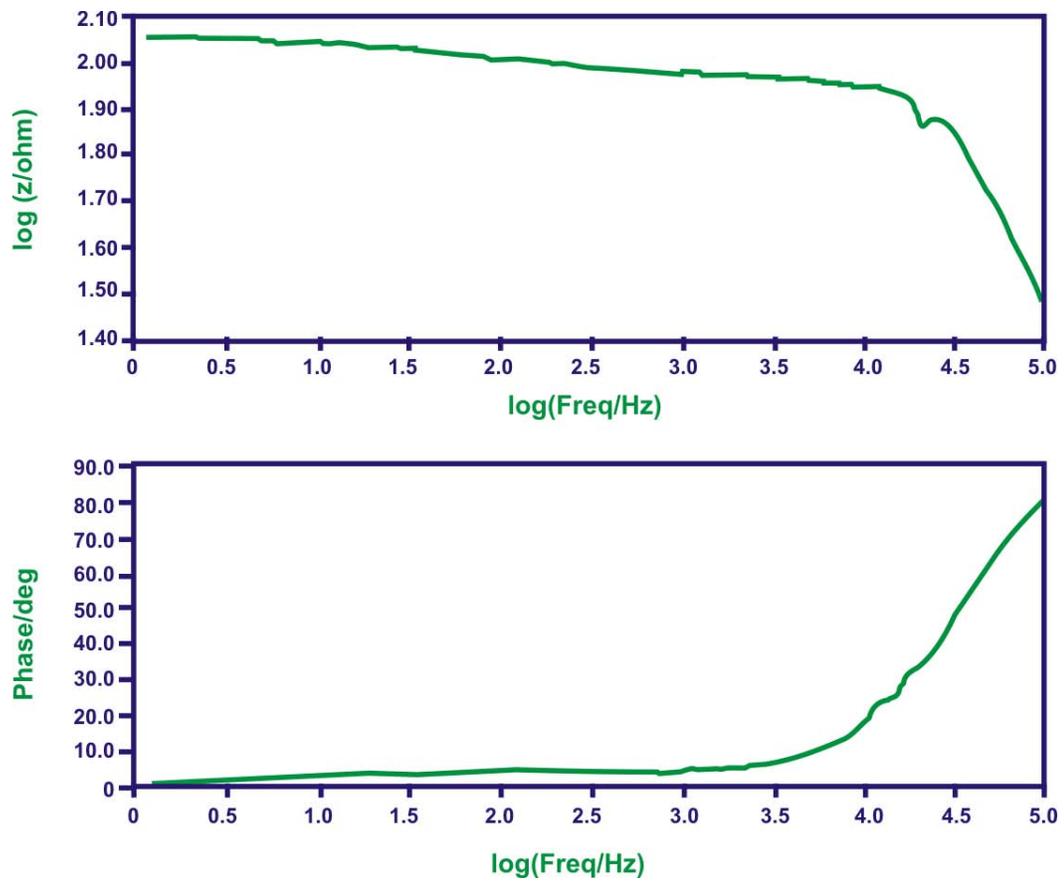


Fig. (4b). Bode plots of carbon steel immersed in well water +50 ppm of ST+10 ppm of Zn^{2+} .

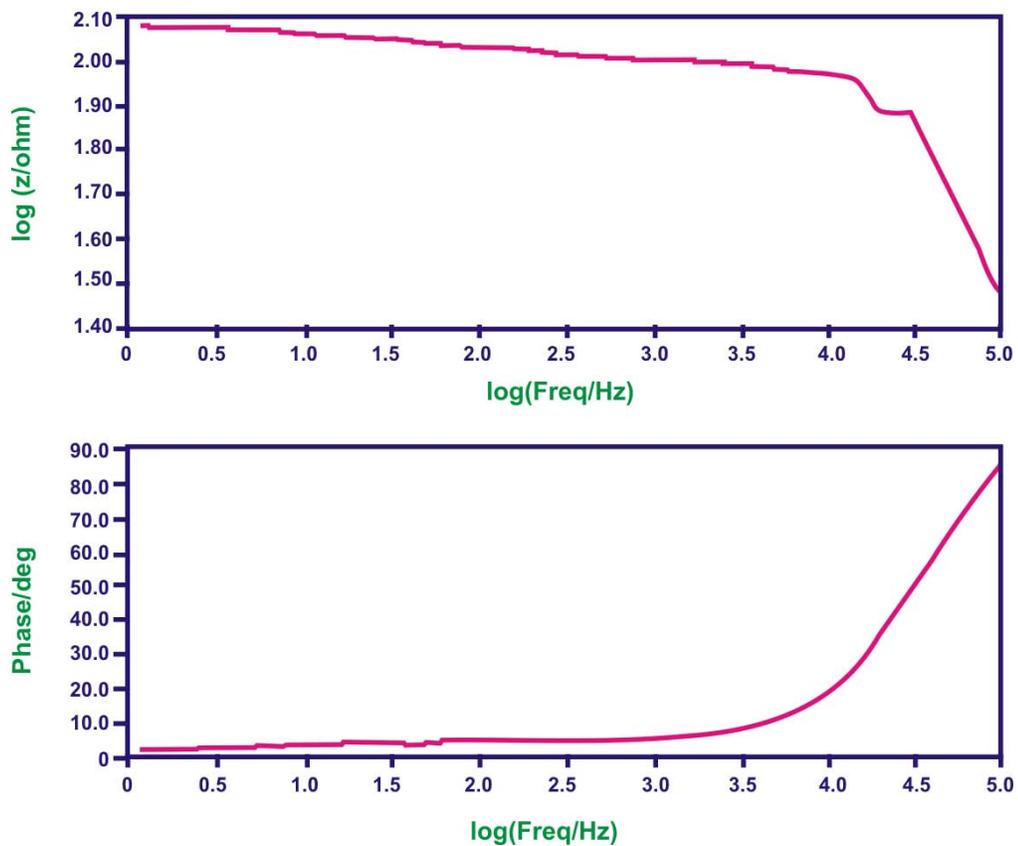


Fig. (4c). Bode plots of carbon steel immersed in well water +50 ppm of ST+10 ppm of Zn^{2+} +150 ppm of NPMIDA.

- 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 [34, 35] 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 [36-40] with the combined application of Zn²⁺ and NPMIDA, the corresponding anodic and cathodic reactions of the metal can be generalized as follows. Zn²⁺ inhibited the local cathodic region and the local anodic region was inhibited by NPMIDA.
- 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 [41]. The released Zn²⁺ 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 carbon steel consists of oxides/hydroxides of iron and zinc. It is also likely to comprise complexes of Fe²⁺/Fe³⁺ and Zn²⁺ with ST as well as with NPMIDA.
- vi. The FTIR spectra of the surface film suggests, the formation of these complexes and the presence of Zn(OH)₂ in the surface.

CONCLUSION

The present study leads to the following conclusions

1. A formulation consisting of Zn²⁺, ST and NPMIDA can be used as a potent inhibitor to prevent the corrosion attack of carbon steel in well water media. NPMIDA plays an excellent synergistic role in the ST-Zn²⁺-NPMIDA system.
2. The ternary system ST (50 ppm)-Zn²⁺(10 ppm)-NPMIDA (250 ppm) is effective and has 98% IE. Significant synergism was attained by the combined application of ST-Zn²⁺-NPMIDA.
3. The concentrations of both ST and Zn²⁺ are reduced and NPMIDA, which is environmentally friendly, is required only at low concentrations. Thus, this new inhibitor formulation is more environment-friendly.
4. The inhibitor formulation acts as an cathodic inhibitor. In presence of the inhibitor, the charge transfer resistance is significantly increased. Also, the double layer capacitance of surface film reduced markedly.
5. Both ST and NPMIDA form stable complexes with metal ions in the metal surface. The protective film consists of Zn(OH)₂ and complexes of Fe²⁺/Fe³⁺ and Zn²⁺ with NPMIDA.

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