Inhibition of Corrosion of Carbon Steel by Resorcinol-Zn^{2+} System in Well Water

Benita Sherine[1]* , A. Jamal Abdul Nasser[2] and S. Rajendran[3]

ABSTRACT

The inhibition efficiencies of inhibitor systems constituting various combinations of resorcinol and zinc ions in controlling corrosion of carbon steel immersed in well water have been evaluated by weight loss method. 75 ppm of zinc has 36% inhibition efficiency (Immersion period =7 days). When 100 ppm of resorcinol is added, the IE increases to 96%. The nature of the protective film formed on the metal surface has been analyzed by FTIR spectra, SEM and AFM analysis. The protective film is found to consist of Fe^{2+} - resorcinol complex and Zn(OH)$_2$.

Keywords: *atomic force microscopy, carbon steel, corrosion inhibition, scanning electron microscopy, synergistic effect.*

1. INTRODUCTION

LOT of interest has been generated in the study of organic compounds as corrosion inhibitors, owing to their usefulness in several industries, during the pickling of metals, cleaning of boilers, acidification of oil wells, etc[1]. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms[2-5]. The presence of hetero atom in an organic compound with unsaturated bonds, causes adsorption on the metal surface thereby reducing metal dissolution. The presence of an hydroxyl group can increase the solubility of the inhibitor, leading to higher inhibition efficiency [6] In most inhibition studies the formation of donor acceptor surface complexes between free or pi-electrons of an inhibitor and vacant d-orbital of a metal were postulated [7]. Kulkarni et al [8] have studied the corrosion inhibition of mild steel in nitric acid, sulphuric acid and hydrochloric acid media by phenols. The trend observed among the phenols in corrosion inhibition efficiency is p-cresol > m-cresol>phenol> 2-naphthol>1-naphthol> 2-nitrophenol. Among naphthols, 2-naphthol was more efficient inhibitor than 1-naphthol. Viswanatham and Haldar have investigated the inhibitory action of methoxy phenol and nonyl phenol on corrosion of N80 steel in 15% HCl at different period of exposure (6 to 24h) and temperature (30 to 110^{0}C). Nonyl phenol and methoxy phenol have shown maximum inhibition of about 83 and 78% at 75mM inhibitor concentration in the acid after 6h at ambient temperature [9]. The aim of this work is to shed more light on the inhibitive action of resorcinol on carbon steel in well water which can be used in cooling water systems and to investigate synergistic corrosion inhibition for the resorcinol and Zn^{2+} combination to carbon steel immersed in well water. The corrosion inhibition efficiency was evaluated using weight loss method, polarization study and the AC impedance spectra. The protective film formed on the metal surface is characterized with the help of surface analytical techniques such as Fourier Transorm Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

2. EXPERIMENTAL SETUP AND OBSERVATIONS

2.1 Preparation of the specimen

Carbon steel specimens (0.03% S, 0.05% P, 0.5% Mn, 0.15%C and the rest iron) of dimensions 1.0 x 4.0 x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies. The environment chosen is well water and the physico-

1   Benita Sherine, Department of Chemistry, Holy Cross College, Tiruchirappalli - 620 002, Tamilnadu, India.Email: beni2@rediffmail.com
2   A. Jamal Abdul Nasser, Department of Chemistry, Jamal Mohammed College, Tiruchirappalli - 620 020, Tamilnadu, India. Email: ajanasser@yahoo.com
3   S. Rajendran, Department of Chemistry, GTN Arts College, Dindigul - 624 005, Tamilnadu,Email: srmjoany@sify.com

chemical parameters of well water are given in Table I.

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Table - I

Physico-chemical parameters of well water

Parameters	Value
pH	8
TDS	2018 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total Hardness	1100 ppm
Conductivity	3110 mhos/cm

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2.2 Weight-loss method

Three carbon steel specimens were immersed in 100ml of the solutions containing well water and various concentrations of the inhibitor in the absence and presence of Zn^{2+} for a period of seven days. The corrosion product is cleaned with Clark's solution [10]. The weights of the specimens before and after immersion were determined using a Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship

IE = $(1-W_2/W_1) \times 100$ %

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

2.3 FTIR spectra

The FTIR spectra were recorded with the Perkin Elmer 1600 spectrophotometer. The protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

2.4 Scanning Electron Microscopic studies (SEM)

The carbon steel immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of the carbon steel were examined using Hitachi S-3000 H computer controlled scanning electron microscope.

2.5 Atomic Force Microscopy Characterization (AFM)

The mild steel specimen immersed in blank and in

the inhibitor for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the mild steel surface were carried by atomic force microscopy (AFM) using Pico SPM 2100 with the software version of Pico scan version 5.4.

2.6 Potentio-dynamic polarization study

Polarization study was carried out in H&CH electrochemical workstation impedance Analyzer Model CHI 660A provided with iR compensation facility, using a three electrode cell assembly. Carbon steel was used as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. After having done IR compensation, polarization study was carried out at a sweep rate of 0.01 V/Sec. The corrosion parameters such as linear polarization resistance (LPR), corrosion potential Ecorr, corrosion current Icorr and Tafel slopes (bc and ba) were measured. 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.

2.7 Alternating Current Impedance Spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part and the imaginary part of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

$R_t = (R_s + R_t) - R_s$
where R_s = solution resistance
$C_{dl} = 1/2 \prod R_t f_{max}$
Where f_{max} = maximum frequency.

AC Impedance spectra were recorded with initial E(v) =0; High frequency (Hz) =1×105, Low frequency (Hz) =1; Amplitude (v) = 0.05 and Quiet time (s) =2.

2.8 Synergism Parameter (SI)

Synergism parameters are indications of synergistic effect existing between the inhibitors [11-13]. If S_1 value is found to be greater than one it suggests that a synergistic effect exists between the inhibitors.

$$S_1 = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

Where,

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$$

θ_1 = Surface coverage (θ) of inhibitor resorcinol

θ_2 = Surface coverage (θ) of inhibitor Zn^{2+}

θ'_{1+2} = Combined surface coverage (θ) of inhibitor resorcinol and Zn^{2+}.

2.9 Analysis of Variance (F-Test)

F-Test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant [14]. If the 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.

3. RESULTS AND DISCUSSION

3.1 Weight loss study

The inhibition efficiency (IE) of sodium salt of resorcinol in controlling corrosion of carbon steel immersed in well water for a period of seven days in the absence and presence of Zn^{2+} is given in Table II. It can be seen from data that Zn^{2+} alone has some IE and resorcinol alone is a poor inhibitor and is found to be corrosive i.e. 50 ppm of resorcinol gives -80 % IE. However, the combination of both shows a better IE. For example, carbon steel immersed in 100 ppm of resorcinol offers -78 % IE and 75 ppm of Zn^{2+} solution gives 36 % while the combination of 100 ppm of resorcinol and 75 ppm of Zn^{2+} gives 96 %. This is found to be the maximum IE offered by the system. This clearly suggests that Zn^{2+} and resorcinol mutually enhance the inhibition efficiency of each other in controlling the corrosion of carbon steel. The synergism is due to the formation of complex with resorcinol and the role of Zn^{2+} is to transport the resorcinol inhibitor from the bulk of the solution onto the metal surface [15-17].

Table - II
Inhibition efficiencies (IE) obtained from resorcinol-Zn^{2+} systems when carbon steel is immersed in well water.
Inhibitor system: resorcinol + Zn^{2+} Immersion period: 7 days

resorcinol ppm	Inhibition efficiency (IE)% Zn^{2+} (ppm)					
	0	10	25	50	75	100
0	0	10	15	25	36	50
50	-80	12	36	83	87	96
100	-78	-3	69	56	96	87
150	-44	-22	-56	54	90	77
200	-36	-37	-38	50	78	73
250	-10	-56	-28	26	62	62

3.2 Influence of immersion period on the IE of resorcinol- Zn^{2+} system

The influence of immersion period on the IE of the sodium salt of resorcinol (100 ppm) - Zn^{2+} (75 ppm) system is given in Table III. It is found that as the immersion period increases, the inhibition efficiency decreases. The inhibitor formulation in well water offers 96 % at the end of 7 days of immersion. However, when the duration of immersion is prolonged, a gradual reduction in IE is noted. This is because the protective film formed on the surface becomes unstable due to the attack of the Cl⁻ ion in the solution. A competition between the formation of two films namely, Fe-resorcinol complex and Fe-chloride complex is found to take place [18]. It appears that initially the formation of Fe-resorcinol complex, which forms a thin film on the surface is favoured; this protects the metal from the attack of Cl⁻. However, Fe-resorcinol film is unable to sustain the attack of Cl⁻ for a long period and the film breaks and pit nucleation occurs. Hence, a decrease in IE with increase in the duration of immersion is observed [19].

Table - III
Influence of Immersion period on the IE of resorcinol -Zn^{2+} system

Immersion period (day)	7	10	15	20	30
System: Well water CR (mpy)	55.43	142.25	304.43	352.80	498.62
System: Well water+ resorcinol (100 ppm) +Zn^{2+} (75 ppm) CR (mpy)	2.21	7.76	15.52	16.62	37.13
IE (%)	96	86	72	70	33

3.3 Synergism Parameter (S_I)

The values of synergism parameters are shown in Table IV. Here the values of S_I are greater than one, suggesting a synergistic effect. SI approaches 1 when no interaction exists between the inhibitor compounds. When S_I>1, this points to synergistic effect.

In the case of S_I< 1, the negative interaction of inhibitor prevails, (i.e. corrosion rate increases). From Table 4, it can be seen that the values of S_I are greater than unity, suggesting that the phenomenon of synergism existing between resorcinol and Zn^{2+}. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} ions to resorcinol is only due to the synergistic effect.

Table - IV

Inhibition efficiencies and synergism parameters for various concentrations of resorcinol- Zn^{2+} systems, when carbon steel is immersed in well water.

resorcinol ppm	Zn^{2+} (ppm)									
	0 ppm	10 ppm	S_I	25 ppm	S_I	50 ppm	S_I	75 ppm	S_I	100 ppm	S_I
0	0	10	-	15	-	25	-	36	-	50	-
50	-80	12	1.84	36	2.39	83	7.94	87	8.86	96	22.50
100	-78	-3	1.55	69	4.88	56	3.03	96	28.48	87	6.84
150	-44	-22	1.06	-56	0.78	54	2.34	90	9.21	77	3.13
200	-36	-37	0.89	-38	0.83	50	2.04	78	3.95	73	2.51
250	-10	-56	0.63	-28	0.73	26	1.11	62	1.85	62	0.88

3.4 Analysis of variance (ANOVA)

To investigate whether, the influence of Zn^{2+} on the inhibition efficiencies of resorcinol is statistically significant, F-test was carried out [20]. The results are given in Table V. The results of Analysis of Variance (ANOVA) shows the influence of 10 ppm, 25 ppm, 50 ppm, 75 ppm and 100 ppm of Zn^{2+} on the inhibition efficiencies of 50,100,150, 200, 250 ppm of resorcinol.

The obtained F-value 2.51 for 10 ppm Zn^{2+}, 2.86 for 25 ppm Zn^{2+} was not statistically significant, since it was 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 10 ppm Zn^{2+}, 25 ppm Zn^{2+} on the inhibition efficiencies of various concentrations of resorcinol is not statistically significant.

The obtained F-value 44.8 for 50 ppm Zn^{2+}, 499.9 for 75 ppm Zn^{2+}, 79.4 for 100 ppm Zn^{2+} was statistically significant, since the obtained F values

Table - V

Distribution of F - value between the inhibition efficiencies of various concentrations of resorcinol (0 ppm Zn^{2+}) and the inhibition efficiencies of resorcinol in the presence of 10, 25, 50, 75, 100 ppm Zn^{2+}.

Zn^{2+} (ppm)	Source of variance	Sum of squares	Degrees of freedom	Mean Square	F	Level of significance of F
10	Between	2016.40	1	2016.40	2.51	p<0.05
	Within	6410	8	801.25		
25	Between	5336.10	1	5336.10	2.86	p<0.05
	Within	14878.40	8	1859.80		
50	Between	28944.40	1	28944.40	44.8	p>0.05
	Within	5160	8	645		
75	Between	43692.10	1	43692.10	499.9	p>0.05
	Within	699.20	8	87.4		
100	Between	41344.90	1	41344.90	79.4	p>0.05
	Within	4164.20	8	520.5		

were 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+}, 75 ppm Zn^{2+}, 100 ppm Zn^{2+} on the inhibition efficiencies of various concentrations of resorcinol are statistically significant.

3.5 FTIR spectra

The FTIR spectrum of pure resorcinol is given in Fig 1a.
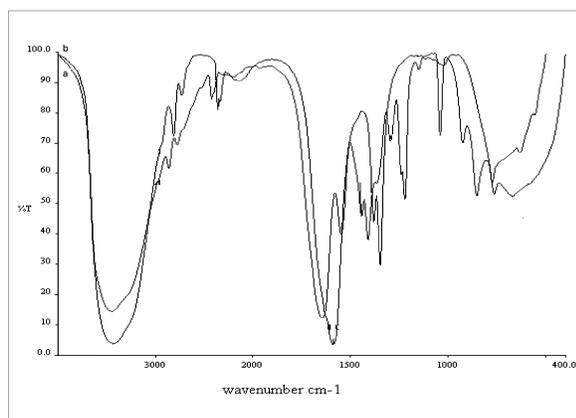
Fig. 1: FTIR spectra (a) pure resorcinol, (b) Film formed on surface of metal after immersion in well water + resorcinol (100 ppm) + Zn^{2+} (75 ppm)

Broad bands at 3434.01 cm^{-1} were observed in the spectrum of resorcinol which indicated the -OH stretching vibration [21]. A peak observed at 1589.17 cm^{-1} were attributable for the aromatic-C=C-stretching frequency. A peak at 670 cm^{-1} is an indicative of C-O stretching of phenolic compounds.

The FTIR spectrum (KBr) of the film formed on the surface of the carbon steel after immersion in well water, 75 ppm of Zn^{2+} and 100 ppm of resorcinol is shown in Fig 1b. The -OH stretching frequency has decreased from 3434.01 cm^{-1} to 3429.40 cm^{-1}. This shows that Fe^{2+} has coordinated through oxygen atoms of OH group in the resorcinol. The aromatic C=C stretching frequency has shifted from 1589.17 to 1591.19 cm^{-1}[22]. This indicates that resorcinol has co-ordinated with Fe^{2+} through Π electrons. The band at 765.26 cm^{-1} may be due to Zn-O stretching vibration. The band at1349.57 may be due to in-plane vibration of -O-H group in $Zn (OH)_2$ [23-24].

3.6 Analysis of Potentiodynamic Polarization Curves

The potentiodynamic polarization curves of carbon steel immersed in well water are shown in Fig 2. The corrosion parameters of carbon steel immersed in various test solution obtained by polarization study are given in Table VI.
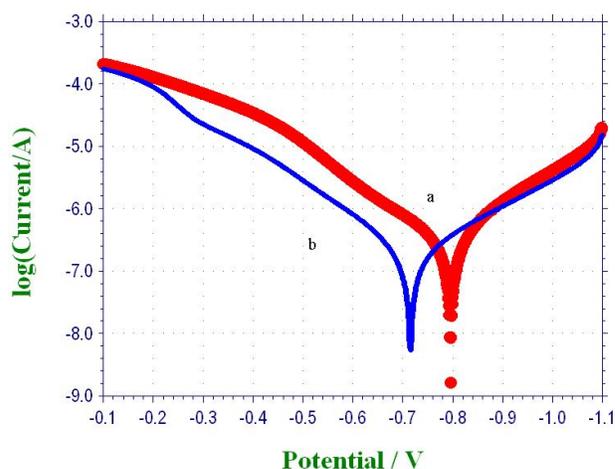
Fig 2: Polarization curves of carbon steel immersed in various solutions well water b)well water + resorcinol (100 ppm) + Zn^{2+} (75 ppm)

Fig 3: AC impedance spectra of carbon steel immersed in various solutions a)well water b)well water + resorcinol (100 ppm) + Zn^{2+}(75 ppm)

When carbon steel is immersed in well water, the corrosion potential (Ecorr) is -796 mV vs SCE. The formulation consisting of 75 ppm of Zn^{2+} and 100
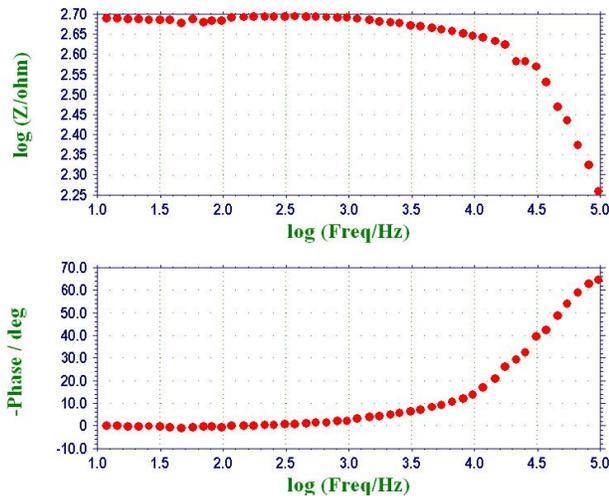
Fig. 4(a) : The Bode plot of carbon steel immersed in well water
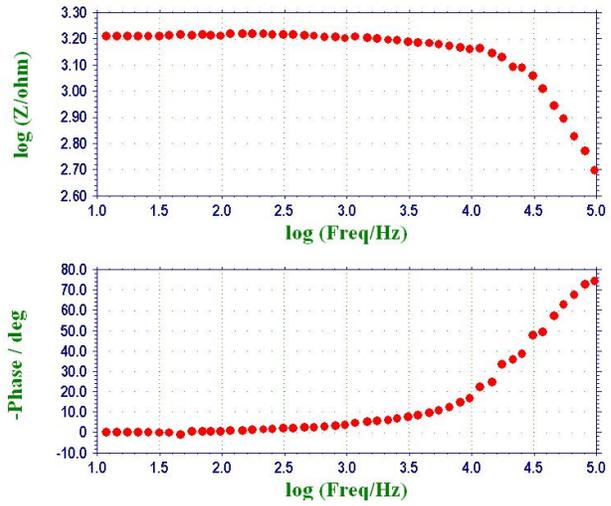
Fig 4(b) : The Bode plot of carbon steel immersed in well water containing resorcinol (100 ppm) + Zn^{2+}(75 ppm)

ppm of resorcinol shifts the corrosion potential to -715 mV vs SCE. It is found that there is no significant variation in the Ecorr values in the presence of inhibitors suggesting that this behaves as a mixed type of inhibitor. The LPR values are found to increase from 1.070×10^5 to 2.007×10^5. As there is not much variation in the Tafel slopes in the presence of inhibitor, it shows that these inhibitors inhibit by adsorption. The inhibitory action of sodium salt of resorcinol increases with the electron density at the oxygen atom constituting the reaction centre. The inhibitive properties of organic compounds depend on the electron densities around the chemisorptions centre; the higher the electron density the more effective is the inhibitor. This fact is supported by the decrease in the corrosion current. The corrosion current for well water is 3.762×10^{-7} A/cm^2. It is decreased to 1.9846×10^{-7} A/cm^2 by the addition of 100 ppm of resorcinol and 75 ppm of Zn^{2+}. The current of the

iron dissolution is decreased significantly, indicating that the metal surface was passivated by the formed inhibitor layer. The passivity of iron is probably due to the formation of a phenolateanion-Fe^{2+} surface layer. The significant reduction in corrosion current for inhibitor formulation may indicate more adsorption of the inhibitors and better inhibition performance [25]. This indicates that a protective film is formed on the metal surface.

3.7 Analysis of AC Impedance spectra

The AC impedance spectra of carbon steel immersed in various test solution are shown in Fig 3(a, b). The AC impedance parameters, namely the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) are given in Table VII. When carbon steel is immersed in well water the R_t value is found to be 424.92 Ω cm^2 and the Cdl value is 1.2002×10^{-8} F/cm^2. When 75 ppm of Zn^{2+} and 100 ppm of resorcinol are added the R_t value has increased

Table - VI

The electrochemical parameters associated with polarization measurements of carbon steel immersed in well water in the presence and absence of inhibitor system (resorcinol- Zn^{2+})

System	E$_{corr}$ mV vs SCE	b$_c$ mV/ decade	b$_a$ mV/ decade	LPR ? cm^2	I$_{corr}$ A/ 0.00785 cm^2
Well water	-796	175.5	196.0	1.070 x 10^5	3.762x10^{-7}
Well water+ Zn^{2+} 75ppm + resorcinol100ppm	-715	202.3	167.2	2.007x10^5	1.984x10^{-7}

Table - VII

Impedance parameters for corrosion of carbon steel immersed in well water in the presence and absence of inhibitor system (resorcinol-Zn^{2+}) obtained from AC impedance curves.

System	R$_t$ Ω cm^2	C$_{dl}$ F/0.00785cm^2	Impedance log (z/ Ω)
Well water	424.92	1.2002x10^{-8}	2.689
Well water+ Zn^{2+} 75ppm + resorcinol 100ppm	1549.5	3.2913x10^{-9}	3.210

Table - VIII

AFM data for carbon steel surface immersed in inhibited and uninhibited environments

Samples	RMS (R_q) Roughness (nm)	Average (R_a) Roughness (nm)	Maximum Peak-to-valley Height (nm)
Polished carbon steel (control)	434	369	2229
Carbon steel immersed in well water (blank)	715	612	2803
Carbon steel immersed in well water containing resorcinol (100 ppm) + Zn^{2+} (75 ppm)	412	352	1765

tremendously from 424.92 Ω cm^2 to 1549.5 Ω cm^2 and C_{dl} value decreases to 3.2913x10^{-9} F/cm^2. The increased R_t value and decreased double layer capacitance value obtained from impedance studies confirms the formation of a protective film on the metal surface and justify the good performance of a compound as an inhibitor in well water [26]. This behavior shows that the film obtained acts as a barrier to the corrosion process that clearly proves the existence and formation of the film [27,28]. Fig.4 represents the Bode plots obtained in the absence and presence of binary 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 [29,30]. The impedance values increases in the presence of inhibitors.

3.8 SEM Analysis of Metal Surface

The SEM image of magnification (X 2000) of carbon steel specimen immersed in well water for 1 day in the absence and presence of inhibitor system are shown in Fig 5 (a,b) respectively.

The SEM micrographs of polished carbon steel surface (control) in Fig 5(a) shows the smooth surface of the metal. This shows the absence of any corrosion products formed on the metal surface.

The SEM micrographs of carbon steel surface immersed in well water in Fig 5(b) shows the roughness of the metal surface which indicates the

(a)   (b)   (c)
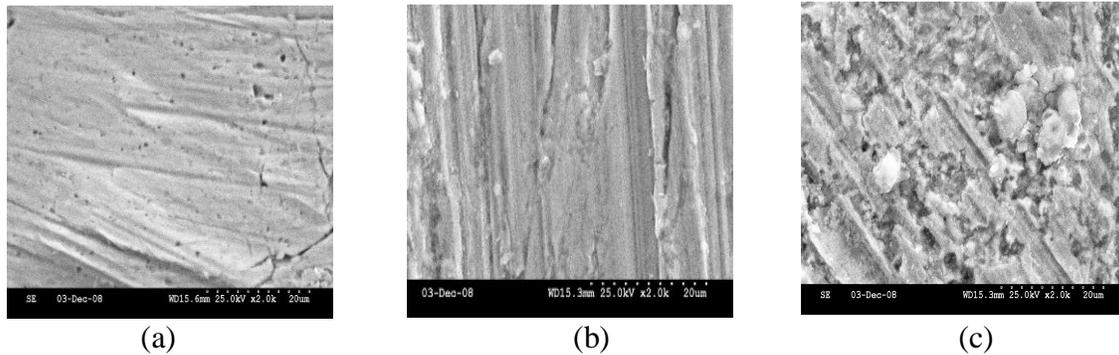
Fig 5: SEM micrographs of (a) Carbon steel (control); Magnification-X 2000 (b) Carbon steel immersed in well water; Magnification -X 2000 (c) Carbon steel immersed in well water containing resorcinol (100 ppm)+ Zn^{2+}(75 ppm); Magnification -X 2000

(a)   (b)   (c)
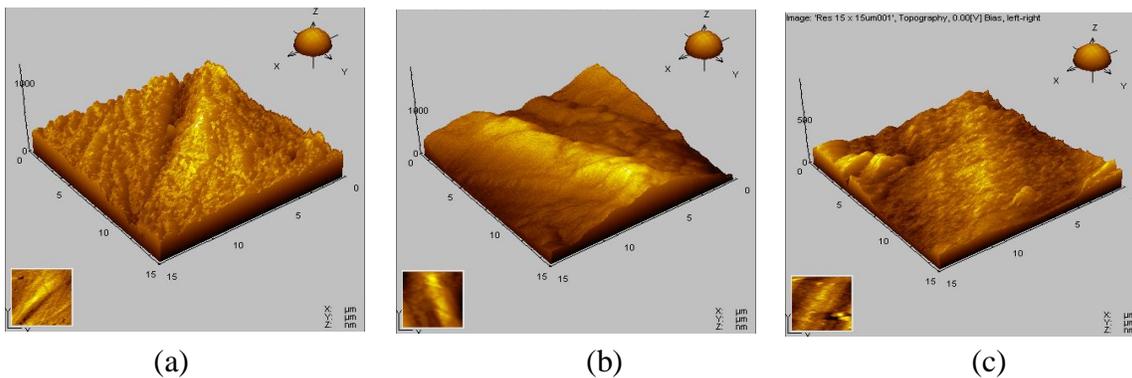
Fig 6: 3D AFM images of the surface of (a) Polished carbon steel (control) (b) Carbon steel immersed in well water (blank) and (c)Carbon steel immersed in well water containing res9orcinol (100 ppm)+Zn^{2+} (75 ppm)

corrosion of carbon steel in well water. Fig 5 (c) indicates that in the presence of 100 ppm of resorcinol and 75 ppm of Zn^{2+} mixture in water, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal (resorcinol- Zn^{2+} inhibitor complex) and the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel [31].

3.9 Atomic Force Microscopy Characterization

All atomic force microscopy images were obtained on a pico SPM 2100 AFM instrument operating in contact mode in air. The scan size of all the AFM images are 15 μ m×15 μ m areas at a scan rate of 2.4 lines per second.

The three dimensional (3D) AFM morphologies for polished carbon steel surface (reference sample), carbon steel surface immersed in well water (blank sample) and mild steel immersed in well water containing the formulation of 100 ppm of resorcinol and 75 ppm of Zn^{2+} are shown in Fig 6. (a, b, c) respectively.

3.10 Root-mean-square roughness, average roughness and peak-to-valley value

AFM image analysis was performed to obtain the average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, R_q (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) [32]. Rq is much more sensitive than Ra to large and small height deviations from the mean [33]. Table VIII is a summary of the average roughness (R_a), rms roughness (R_q) maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments.

The value of R_q, R_a and P-V height for the polished mild steel surface (reference sample) are 434 nm, 369 nm and 2229 nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth . Fig 6a displays the uncorroded metal surface. The slight roughness observed on the polished mild steel surface is due to atmospheric corrosion. The rms roughness, average roughness and P-V height values for the mild steel surface immersed in well water are 715 nm, 612 nm and 2803 respectively. These data suggests that mild steel surface immersed in well water has a greater surface roughness than the polished metal surface, which shows that the unprotected mild steel surface is rougher and was due to the corrosion of mild steel in well water. Fig 6(b) displays corroded metal surface with few pits.

The presence of 100 ppm of resorcinol and 75 ppm of Zn^{2+} in well water reduces the R_q to 412 nm from 715 nm and the average roughness is significantly reduced to 352 nm when compared with 612 nm of carbon steel surface immersed in well water. The maximum peak-to-valley height also was reduced to 1765 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} -resorcinol complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of mild steel. The above parameters observed for carbon steel are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.

4. CONCLUSIONS

The study shows that results of the weight loss are due to the formulation of 100 ppm of resorcinol and 75 ppm of Zn^{2+} which has 96% inhibition efficiency in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and resorcinol. Polarization study reveals that the formulation behaves as mixed inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra revealed that the protective film consists of Fe^{2+}-resorcinol complex and $Zn(OH)_2$. In order to explain the facts the following mechanism of corrosion inhibition is proposed:

- When the formulation consisting of 100 ppm of resorcinol and 75 ppm of Zn^{2+} is prepared, there is formation of Zn^{2+} - resorcinol complex in solution.
- When carbon steel is immersed in this solution, the Zn^{2+} -resorcinol complex diffuses from the bulk of the solution towards the metal surface.
- On the metal surface, Zn^{2+} -resorcinol complex is converted in to Fe^{2+} -resorcinol complex on the anodic sites. Zn^{2+} is released and $Zn(OH)_2$

is formed.

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

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$$
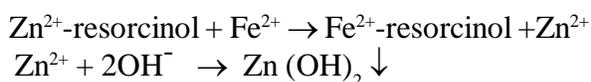
- Thus the protective film consists of Fe^{2+} - resorcinol complex formed on anodic sites of the metal surface and $Zn(OH)_2$ deposited on cathodic sites of the metal surface.

- The SEM micrographs and AFM images confirm the formation of protective layer on the metal surface.

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