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Surface and Electrochemical Characterization of Corrosion Inhibition of Stainless steel in Acid Medium

P. Selvakumar[1,*], B. Balanaga Karthik[2], C. Thangavelu[3]
[1,*]*Department of chemistry, Chettinad College of Engineering and Technology, Karur, Tamil Nadu, India.*
[2]*Department of chemistry, KCG College of Technology, Chennai, Tamil Nadu, India.*
[3]*Department of Chemistry, Periyar EVR College (Autonomous), Tiruchirappalli, Tamil Nadu, India.*

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[*]*Corresponding Author. E-mail: ppselva@gmail.com ; Tel: (+919843289593)*

Abstract

The corrosion inhibition of stainless steel in 0.5M H_2SO_4 solutions by diethylenetriaminepenta(methylene phosphonic acid) (DTPMP) and Sodium Gluconate (SG) has been investigated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic techniques (EIS). The results obtained reveal that DTPMP-SG performs a mixed type of inhibitor. Electrochemical Impedance spectroscopy (EIS) results confirm the adsorption of the inhibitors at stainless steel/acid interface. The adsorption of the inhibitor molecules on the stainless steel surface obeys Tempkin adsorption isotherm and occurs spontaneously. The heat of adsorption (Q_{ads}) as well as other thermodynamic parameters for the inhibition process is calculated. These thermodynamic parameters show strong interaction between inhibitor and stainless steel surface. The nature of the protective film formed on the metal surface has been characterized by FTIR, SEM and AFM analysis.

Keywords: Corrosion inhibition, Stainless steel, Polarization, FTIR, SEM, AFM.

Introduction

In the Maritime field and in the Industrial domain, stainless steel is the material that is frequently used against corrosion because of its excellent resistivity. In many destructive environments, it is resistant to corrosion because of its covering made up of chromium oxyhydroxide, a highly protective film. So, in order to reduce the corrosion rate to safe level, various kinds of inhibitors are used with the solution [1-2]. The organic compounds posses multiple bonds acts as adsorption centers or those posses heteroatom's such as nitrogen, sulphur and oxygen with high electron density, are as effective as corrosion inhibitors [3-10]. Inhibitors are used during acid treatment of scaled parts in multistage flash (MSF) desalination plants [11]. The aim of this study is the investigation of inhibition effects of the diethylenetriaminepenta(methylene phosphonic acid) (DTPMP) – Sodium Gluconate (SG) on the corrosion of stainless steel in 0.5M H_2SO_4 solutions. The best isotherm has been selected and the effects of temperature on the corrosion behavior of stainless steel in absence and presence of inhibitors have been investigated.

2. Materials and methods

2.1. Preparation of working electrode

Grade 304 Stainless steel strips were cut into 4 cm x 1 cm x 0.2 cm having the following compositions (C – 0.021 %, Si – 0.888 %, Mn – 1.42 %, P – 0.0177 %, S – 0.0268 %, Cr – 18.20 %, Mo – 0.0373 %, Ni – 9.43 %, Cu – 0.507 %, V – 0.1 %, and Fe – 69.36 %) were used for weight-loss studies, while coupons of size 1 cm^2 were used for electrochemical studies and SEM analysis. The stainless steel strips were cut and polished to mirror finish by table grinding wheels and degreased with Trichloroethylene.

2.2 Preparation of 0.5 M H_2SO_4

0.5 M H_2SO_4 solution was prepared by diluting 27.8 ml of 18 M AR-Grade H_2SO_4 to 1000 ml using double distilled water.

2.3 Preparation of diethylenetriaminepenta(methylene phosphonic acid)

1g of diethylenetriaminepenta(methylene phosphonic acid) (DTPMP) was dissolved in double distilled water and made up to 100 ml in a standard measuring flask. 1 ml of this solution was diluted to 100 ml to get 100 ppm of DTPMP.

2.4 Preparation of Sodium Gluconate solution

1 g of sodium gluconate was dissolved in double distilled water and made up to 100 ml in a standard measuring flask. 1 ml of this solution was diluted to 100 ml to get 100 ppm of sodium gluconate.

2.5 Electrochemical methods

Electrochemical measurements were performed using a CHI electrochemical analyzer model 760D instrument with CHI 760D operating software. A three-electrode electrochemical setup was used. A working stainless steel electrode embedded in Teflon holder was dipped in test solution. A saturated calomel electrode (SCE) and a platinum electrode were used and the reference and counter-electrode respectively. In the case of polarization and electrochemical impedance spectroscopy, prior to each measurement a stabilization period of 30 min was allowed to establish a steady-state open circuit potential (OCP) ± 200 mv ranges a sweep rate of 2 mV/s. The electrochemical impedance spectroscopy measurements were carried out in the frequency range from 100 kHz to 0.1 Hz with a signal amplitude perturbation of 5 mV. The double-layer capacitance (C_{dl}) and charge-transfer resistance (R_{ct}) were calculated from Nyquist plots as described elsewhere [12].

2.6 Surface Characterization

2.6.1 FT-IR Analysis

FT-IR spectra are recorded with a frequency ranging 4000 to 400 cm-1 for the inhibitor as well as the inhibitor adsorbed on stainless steel in 0.5 M H_2SO_4 solution using Shimadzu IR affinity –1 KBr dei set method.

2.6.2 SEM Analysis

Surface analysis was carried out using scanning electron microscope (SEM). The stainless steel specimens were immersed in 0.5 M H_2SO_4 solution without and with inhibitor for about 6 hours. After 6 hours, immersed specimens were drawn from the test solution, cleaned with double distilled water and dried at room temperature. A SEM experiment was performed by using a model JSM 6390 scanning electron microscope.

2.6.3. AFM Analysis

The stainless steel specimens immersed in various test solutions for one day are taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the stainless steel surface are analyzed using Park XE-100 atomic force microscopy (AFM).

3. Results and discussion

3.1. Weight Loss Study

Inhibition efficiency of diethylenetriaminepenta(methylene phosphonic acid) in controlling corrosion of stainless steel immersed in 0.5 M H_2SO_4 solutions in absence and presence of sodium gluconate are determined. The results obtained from the weight loss measurements for the stainless steel are listed in Table 1. It is evident from these results that inhibition efficiency of stainless steel increases on addition of inhibitors. As the temperature increases the corrosion rate increases and the inhibition efficiency decreases. The corrosion rate decreases and inhibition efficiency increases with increasing inhibitor concentrations, which suggest that the inhibitor molecules are adsorbed on the metal surface. 200 ppm of DTPMP has 53% inhibition efficiency and 100 ppm of SG has 47% inhibition efficiency. When DTPMP is combined with SG, it is found that inhibition efficiency increases up to 91%.

Table 1: Weight loss values of Corrosion rates and inhibition efficiencies of stainless steel in presence and absence of inhibitors at different temperatures.

Medium	Conc. Of DTPMP (ppm)	Conc. Of SG (ppm)	Corrosion Rate	IE	Surface coverage (θ)
0.5 M H_2SO_4	0	0	41.56	--	--
	200	0	19.40	53.33	0.5333
	0	100	22.17	46.67	0.4667
	200	25	29.09	30.00	0.3000
	200	50	18.84	54.67	0.5467
	200	75	11.08	73.33	0.7333
	200	100	3.60	91.33	0.9133
	200	125	4.99	88.00	0.8800

3.2. Potentiodynamic Polarization

The potentiodynamic polarization curves of SS in 0.5 M H_2SO_4 solution without and with the addition of various concentration of inhibitor are shown in Figure 1.

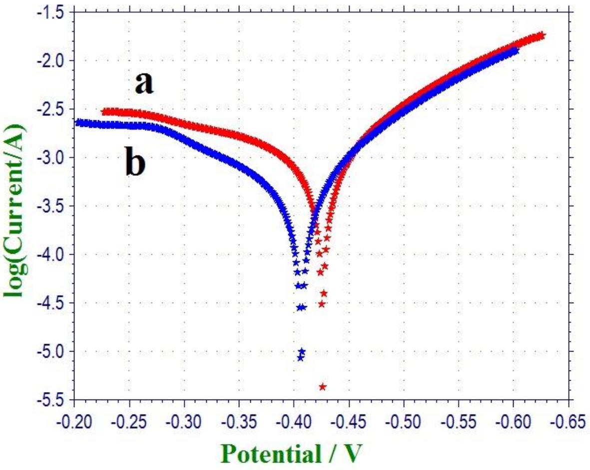


Figure 1: Potentiodynamic polarization curves for stainless steel in 0.5 M H_2SO_4solution in (a) absence (b) presence of SG

The values of associated electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic tafel slopes (b_c), anodic tafel slopes (b_a) and percentage inhibitor efficiency (IE %) values were calculated from the polarization curve and listed in Table 2.

Table 2: Electrochemical parameters of stainless steel in 0.5M H_2SO_4 solutions obtained by polarization method.

System	b_a mV	b_c mV	E_{corr} mV V SCE	I_{corr} A/cm^2	IE %
Blank	2.66	7.22	-0.426	15.55 x 10^{-4}	-----
200 ppm DTPMP +100 ppm SG	5.48	7.93	-0.406	6.03 x 10^{-4}	61.22

$$\mathbf{IE}\ (\%) = \frac{\mathbf{I_{corr}} - \mathbf{I_{corr(inh)}}}{\mathbf{I_{corr}}}\ \mathbf{X\ 100}$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current densities without and with inhibitor respectively[13]. When the stainless steel is immersed in H_2SO_4 the corrosion current I_{corr} is 15.55×10^{-4} A/cm^2. When 200ppm DTPMP and 100ppm SG are added, it decreases to 6.03×10^{-4} A/cm^2. The significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of inhibitor. From table 2, it is also clear that there is a shift towards anodic region in the values of corrosion potential E_{corr}. In the literature [14-16] it has been reported that E_{corr} values of up to ±85 mV can be attributed to a mixed type of inhibitor. This indicates that a protective film is formed on the metal surface [17-18].

3.3. Electrochemical impedance spectroscopy

The corrosion behavior of mild steel in 0.5M H_2SO_4 was also investigated by electrochemical impedance spectroscopy (EIS). Figure 2 shows the Nyquist plots of various concentration of the inhibitor at 30°C. The double layer capacitance (C_{dl}) is calculated from the following equation [19]

$$\mathbf{C_{dl}} = \frac{\mathbf{1}}{\mathbf{2\ \pi\ R_{ct}\ f_{max}}}$$

In the presence of 0.5M H_2SO_4 solution R_{ct} value is 22.52 Ω cm^2 and C_{dl} value is 6.24×10^{-4}µF cm^2. When 200ppm DTPMP and 100ppm SG are added to this solution, R_{ct} value increases to 45.84 Ω cm^2 [20] and C_{dl} value decreases to 1.50×10^{-4}µF cm^2[21]. This confirms that the formation of a protective film on the metal surface [22-23]. The EIS parameters namely, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are given in table 2.

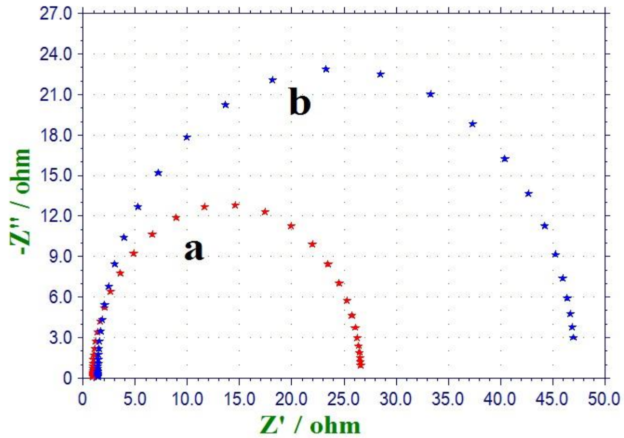


Figure 2: Electrochemical impedance curves for stainless steel in 0.5M H_2SO_4solution in (a) absence (b) presence of the inhibitor.

Table 3: Electrochemical parameters of stainless steel in 0.5M H_2SO_4 solutions are obtained by impedance method.

Systems	R_{ct} Ωcm^2	C_{dl} μF cm^2
Blank	22.52	6.24×10^{-4}
200 ppm DTPMP + 100 ppm SG	45.849	1.508×10^{-4}

3.4. FT-IR Spectra

The FTIR spectrum of pure DTPMP is shown in Figure 3 a. The stretching frequency of P-O & C-N appears at 1059cm^{-1}& 1111cm^{-1}.The FTIR spectrum of pure SG is shown in figure 3 b. The stretching frequency of C=O appears at 1627cm^{-1}. The FTIR spectrum of film formed on the stainless steel surface after immersion in the solution containing 200 ppm of DTPMP and 100 ppm of SG are shown in Figure 3 c. The C-N stretching frequency of DTPMP shifts from 1111cm^{-1}to 1103cm^{-1}. The P-O stretching frequency shifts 1059 cm^{-1}to 946 cm^{-1}. The C=O stretching frequency of SG shifts from 1627 cm^{-1} to 1680 cm^{-1}. This suggests the formation of Fe^{2+} - SG complex on the metal surface. DTPMP has co-ordinates with Fe^{2+} through N, P and O atoms of phosphonic acid. SG coordinates with Fe^{2+} through oxygen atoms of carbonyl group [24-26].

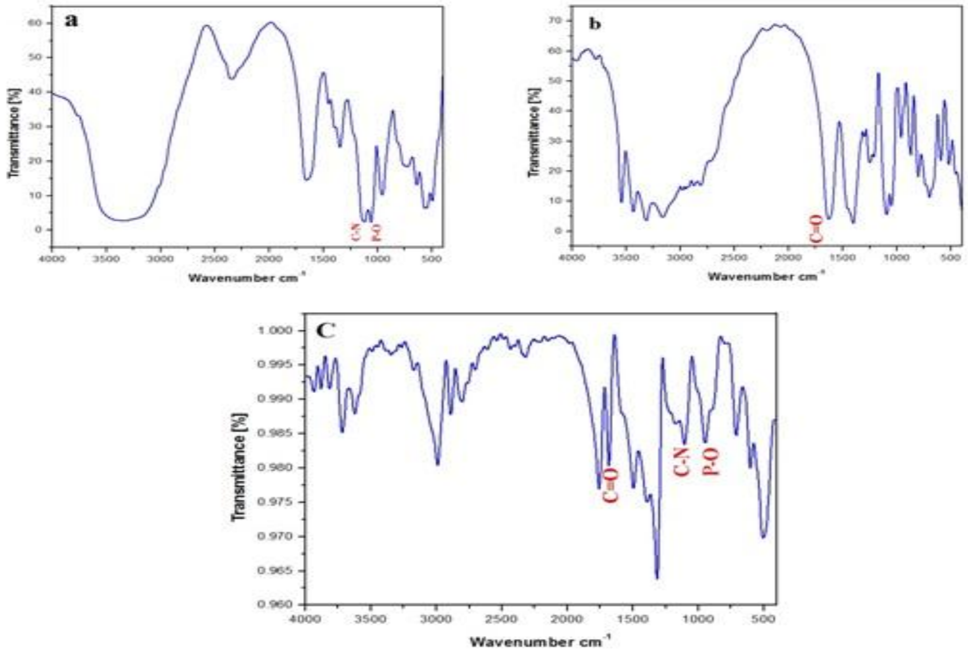


Figure 3: (a) FT-IR spectrum of pure DTPMP (b) FT-IR spectrum of pure SG
(c) FT-IR spectrum of stainless steel in 0.5 M H_2SO_4 solution with DTPMP and SG

3.5. Thermodynamic Parameters

Table 4. Shows that the calculated values of heat of adsorption (Q_{ads}), entholpy of activation (ΔH_{ads}) and entropy of activation (ΔS_{ads}) for stainless steel in 0.5 M H_2SO_4 solutions with and without various concentration of DTPMP – SG at 303, 313, 323 and 333K are calculated from the following equation (27).

$$\boldsymbol{Q_{ads} = 2.303\, R \left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right] X\, \frac{T_1\,.\,T_2}{T_2 - T_1}}$$

Where Q_1 and Q_2 are the surface coverage of inhibitors at temperature T_1 and T_2 respectively.

Table 4: Thermodynamic parameters of Q_{ads}, ΔH and ΔS for stainless steel in 0.5 M H_2SO_4 with and without inhibitors

Medium	Conc. Of DTPMP (ppm)	Conc. of SG (ppm)	$-Q_{ads}$ KJ/mol			-ΔH KJ/mol	ΔS KJ/mol
			303 – 313K	313 – 323K	323 – 333K		
0.5 M H_2SO_4	0	0	0	0	0	2.7664	0
	200	25	11.23	14.30	20.26	2.7641	0.0304
	200	50	13.75	17.41	23.74	2.7586	0.0323
	200	75	16.56	24.16	26.30	2.7530	0.0345
	200	100	25.66	32.03	33.92	2.7411	0.0407

The negative value of (Q_{ads}) confirms that the degree of surface coverage decreased and also inhibition efficiency decreased with raise in temperature [28]. The enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are calculated using the following equation (29).

$$\boldsymbol{\Delta H = E_a - RT}$$

$$\boldsymbol{\Delta S = \frac{\Delta H - \Delta G}{T}}$$

The negative values of enthalpy of adsorption (ΔH_{ads}) indicate that the adsorption of DTPMP – SG onto the stainless steel surface is exothermic [30]. The positive values of entropy change confirming that the corrosion process is entropically favorable [31].

3.6 Adsorption Isotherm

Adsorption isotherm is very important in establishing the mechanism of electrochemical reactions [32]. Since the corrosion inhibition process is based on the adsorption of the DTPMP-SG molecules on the metal surface, it is essential to know the mode of adsorption and the adsorption isotherm that fits the experimental results [33]. The most frequently used adsorption isotherms are Langmuir, Tempkin and Frumkin with general formula [34-36]. The best fit is obtained with Tempkin adsorption isotherm, where the surface coverage (θ) values are plotted against the concentration of the inhibitor. The values of surface coverage for the inhibitor are acquired from the weight loss measurements. The plots of θ against log C, as presented in Figure 4 gives linear relationship, which shows that adsorption data fitted Tempkin adsorption isotherm.

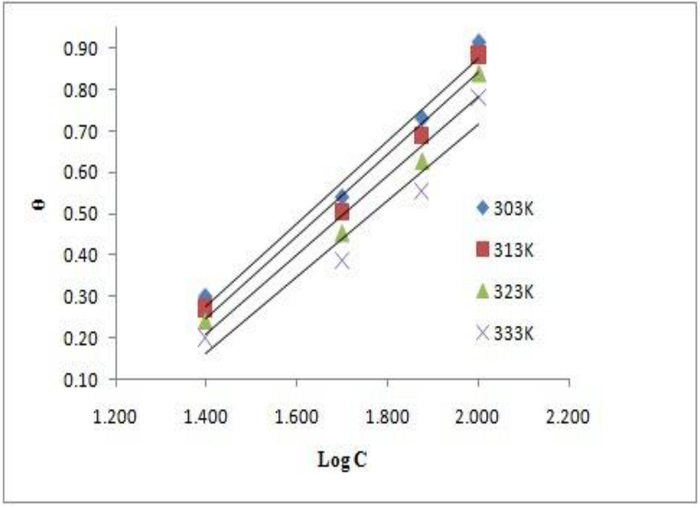


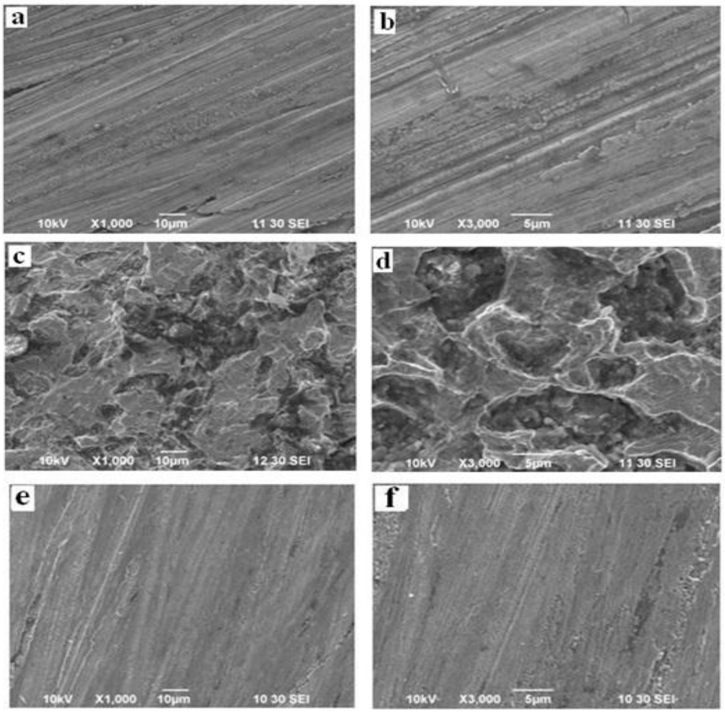
Figure 4: Tempkin adsorption isotherm of DTPMP – SG on the stainless steel in 0.5 M H_2SO_4 (303–333K)

3.7. Scanning Electron Microscopy

The surface morphology of stainless steel studied by scanning electron microscope (SEM) surface was observed after 6 hours, immersion of 0.5 M H_2SO_4 before and after addition of DTPMP-SG. Figure 5 (a & b) show the polished metal surface of stainless steel before corrosion. Figure 5 (c & d) show the metal surface after immersion of 0.5 M H_2SO_4 solutions. It can be observed that in the absence of DTPMP–SG, a non-uniform layer is formed on stainless steel surface. According to this, when the stainless steel is immersed in 0.5 M H_2SO_4 solutions, the surface of stainless steel is not stable and the composition can be changed by incorporation of ions and molecules. In the presence of DTPMP–SG, the film formed on the stainless steel surface is different from that in the absence of DTPMP–SG is shown in Figure 5 (e & f). The uniformity of DTPMP–SG adsorbed on the surface of metal can be observed [37].

3.8. Atomic Force Microscopy

AFM is a dynamic tool to examine the surface morphology from nano to micro scale and has become a new choice to study the nature of protective layer formed over the surface of stainless steel [38]. The 2D and 3D AFM images of polished stainless steel (control), stainless steel in 0.5 M H_2SO_4 (blank) and stainless steel in 0.5 M H_2SO_4 with 200 ppm of DTPMP and 200 ppm of SG, respectively are shown in Fig. 6 (a – f). As can be seen from the AFM images, the surface is very clear for polished stainless steel (Fig. 6 a & d) whereas in stainless steel immersed in 0.5 M H_2SO_4 (Fig. 6 d & e) the surface is severely damaged by aggressive acid solution. In (Fig. 6 c & e) the surface is protected from acid attack by the protective layer formed by the inhibitor molecules. From the results, it is clear that, the inhibition of stainless steel corrosion in 0.5 M H_2SO_4 is mainly due to the formation of protective layer by adsorption of inhibitor molecules over the surface of stainless steel. AFM data for stainless steel is given in table 5.



Figures 5:

1. (a & b) SEM micrograph of polished Stainless steel (control
2. (c & d) SEM micrograph of Stainless steel in 0.5 M H_2SO_4 solution (Blank)
3. **(**e & f) SEM micrographs of Stainless steel in 0.5 M H_2SO_4 solution with 200 ppm DTPMP and 100 ppm SG
4.

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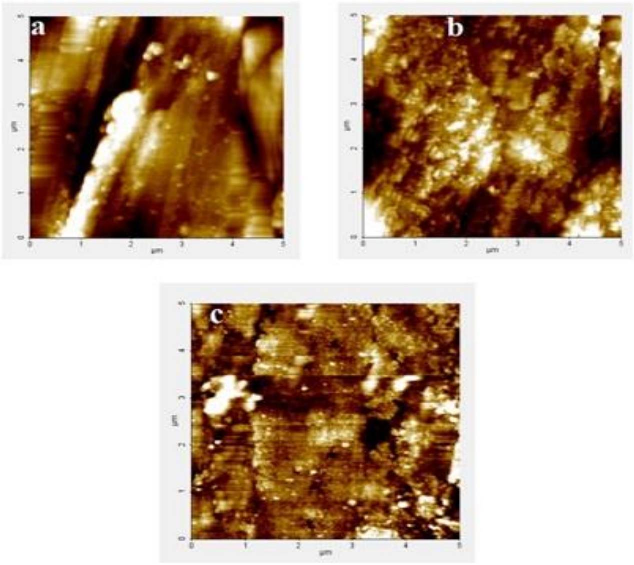
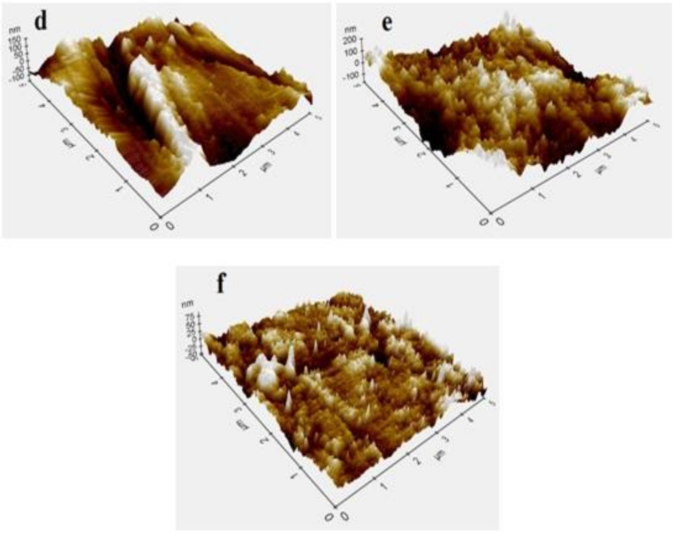
Table 5: AFM data for stainless steel immersed in inhibited and uninhibited environments.

Samples	**Average Roughness (Ra) nm**	**Root-mean- square Roughness (Rq) nm**	**Maximum peak-to-valley height (P-V) nm**
Polished Stainless steel (Control)	16.83	25.44	157.75
Stainless steel immersed in 0.5 M H_2SO_4 (Blank)	63.28	73.08	295.29
Stainless steel immersed in 0.5 M H_2SO_4 containing DTPMP (200 ppm) and SG (100 ppm)	28.43	34.57	168.24





Figures 6: 2D AFM images of stainless steel surface.
(a) Polished stainless steel (control)
(b) Stainless steel immersed in 0.5 M H_2SO_4 solution (blank)
(c) Stainless steel immersed in 0.5 M H_2SO_4 solution containing DTPMP (200 ppm) + SG (100 ppm)

Figures 6: 3D AFM images of stainless steel surface.
(d) Polished stainless steel (control)
(e) Stainless steel immersed in 0.5 M H_2SO_4 solution (blank)
(f) Stainless steel immersed in 0.5 M H_2SO_4 solution containing DTPMP (200 ppm) + SG (100 ppm)

Conclusion

In this study, inhibition efficiency of DTPMP – SG shows a significant corrosion inhibitors effect as evident from the results of weight loss studies. According to this results these DTPMP – SG are good inhibitors for stainless steel in 0.5 M H_2SO_4 solutions. The obtained inhibition efficiency of DTPMP – SG from polarisation and impedance curves has the same trend. From the polarization study it is found that inhibitors affect both anodic and cathodic reaction and act as mixed type of inhibitors. EIS confirms that presence of inhibitors into the acid media leads to the increase in the charge transfer resistance and decrease in the double layer capacitance. The adsorption of the inhibitors on the stainless steel surface obeys Tempkin adsorption isotherm. The negative values of (ΔH_{ads}) indicate that adsorption is exothermic process. The results of FT-IR, SEM and AFM studies have proved the formation of the protective layer over stainless steel surface.

References

1. Abdallah. M., *Corros. Sci*. 44 (2002) 717.
2. Abdallah. M., *Mater. Chem. Phys.* 82 (2003) 786.
3. Ismail. K.M., *Electrochim. Acta,* 52 (2007) 7811.
4. Benabdellah. M., Touzani. R., Aouniti. A., Dafali. A., El Kadiri. S., Hammouti. B., Benakaddour. M., *Mater. Chem. Phys.* 105 (2007) 114.
5. Bouklah. M., Ouassini. A., Hammouti. B., El Idrissi. A., *Appl. Surf. Sci.* 250 (2005) 50.
6. Yurt. A., Butun. V., Duran. B., *Mater. Chem. Phys.* 105 (2007) 114.
7. Popova. A., Chirstov. M., Vasilev. A., *Corros. Sci.* 49 (2007) 3290**.**
8. Bentiss. F., Lebrini. M., Lagrenee. M., Traisnel. M., Elfarouk.A., Vezin. H., *Electrochim, Acta* 52 (2007) 6865.
9. Sherif. E.M., Erasmus. R.M., Comins. J.D., J. *Colloid Interface Sci*, 311 (2007) 144.
10. Tebbji. K., Faska. N., Tounsi. A., Oudda. H., Benkaddour. M., Hammouti. B., *Mater. Chem. Phys.* 106 (2007) 260.
11. Report No. SWCC (RDC) – 36, Saline Water Conversion Corporation, Saudia Arabia, March 1995.
12. Ashassi-Sorkhabi. H., Shaabani. B. Seifzadeh. D., *Electrochem. Acta* 50, (2005) 3446
13. Lowmunkhong. P., Ungthararak. D., Sutthivaiyakit. P., *Corros. Sci.* 52 (2010) 30-36
14. Ferreira. S., Giancomelli. C., Giacomelli. F.C., Spinelli. A., *Mater. Chem. Phys.* 83 (2004) 129-134
15. Ashassi – S0rkkhabi. H., Majidi. M.R., Seyyedi. K., *Appl. Surf. Sci*. 225 (2004) 176-185
16. Riggs Jr. O.L., Corrosion inhibition, second ed., C.C. Nathan, Houston, Tx, 1973.
17. Rajendran S., Joany R. M., and Apparao. B.V., *Indian journal of Chemical Tech*, 9 (2002) 197 -200
18. Hariharaputhran R., Subramanian Alice Arul Anthony A., Manisankar P., Vasudevan T., VenkatakrishnaIyer S., *Anti corrosion methods and mater*, 46 (1999) pp 35-39
19. Khaled K.F., *Electrochim. Acta*, 48, (2003) 2493
20. Hileli S., Abdelghani. A., Tlili. A., *Sensors*, 3, (2003) 472
21. De Souza. F.S., and Spinelli. A., *Corros. Sci.* 51 (2009) 642
22. Kalman. E., Varhegyi. B., Felhosi. I., Karman. F.H., Shaban. A., *J. Electrochem. Soc.* 141 (1994) 3357
23. Bonnel. A., Dabosi. F., Deslovis. C., Duprat. M., Keddam. M., Tribollet. B., *J. Electrochem. Soc*, 130 (1983) 753
24. Cross, Introduction to practical infrared spectroscopy, Butter worths, scientific publication, London (1990) 73.
25. Nakamoto. K., Infrared and Raman spectra of inorganic and coordination compounds, Wiley Interscience, New York, 1986 (168)
26. Silverstein R.M., Bassler G.C., Moril T., Spectrometric identification of organic compound, John Wiley and sons, New York, 198.
27. Subramanian N., and Ramakrishnaiah K., *Indian. J. Tech*, 8 (1970) 369
28. Bhajiwala H.M., and Vashi R.T., *Bull Electrochem*, 17(2001) 441
29. AyssarNahie, Ibrahim Abdel – Rahman and MohamadAlfarouk, *Bull. Electrochem.* 21 (2005) 353-361
30. Solmaz. R., Kardas. G., Culha. M., Yazici. B., and Erbil. M., *Electrochim Acta*, 53 (2008) 5941 – 5952
31. Issa. R.M., El – Sonbati. A.Z., El-Bindary. A.A., and Kera. H.M., *Eu. Poly. J*. 38 (2002) 561
32. Wu. X., Ma. H., Chen. S., Xu. Z., Sui. A., J. *Electrochem. Soc*, 146 (1999) 1847
33. Senthil Kumar. A.N., Tharini. K., and Sethuraman. M.G., *Surf. Rev. Lett.* 16 (2009) 141 147
34. Bilgic. S., and Caliskan.N., *Journal of applied electrochemistry*, 31 (2001) 441-448
35. BouyanzerA., and Hammouti. B., *Pigment & Resin Technology*, 33 (2004) 287 – 292
36. Ebenso. E.E., Eddy. N.O., and Odiongenyi. A.O., *Portugaliae Electrochimica Acta*, 27 (2009) 13 – 22
37. Rafaey. S.A.M., Taha. F., Abd El-Malak. A.M., *Applied Surface Science*, 263 (2004) 175
38. Satapathy. A.K., Gunasekaran. G., Sahoo, Kumar. S.C., Amit, Rodrigues. P.V., *Corros. Sci*, 51 (2009) 2848

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