Application of 1,2,3-Benzotriazole as Corrosion Inhibitor for Mild Steel in Sulphuric Acid Medium at Different Temperature

Harish Kumar[1,*,iD] and Tilak Dhanda[2,iD]

[1]Electrochemistry Laboratory, Department of Chemistry, School of Chemical Sciences, Central University of Haryana, Mahendergarh-123031, India
[2]Material Science and Electrochemistry Laboratory, Department of Chemistry, Chaudhary Devi Lal University, Sirsa-125055, India

*Corresponding author: E-mail: harimoudgil1@gmail.com

Corrosion inhibition property of 1,2,3-benzotriazole for mild steel in 0.1 N sulphuric acid was evaluated at different concentrations and temperatures using weight loss, electrochemical polarization, differential pulse, stripping voltammetry and impedance spectroscopy. The surface study was carried out using metallurgical research and SEM microscopy. Increase in Warburg impedance and capacitive current and decrease in Faradaic current and capacitive loop was observed with increase in concentration of inhibitor. 1,2,3-Benzotriazole was found as a best corrosion inhibitor (94 %) for mild steel as compared to other inhibitors suggesting 1,2,3-benzotriazole as a potential alternate corrosion inhibitor for mild steel in H_2SO_4.

Keywords: Corrosion, 1,2,3-Benzotriazole, Sulphuric acid, Mild steel, Electrochemical polarization.

INTRODUCTION

Mild steel (MS) is a very common and useful metal used in industries and household due to its low-cost, easy availability and good mechanical properties. Mild steel corrodes heavily when comes in contact with corrosive environment especially acidic environment. To protect metal and their alloys from corrosion, corrosion inhibitors are essentially required [1-4]. Corrosion inhibitors containing some hetero atoms are preferred as they have strong affinity for surface adsorption [5-8]. Some researchers have tested amide derivatives as corrosion inhibitors for mild steel in 1 M HCl as a corroding medium [9]. Others have tested ethanolamine and ethylamine as corrosion inhibitors for mild steel in 1 M H_2SO_4 solution at room temperature [10]. Singh *et al.* [11] studied ceftadizime as corrosion inhibitor for mild steel and reported the decrease in roughness of mild steel surface with increasing ceftadizime concentration. Diallylamine, 1-benzylimidazole and 5-amino-tetrazole were tested as vapour phase corrosion inhibitors for mild steel in different aggressive atmospheric conditions [12,13]. Neznamova *et al.* [14] have reported benzotriazole as a corrosion inhibitor for copper metal in neutral and acidic

environment. Khan *et al.* [15] have studied corrosion characteristics of benzotriazole for copper metal under flow conditions. Mennucci *et al.* [16] have studied corrosion inhibition properties of benzotriazole for carbon steel reinforced in concrete in 3.5 % NaCl solution. To the best of our knowledge, no work has been reported on the corrosion inhibition property of 1,2,3-benzotriazole for mild steel in 0.1 N H_2SO_4 solution at different temperature.

In the present study, the corrosion inhibition properties of 1,2,3-benzotriazole (BTA) were investigated on mild steel at different temperatures (25, 30 and 35 °C) and concentrations (200 to 1000 ppm) by weight loss, electrochemical polarization, electrochemical impedance spectroscopy, differential pulse and striping voltammetry followed by surface study techniques like metallurgical research and scanning electron microscopy.

EXPERIMENTAL

Material and sample preparation: Mild steel specimens used for investigation had following composition: C, 0.17; Si, 0.35; Mn, 0.42; S, 0.05; P, 0.20; N, 0.01; Cu, 0.01; Cr, 0.01

and rest Fe (w/w). Sequential mechanical polishing of the metal specimens was carried out by using silicon carbide papers of different grade *i.e.* 100 to 600 microns. The mild steel specimen of size 3 cm × 1.5 cm and 1 cm × 5 cm were used for weight loss and electrochemical polarization experiments, respectively. Subsequently, the working electrode (mild steel coupons) were degreased with acetone, rinsed with double distilled water and dried in hot air stream. All the test solutions were prepared in double distilled water (conductivity 4.3 μS/m). 1,2,3-Benzotriazole was procured from Fischer Scientific Pvt. Ltd. and was of AR grade. Single pan analytical balance of Mettler Toledo, Japan (Model AB 135-S/FACT) with precision 0.01 mg was used for measuring the exact weight of corroded specimen.

Weight loss tests: After mechanical polishing, mild steel specimens were exposed to 0.1 M H_2SO_4 solution for 24 h at 25, 30 and 35 °C in presence and absence of BTA. Corrosion rate (CR) and percentage corrosion inhibition efficiency (PCIE) were found out using NACE ASTM standard technique (ASTM G31).

Electrochemical tests: Potentiodynamic anodic polarization and electrochemical impedance spectroscopy experiments were carried out using a potentiostat/galvanostat Metrohm Autolab, Netherland (PGSTAT128N). Only 1.0 cm × 1.0 cm area of specimen was used as working area and rest of the area was covered with lacquer except the top end of the specimen which was used for making electrical connections with the potentiostat. A three electrode glass cell (double wall jacketed) was used for electrochemical experiments having Ag/AgCl as a reference electrode and platinum wire an auxiliary electrode. All the potential mentioned in this work including open circuit potential (OCP) are with reference to this Ag/AgCl reference electrode.

Linear polarization resistance (LPR) measurements were carried out potentiostatically by scanning through potential range of +500 mV above and 200 mV below the OCP value in a scanning rate of 0.5 mV s⁻¹. Experiments were carried out in absence and presence of inhibitors (200, 400, 600, 800 and 1000 ppm concentration) at 25, 30 and 35 °C. The change in current density, resistance and capacitance were recorded as a function of time and frequency using A.C. sinusoidal signal in frequency range of 1 to 100 kHz and AC perturbation amplitude of 10 mV. Nyquist plots were obtained in potentiostatic mode at a constant potential of corrosion at AC perturbation amplitude of 10 mV in a frequency range of 1 to 100 kHz with 10 points per decade.

Surface study (metallurgical research and scanning electron microscopy): The morphology of the corroded samples was studied under a metallurgical research microscopy (Kyowa-Getner, Japan) and SEM (JEOL JSM 6510 LV). Formation of pits, crevice, intergranular or uniform type of corrosion was investigated by these techniques. Metallurgical research and SEM image of the specimen were recorded up to micro (10^{-6} m) and nanoscale (10^{-9} m), respectively.

RESULTS AND DISCUSSION

Weight loss technique: Table-1 shows the comparative study of corrosion rate (CR) and percentage corrosion inhibition efficiency (PCIE) of BTA in 0.1 N H_2SO_4 medium at 25, 30 and 35 °C temperature with other investigated corrosion inhibitors. PCIE increases with increase in the concentration of BTA from 200 to 1000 ppm. 1,2,3-Benzotriazole (BTA) acts as a good corrosion inhibitor even at low concentration (200 ppm) in 0.1 N sulphuric acid. The maximum PCIE shown by BTA *i.e.* 94.84 % is far better than other four corrosion inhibitors *i.e.* polyethylene glycol methyl ether at 25 °C shows 84.2 % [17], Schiff base at 30 °C shows 86.43 % [18], *n*-octylamine at 30 °C shows 68 % [19] and N,N-dimethyl-N-(2-phenoxyethyl) dodecan-1-aminium bromide at 25 °C shows 90 % [20] at same concentration and corroding medium.

Linear dependency of PCIE was observed with concentration of BTA. It is observed from Table-2 that anodic and cathodic over-potential decreases with increase in concentration of BTA. A typical passive behaviour is observed at a potential near to corrosion potential (E_{corr}). Corrosion current density (I_{corr}) decreases with increasing BTA concentration.

TABLE-1
PERCENTAGE CORROSION INHIBITION EFFICIENCY (PCIE) FOR MILD STEEL COUPONS IN SULPHURIC
ACID AS CORRODING MEDIUM OBTAINED BY WEIGHT LOSS METHOD BY 1,2,3-BENZOTRIAZOLE
AND OTHER CORROSION INHIBITORS AT 25, 30 AND 35 °C

Corrosion inhibitor	Inhibitor concentration	CR 25 °C (mpy)	PCIE at 25 °C	CR 30 °C (mpy)	PCIE at 30 °C	CR 35 °C (mpy)	PCIE at 35 °C
Blank	0	119.889	–	144.689	–	147.11	–
1,2,3-Benzotriazole	200 ppm	30.236	74.78	31.495	78.23	34.141	76.79
	400 ppm	15.732	86.87	16.964	88.27	25.694	82.53
	600 ppm	11.523	90.38	13.565	90.62	10.719	92.71
	800 ppm	8.752	92.69	8.060	94.42	9.502	93.54
	1000 ppm	6.931	94.21	7.455	94.84	8.697	94.08
Polyethylene glycol methyl ether (PEGME) [17]	10^{-3} (M) in 1.0 N H_2SO_4		84.2		NDA		90.0
Schiff base [18]	0.10 (mM) in 1.0 M H_2SO_4		NDA		86.43		NDA
n-Octylamine [19]	10^{-3} (M) in 0.5 M H_2SO_4		NDA		68.0		NDA
N,N-dimethyl -N-(2-phenoxy ethyl) dodecan -1-aminium bromide (DPDAB) [20]	10^{-3} (M) in 0.5 M H_2SO_4		90.0		85.5		NDA

Note: NDA stands for no data available.

TABLE-2
OCP, I_{corr}, R_p, β_a, β_c, CR AND PCIE OF 1,2,3-BENZOTRIAZOLE FOR MILD STEEL IN 0.1 N H$_2$SO$_4$ AT 25, 30 AND 35 °C. POTENTIOSTATIC MODE SCANNING THROUGH POTENTIAL OF +500 mV ABOVE OCP AT A SCAN RATE OF 0.5 mV s^{-1}

Inhibitor	Conc. (ppm)	β_a (mV d^{-1})	β_c (mV d^{-1})	R_p (Ω cm^2)	OCP (mV vs. SCE)	I_{corr} (mA cm^{-2})	PCIE
Blank	0	426	1479	27.92	-0.450	5.14	–
BTA at 25 °C	200	503	1463	74.71	-0.498	2.17	57.78
	400	631	1253	110.84	-0.525	1.64	68.09
	600	558	1498	124.23	-0.501	1.42	72.37
	800	479	1292	137.10	-0.528	1.10	78.59
	1000	437	1194	159.66	-0.540	0.87	83.07
Blank	0	423	1315	14.6	-0.489	9.61	–
BTA at 30 °C	200	763	1097	90.4	-0.510	2.16	77.52
	400	643	906	83.5	-0.500	1.95	79.70
	600	611	905	80.5	-0.487	1.96	79.60
	800	550	864	77.6	-0.494	1.88	80.43
	1000	583	929	87.5	-0.530	1.77	81.58
Blank	0	588	1370	11.20	-0.480	15.9	–
BTA at 35 °C	200	880	1070	90.3	-0.504	2.34	85.28
	400	756	893	83.2	-0.498	2.13	86.60
	600	590	926	81.3	-0.486	1.92	87.92
	800	562	852	77.0	-0.494	1.90	88.05
	1000	628	804	85.1	-0.510	1.79	88.74

Electrochemical polarization results indicate that BTA acts as a very good corrosion inhibitor for mild steel in 0.1 N sulphuric acid. It is evident from anodic and cathodic Tafel slope that BTA acts as mixed type of corrosion inhibitor, confirmed by decrease in rate of anodic metal dissolution and cathodic H$_2$ evolution reaction [21].

Electrochemical impedance spectroscopy: Table-3 shows Warburg impedance, Z_w (Laplace transform), Faradaic current and capacitive current for mild steel samples in 0.1 N H$_2$SO$_4$ solution in absence and presence of different concentrations of 1,2,3-benzotriazole at 25.0 °C. Table-4 shows electrochemical impedance data for mild steel in 0.1 N H$_2$SO$_4$ solution in presence and absence of BTA at 25, 30 and 35 °C. R_{ct} and PCIE were found to increase with increase in the concentration of inhibitor. Figs. 1-3 shows the Nyquist plots for mild steel immersed in 0.1 N H$_2$SO$_4$ in absence and presence of different concentrations of BTA at 25, 30 and 35 °C, respectively. Nyquist plots show the increase in the value of double layer capacitance (C_{dl}) with increase in concentration of BTA from 200 to 1000 ppm. This is due to the increase in effective thickness of inhibitor film over the surface of mild steel with increase in concentration of BTA. The increase in film resistance is clearly visible from Nyquist plots in the form of distinctive semicircle graph which increase significantly with increase in concentration of BTA. Increase in the value of charge transfer resistance further proves the formation of non-porous, uniform film over the surface of mild steel with increase in concentration of inhibitor. Maximum PCIE was observed for 1000 ppm concentration of BTA. Thickening of surface film is indicated by increase in area under the peak with the concentration of the inhibitor at all the investigated temperatures. Fig. 4 shows equivalent circuit (Randles circuit) at 1000 ppm concentration of BTA at 25 °C. Impedance measurements were performed in potentiostatic mode at OCP with AC perturbation amplitude of 10.0 mV/s in a frequency range of 1 to 100 kHz with 10 points/decade. It includes a resistor (R_{ct}) which is due to formation of electrified interface at the surface of working electrode
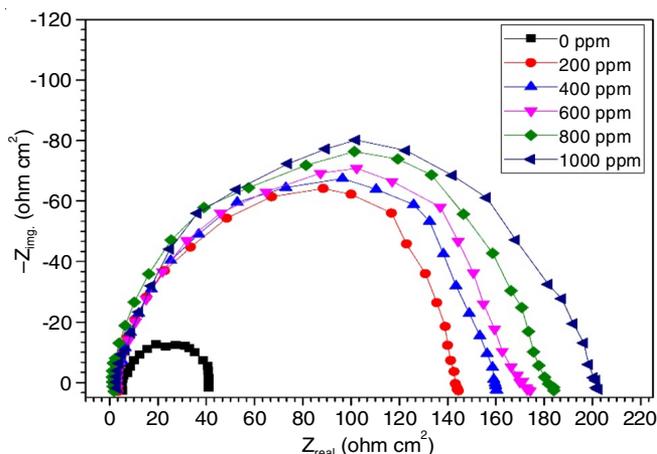

Fig. 1.   Nyquist plots (EIS) of mild steel immersed in 0.1 N H$_2$SO$_4$ in absence and presence of different concentrations of BTA at 25 °C. Obtained in potentiostatic mode at OCP with AC perturbation amplitude of 10.0 mV/s in a frequency range of 1 to 100 kHz with 10 points/decade
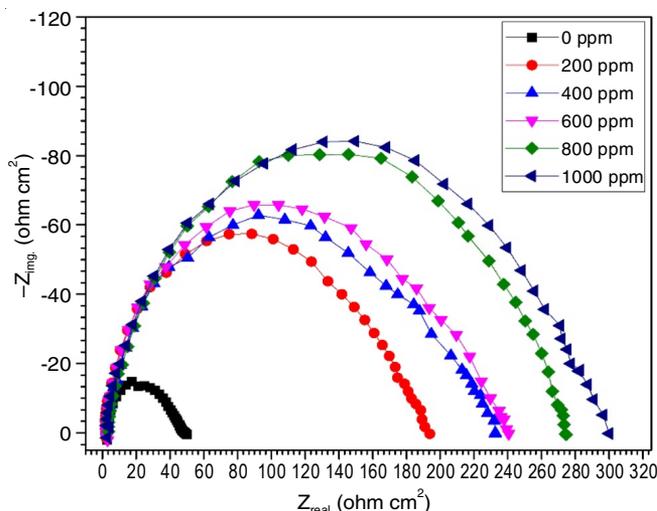

Fig. 2.   Nyquist plots (EIS) of mild steel immersed in 0.1 N H$_2$SO$_4$ in absence and presence of different concentrations of BTA at 30 °C

TABLE-3
WARBURG IMPEDANCE (Z_w), FARADAIC CURRENT AND
CAPACITIVE CURRENT COMPONENT FOR MILD STEEL
SAMPLES IN 0.1 N H_2SO_4 SOLUTION IN ABSENCE AND
PRESENCE OF DIFFERENT CONCENTRATIONS OF
1,2,3-BENZOTRIAZOLE AT 25 °C

Conc. (ppm)	Warburg impedance, Z_w (S/cm)	Faradaic current, I_F ($\mu A\ cm^{-2}$)	Capacitive current, I_C ($\mu A\ cm^{-2}$)
Blank	0.3	4.37	0.77
200	3.6	1.89	0.94
600	8.3	1.12	1.43
800	9.9	0.86	2.02
1000	12.4	0.67	2.35

Fig. 4. Equivalent circuit (Randles circuit) corresponding to 1000 ppm concentration of 1,2,3-benzotriazole as corrosion inhibitor for mild steel at 25 °C
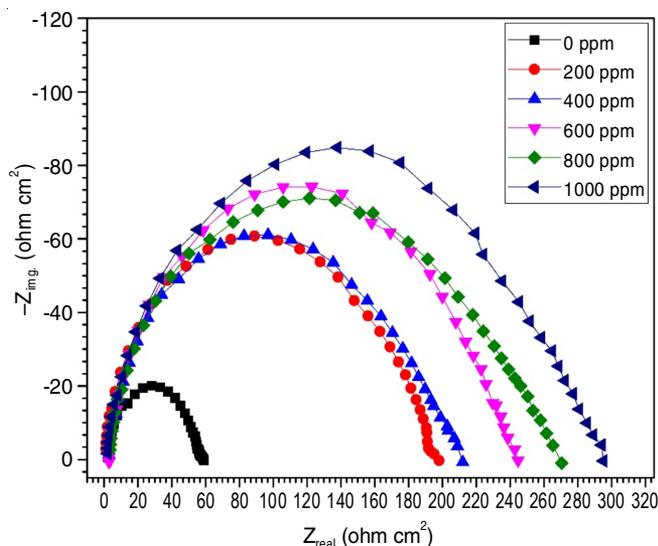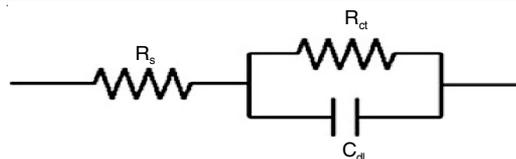

Fig. 3. Nyquist plots (EIS) of mild steel immersed in 0.1 N H_2SO_4 in absence and presence of different concentrations of BTA at 35 °C

TABLE-4
ELECTROCHEMICAL IMPEDANCE PARAMETERS FOR
MILD STEEL SAMPLES IN 0.1 N H_2SO_4 SOLUTION IN ABSENCE
AND PRESENCE OF DIFFERENT CONCENTRATIONS OF 1,2,3-
BENZOTRIAZOLE AT 25.0, 30.0 AND 35.0 °C. RECORDED IN
POTENTIOSTATIC MODE AT OCP AND AC PERTURBATION
AMPLITUDE OF 10.0 mV/s IN FREQUENCY RANGE FROM
1 to 100 kHz WITH 10 POINTS/DECADE

| Corrosion inhibitor	Conc. (ppm)	C_{dl} ($F\ cm^2$)	R_{ct} ($\Omega\ cm^2$)	IE (%)
Blank	0	3.8×10^{-2}	41	–
BTA at 25.0 °C	200	10.9×10^{-3}	145	71.72
	400	9.9×10^{-3}	160	74.37
	600	9.1×10^{-3}	174	76.43
	800	8.6×10^{-3}	185	77.83
	1000	7.8×10^{-3}	202	79.70
Blank	0	3.18×10^{-2}	50	–
BTA at 30.0 °C	200	8.1×10^{-3}	195	74.46
	400	6.8×10^{-3}	232	78.48
	600	6.6×10^{-3}	240	79.15
	800	5.7×10^{-3}	274	81.78
	1000	5.3×10^{-3}	299	83.32
Blank	0	3.18×10^{-2}	59	–
BTA at 35.0 °C	200	8.0×10^{-3}	198	74.71
	400	7.5×10^{-3}	211	76.31
	600	6.5×10^{-3}	244	79.52
	800	5.8×10^{-3}	270	81.48
	1000	4.0×10^{-3}	295	83.03
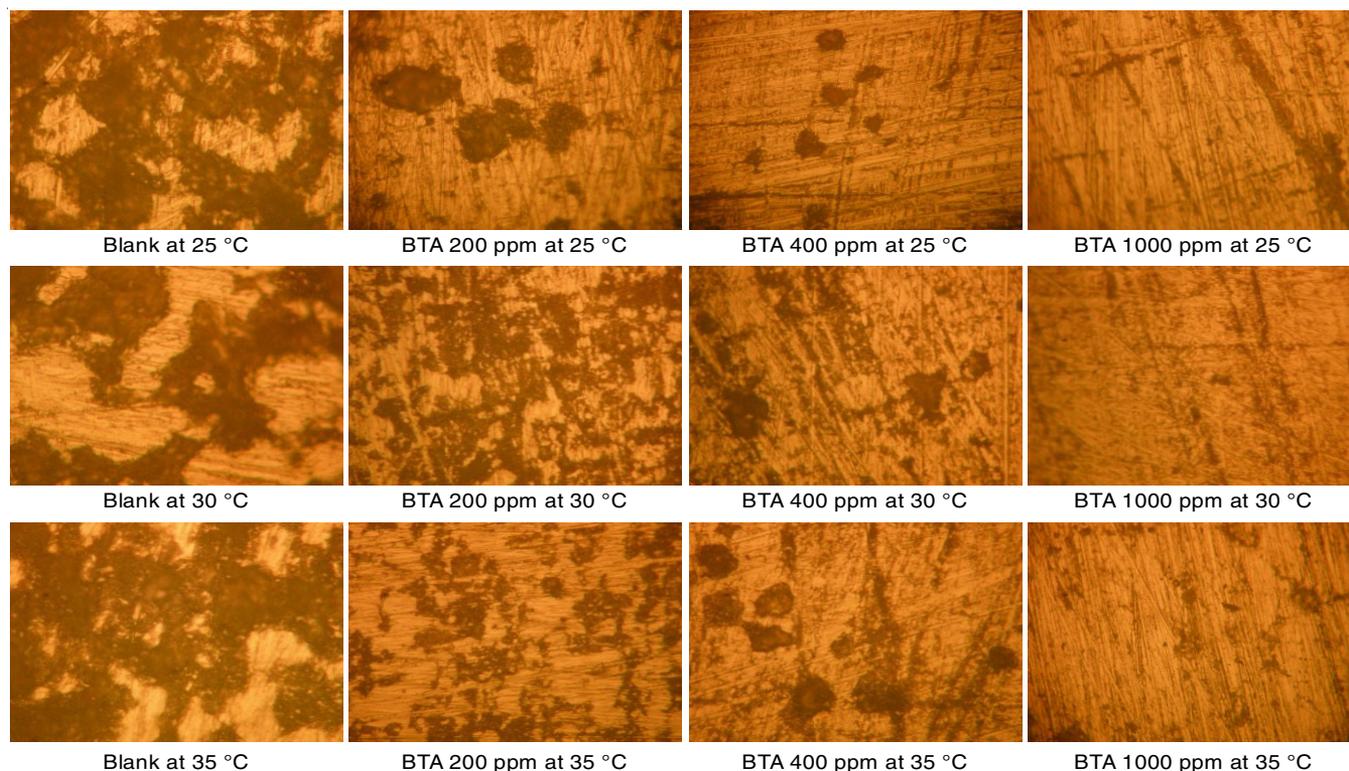
Fig. 5. Metallurgical research micrographs of mild steel samples with and without BTA at different concentrations and temperatures

termed as charge-transfer resistance which is connected in parallel with a capacitor (C_{dl}) *i.e.* a double layer-capacitance and this whole RC electrical unit is connected in series with another resistor, R_s.

Differential pulse voltammetry and anodic stripping voltammetry techniques were used to separate Faradaic and capacitive component of current. Values of Warburg impedance, Z_w (Laplace transform) and Faradaic current decreases whereas capacitive current and capacitive loop in Nyquist plots increases with increase in concentration of BTA (Table-3). Magnitude

of Warburg impedance was found to be higher in the concentration of 600 and 800 ppm of BTA at 25.0 °C and shows a phase shift of 450 in low frequency region (Fig. 1).

Metallurgical research microscopy technique: Morphology of the corroded samples of the mild steel was studied under a metallurgical trinocular research microscope attached to a computer and the micrographs were recorded. The micrographs obtained for corroded samples with and without corrosion inhibitors clearly gave an idea about the effectiveness of the corrosion inhibitor. Porosity, coating thickness, length of pores,
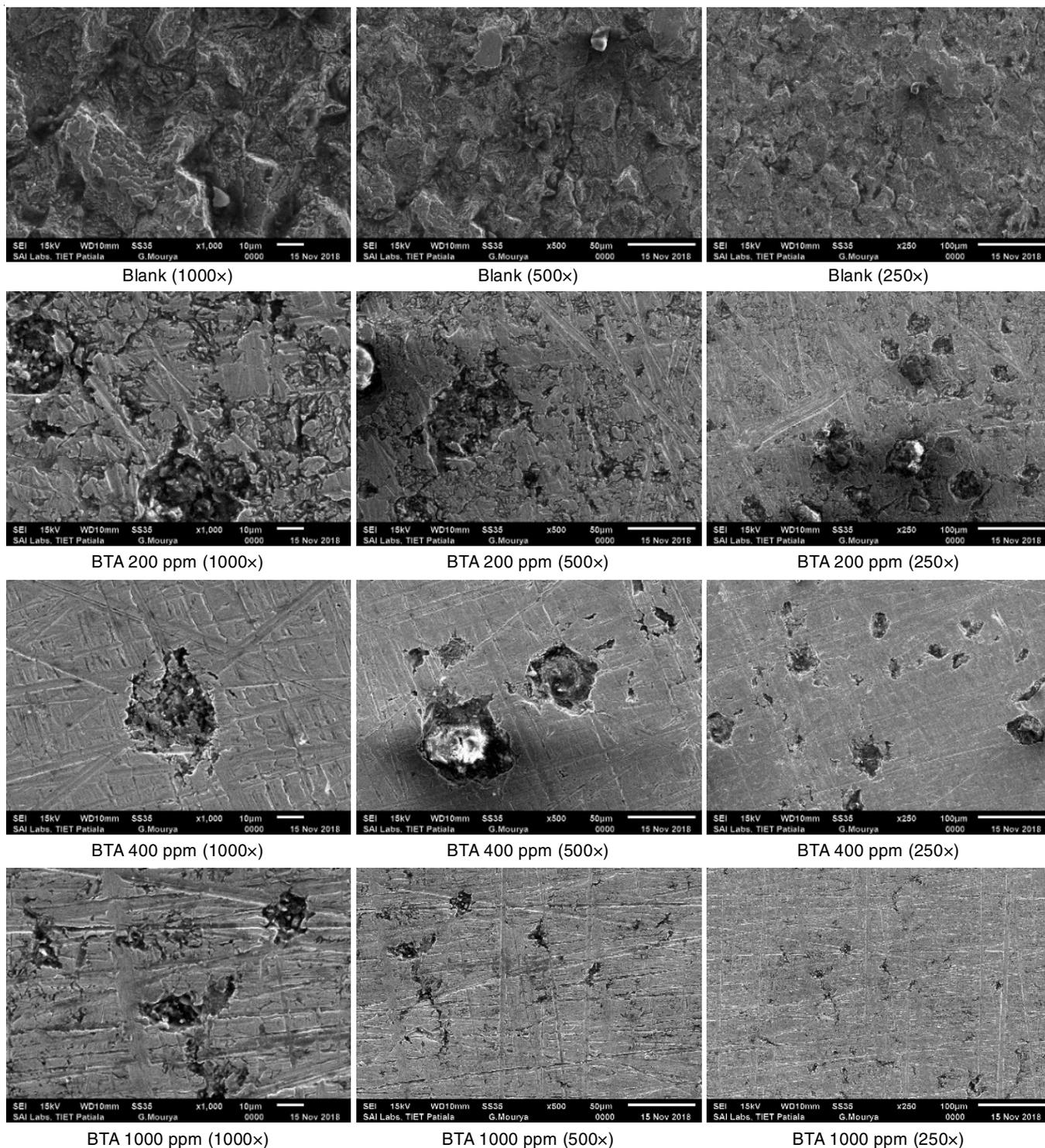

Fig. 6. SEM images of mild steel samples without and with different concentrations of BTA at 25 °C

maximum and minimum perimeter was measured on the surface of mild steel. Micrographs of blank specimen and specimen with different concentrations of corrosion inhibitor were taken after immersion in 0.1 N H_2SO_4 for 24 h and are shown in Fig. 5. Data obtained from metallurgical microscopy study of blank and corrosion inhibitor exposed samples after 24 h of immersion time is tabulated in Table-5. Data shows that the surface becomes porous after exposing specimen in 0.1 N H_2SO_4 as a corroding medium.

As the concentration of BTA was increased from 200 to 1000 ppm, porosity of mild steel surface decreases with increase in concentration of inhibitor. Length of pores also decreases with increase in concentration of BTA. SEM images of mild steel surface reveals that roughness of mild steel surface decreases with increase in concentration of BTA. In presence of BTA, no pit and corrosion products were visible on the surface of mild steel. However, at very high resolution (1000 X) very slight sign of roughness was observed on the surface of mild steel. From the SEM images, it is clear that BTA provides significant protection to mild steel even at 200 ppm concentration

at all the three investigated temperatures *i.e.* 25, 30 and 35 °C.

SEM analysis: To understand the nature and thickness of the surface film in the absence and presence of inhibitor and the extent of corrosion on mild steel, SEM images of corroded and blank samples were taken. Figs. 6-8 shows SEM image of mild steel samples at three different magnifications and temperatures *i.e.* 25, 30 and 35 °C, respectively. It is clear from the SEM images that mode of action of BTA is through physical adsorption over the surface of mild steel by forming a thin, uniform, transparent, continuous, barrier film which reduces the rate of corrosion.

Conclusion

Addition of BTA as corrosion inhibitor for mild steel in 0.1 N H_2SO_4 solution results in significant decrease in corrosion rate. Improvement in corrosion inhibition properties are far superior than other organic corrosion inhibitors suggesting that BTA is a potential alternate to them for inhibiting corrosion of mild steel in 0.1 N sulphuric acid medium. The increase in corrosion resistance properties of BTA was associated with
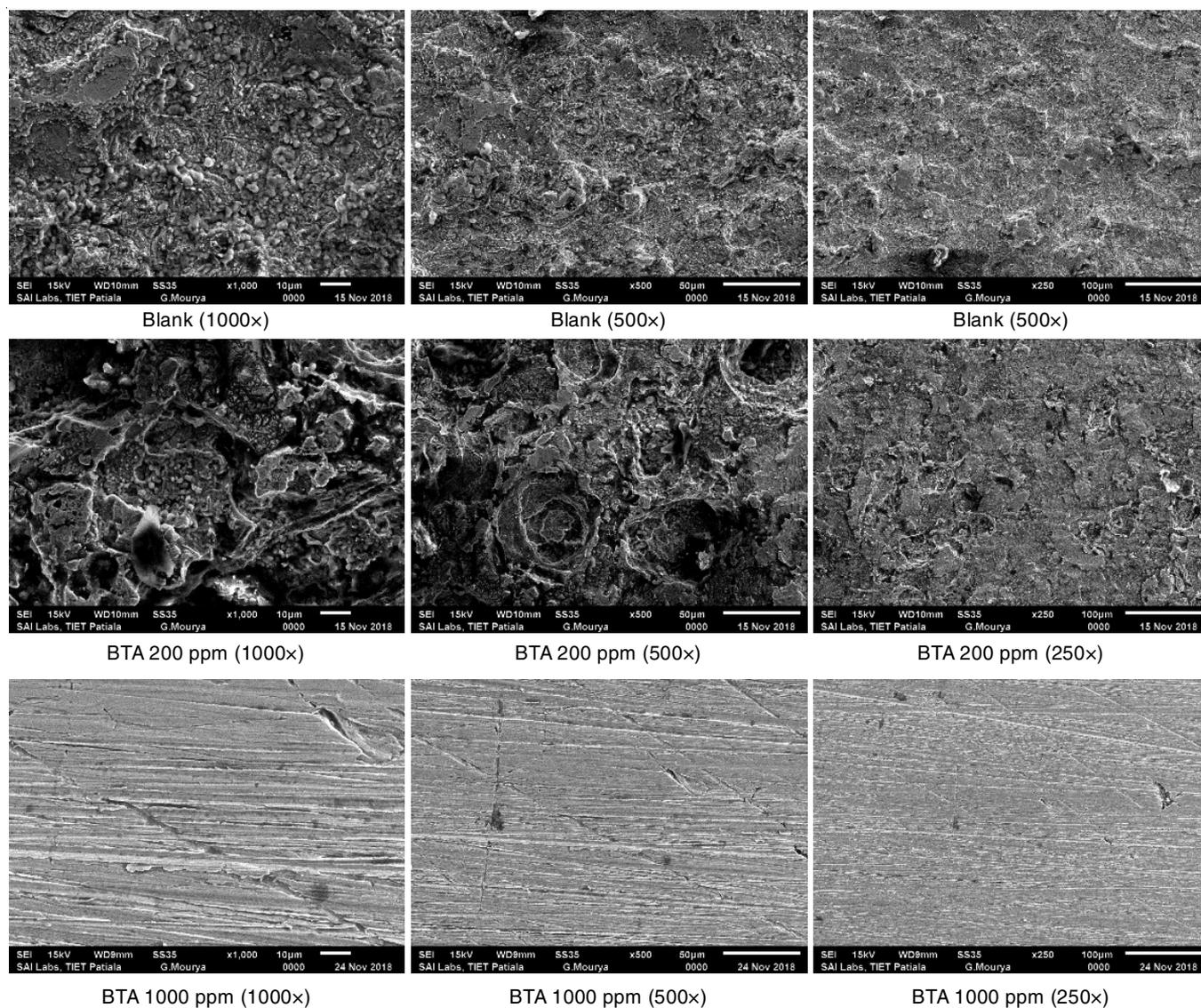

Fig. 7. SEM images of mild steel samples without and with different concentrations of BTA at 30 °C

TABLE-5
COATING THICKNESS (μ, PERCENTAGE POROSITY, MAXIMUM AREA COVERED AND PORE LENGTH (μ) OF MILD STEEL SAMPLES WITH AND WITHOUT CORROSION INHIBITOR AT THREE DIFFERENT TEMPERATURES

Temperature (°C)	Conc. of inhibitor (ppm)	Max. perimeter (Micron)	Max. area covered (micron)^2	Porosity (%)	Coating thickness (micron)	Length of pores (micron)
25	0	7712.58	485803.32	93.36	94.74	185.28
	200	2025.76	37991.69	22.41	352.63	80.34
	400	1858.89	13843.49	20.62	436.84	143.29
	600	1275.89	14452.91	17.77	550.00	51.70
	800	1739.18	17714.68	13.20	702.63	121.31
	1000	1672.73	18621.88	8.91	813.16	86.27
30	0	6766.84	490304.71	92.70	78.95	265.80
	200	3203.34	19653.74	28.98	255.26	78.95
	400	2910.69	39203.60	27.87	310.51	76.32
	600	6023.52	57714.68	23.76	455.26	69.08
	800	2138.02	17998.61	16.10	494.74	39.12
	1000	3949.26	23407.20	13.55	744.73	28.95
35	0	4222.91	511620.49	96.42	268.42	255.38
	200	2713.99	23213.29	30.32	334.21	145.33
	400	2703.45	19016.62	27.93	242.10	118.27
	600	2577.98	24141.27	21.46	634.21	100.03
	800	1752.42	13469.53	16.69	550.00	89.82
	1000	1262.73	7278.39	10.89	647.37	73.73

Blank (1000×)   Blank (500×)   Blank (250×)

BTA 200 ppm (1000×)   BTA 200 ppm (500×)   BTA 200 ppm (250×)

BTA 1000 ppm (1000×)   BTA 1000 ppm (500×)   BTA 1000 ppm (250×)

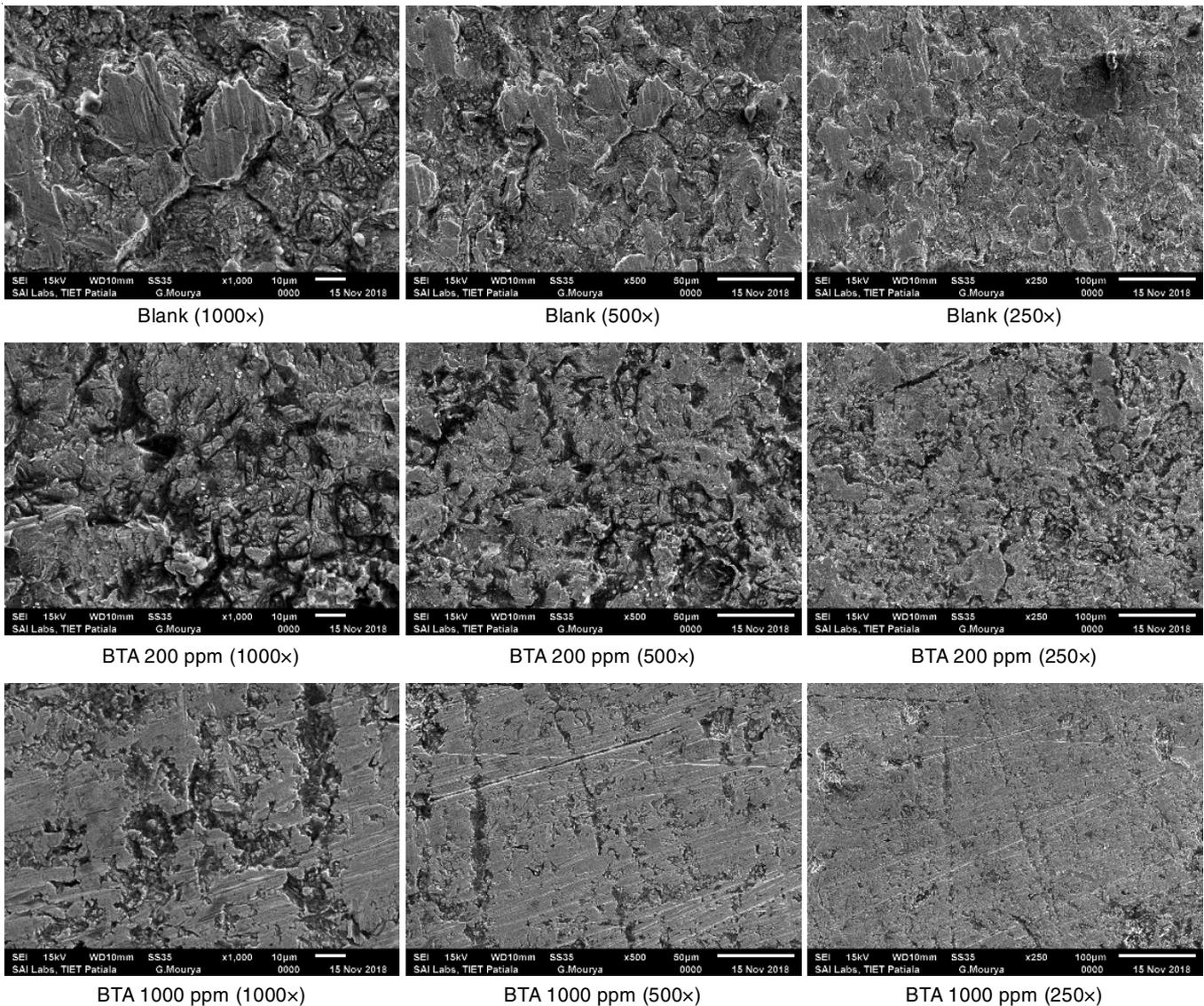Fig. 8. SEM images of mild steel samples without and with different concentrations of BTA at 35 °C

the formation of uniform, non-porous, barrier film over the surface of mild steel as observed in SEM, metallurgical research microscopy and impedance spectroscopy which was further confirmed by increase in Warburg Impedance (Z_w) and Capacitive current and decrease in Faradaic current and capacitive loop with increase in concentration of BTA. The thickness of the film increases with increase in concentration of the BTA and decreases with increase in temperature of the corroding medium. Electrochemical polarization, impedance spectroscopy, anodic striping voltammetry and differential pulse voltammetry experiments proves that BTA acts as potential alternate corrosion inhibitor for mild steel in 0.1 N sulphuric acid medium.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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