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Synthesis of Novel Corrosion Inhibitor *N*-(1,3-Benzothiazol-2-yl)-4-aminobenzamide in 1 N Hydrochloric Acid Medium

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A novel corrosion inhibitor *i.e.* *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide was synthesized and its corrosion inhibitor on controlling the rate of mild steel material in hydrochloric acid medium (1 N) at different temperatures was investigated. Rate of corrosion and inhibition efficiency were analyzed and calculated using mass loss method and electrochemical studies. As the concentration of the inhibitor increase the inhibitor efficiency also increases gradually with decrease in the rate of corrosion. Therefore from this study the efficiency of the inhibitor was good at different temperature in 1 N HCl. The relative corrosion inhibition efficiency of synthesized organic compound has been explained on the basis of its structure dependent-electron donating properties of the inhibitor. Further the structure and compound present in the synthesized organic inhibitor compound was confirmed by FTIR and NMR studies.

Keywords: Mild steel, Aminobenzamide, Corrosion, EIS, Impedance.

INTRODUCTION

In many industrial sectors and in construction purposes, mild steel plays a very important role. The loss in weight of the metal causes due to environmental condition where the metal react either chemically or electrochemically with the metal. Due to this reaction the metal may have physical damages, which can be classified as corrosion-erosion; corrosive-wear or fretting-corrosion, which occurs due to chemical and electrochemical reaction [1,2]. Not only metal gets corroded, materials like plastic, ceramics also get corroded. Not only in India in many countries, there is a major economic loss due to corrosion for this reason more efforts and techniques were carried out to reduce corrosion [3]. A huge amount is spent for the prevention corrosion, which is roughly estimated around 6% of GDP of nation economic value in India. Adsorption takes places on the metal surface with the help of organic synthesized inhibitor, which has high electron density of nitrogen atoms present in the heterocyclic organic compounds. In order to minimize the corrosion attack over mild steel due to the aggressive nature of hydrochloric acid solution inhibitors were used [4-6].

Various organic inhibitors are reported for the prevention of mild steel in various acidic mediums. In a recent study, 5-amino-2-chloro-3-picoline (ACP) corrosion inhibitor were used in 1.1 N HCl medium having efficiency of 85.39% [7]. Similarly, formazan of *p*-dimethylamino benzaldehyde was used as inhibitor in 1.1 N HCl medium with high inhibition efficiency value of 79.21% [8]. A series of oxadiazoles compound were also used as corrosion inhibitors against mild steel in 1 M HCl, having an inhibitor efficiency of > 90%, than in 1 M H_2SO_4 (70%) [9]. However, in 1 M HCl, Schiff's base of triazole shows a better inhibition efficiency of 96.8% [10]. Effective inhibition action of indoles [11], azoles [12], triazoles [13] and a quaternary ammonium salt [14] also showed the corrosion inhibition efficiency around 80% in H_2SO_4 medium. Therefore, in this investigation, 1 N HCl acidic medium and *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide were used as inhibitor, where the inhi-bitor corrosion studies were performed in presence and absence of inhibitor at different temperatures and confirmed by mass loss method and electrochemical method.

EXPERIMENTAL

Preparation of specimens: Mild steel strips were cut into pieces of 5 cm × 1 cm having the composition as Fe = 99.712%, Ni = 0.013%, Mo = 0.018%, Cr = 0.041%, S = 0.013%, P =

0.014%, Si = 0.005%, Mn = 0.169 and C = 0.015%. For electrochemical analysis, mild steel plate were cut into 1 cm × 1 cm × 0.3 cm dimensions. Upper face of the electrode was covered with araldite and lower surface 1 cm^2 were exposed to the acidic medium. Using various grade of emery sheet ranges from 400-1200 grit were used for polishing the surface of the metal and further degreased with acetone [15].

A.C. impedance cell: Using double walled glass cell of capacity which has a provisions of inlet for nitrogen gas, luggin capillary, working electrode and counter platinum electrode and. Through the luggin capillary the potential of the working electrode calomel electrode (SCE) was measured.

Synthesis of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide: A mixture of 2-aminobenzothiazole (5 g, 0.033 mol) in 100 mL THF containing triethylamine (14.1 mL, 0.101 mol) was stirred for 10 min at 0-5 ºC in ice bath. Then to the reaction mixture, 4-aminobenzoyl chloride (6.78 g, 0.036 mol) was added. The resulting reaction mixture was allowed and stirred at room temperature for 12 h. The progress of reaction was monitored by TLC. The reaction solution was concentrated under reduced pressure and extracted using ethyl acetate (250 mL) and water (200 mL). The combined ethyl acetate layer was washed with 2 N HCl (1 × 75 mL), 10% $NaHCO_3$ (1 × 100 mL), brine (1 × 200 mL) and dried over anhydrous Na_2SO_4. The resulting ethyl acetate layer was washed and concentrated under reduced pressure to afford compound. Pale yellow solid; Yield 88%; m.p.: 265-266 ºC. IR (KBr, ν_{max}, cm^{-1}): 3428 (NH *str.*), 3136 (CH *str.*, arom.), 1649 (C=O *str.*), 1401 (C-C *str.*), 1315 (NO_2 *str.*), 931 (CH bend, in-plane), 752 (C-S, *str.*), 710 (CH bend, out-of-plane); ^1H NMR (300 MHz, DMSO-d_6) δ ppm: 7.43 (1H, td, *J* = 0.9, 7.8 Hz), 7.55 (1H, td, *J* = 0.9, 7.8 Hz), 7.85 (1H, d, *J* = 7.8 Hz), 8.10 (1H, d, *J* = 7.5 Hz), 8.40-8.47 (4H, m); ^{13}C NMR (300 MHz, DMSO-d_6) δ ppm: 120.3, 122.4, 124.0, 124.3, 126.8, 130.3, 131.5, 138.4, 150.1; LC-MS (ESI) *m/z*: 299.9 $(M+H)^+$. From stock solutions various concentration of inhibitor such as 10, 20, 40, 60, 80, 100 ppm were prepared.

Thin layer chromatography: For the checking of purity of product as well as monitoring the progress of the reactions were done by TLC run on silica gel GF_{254} pre-coated aluminium sheets, Merck (Germany). The solvent system used was $CHCl_3$:CH_3OH (9:1), $CHCl_3$:CH_3OH (9.5:0.5), hexane: ethyl acetate (7:3), hexane:ethyl acetate (5:5) and ethyl acetate:CH_3OH (9:1). The resulting final products were detected by irradiating with UV light or reacting with $KMnO_4$ or reacting with ninhydrin or reacting with iodine vapour.

Characterization: Infrared spectra were recorded using KBr discs (4000-400 cm^{-1}) on Perkin-Elmer. The ^1H & ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ solvents on Bruker 300 MHz NMR using tetramethylsilane as an internal standard. The mass spectra were recorded on a Waters-Synapt G2 by electrospray ionization (ESI) technique with a flow rate of 0.5 mL/min on C-18 column and total run time of 45 min. The sample used for recording the mass spectrum was prepared by dissolving 0.4 mg of compound in 10 mL of CH_3OH:CH_3CN (7:3).

Mass loss measurement: A cold-rolled mild steel specimens were immersed 1 N HCl at a different temperature range of 303, 318 and 333 K in various inhibitor concentrations. After 1 h, the specimen were removed and washed with doubled distilled water and acetone. Mass loss data such as corrosion rate and inhibitor efficiency was calculated using the formula:

$$CR = \frac{87.6 \times W}{D \times A \times T}$$

where, W = weight of the specimen, D = density of mild steel, A = area of the specimen and T = exposure time.

Similarly, inhibition efficiency (IE):

$$IE\ (\%) = \frac{W_o - W_i}{W_o} \times 100$$

where W_o and W_i are the values of the weight loss (g) of mild steel in the absence and presence of inhibitor, respectively.

Electrochemical studies: Electrochemical studies were performed by preparing the coupons of mild steel material were cut into 1 cm × 1 cm. After molding the working electrode with araldite, 1 cm^2 area of the working electrode was exposed into the test solution by polishing the electrode with 400-1200 grit emery papers and degreased with acetone. In a three-electrode polarization cell 100 mL of the test solution was introduced. The test solution in the polarization cell was allowed to attain a steady potential value for 20 min [16]. By applying constant potential the resultant current was measured. The experimental set-up were carried out at an approximate voltage of ± 200 mV from corrosion potential. At different temperatures, the experiments were carried out in the presence and absence of the inhibitor. The values of β_a and β_c, current density and Tafel slopes were obtained by the extrapolation of the values obtained from polarization curves. Inhibition efficiency was calculated from the following formula:

$$IE\ (\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

where, I_{corr} = corrosion current density in the absence of inhibitor; $I_{corr(i)}$ = corrosion current density in the presence of inhibitor.

RESULTS AND DISCUSSION

The resulting compound *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide was characterized using FT-IR, NMR and LC-MS. The IR spectrum of compound *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide showed absorption band at 3456 and 3222 cm^{-1} region resulting from the NH stretching of amine (Fig. 1). The absorption band at 1601 cm^{-1} is due to NH bending vibration of amine. The carbonyl C=O stretching frequency of compound *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide showed strong absorption band at 1636 cm^{-1}. In the ^1H NMR spectra of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide a characteristic amine protons (NH_2) signal appeared at δ 6.05 ppm as a broad singlet. Six protons of aromatic displayed doublet and remaining two aromatic protons appeared as a triplet in the region between δ 6.61 and δ 7.97 ppm (Fig. 2). The amide NH proton resonated at δ 12.33 ppm as a broad singlet.

In the ^{13}C NMR, a characteristic C=O signals appeared at around δ 153.9 ppm. The amine attached carbon was resonated

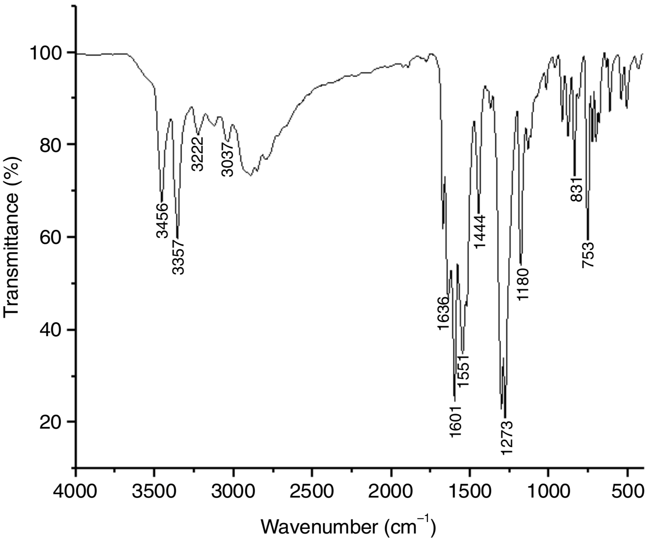

Fig. 1. FT-IR spectrum of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide

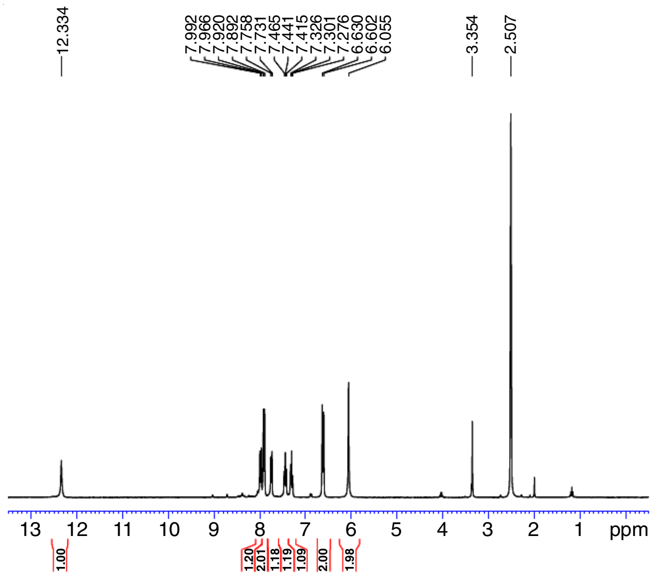

Fig. 2. ^{1}H NMR spectrum of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide

at δ 149.4 ppm. From the ^{13}C NMR of the synthesis compound, the aromatic carbon signals of the synthesized compound were found in the range of δ 113.1-132.0 ppm (Fig. 3). The mass spectrum of *N*-(1,3-benzothiazol-2-yl)-4-nitrobenzamide) as showed in Fig. 4 represent the molecular ion peak *m/z* 269.3 (M-H) equivalent to the correct molecular formula $C_{14}H_{11}N_3OS$.

Mass loss measurement: Mild steel specimen 5 cm × 1 cm were taken and numbered at the top of the plate. Now the plates were immersed in different concentrations of the inhibitor in acidic medium and study was performed at three different temperatures *viz*. 303, 318 and 333 K. The calculated corrosion rate and inhibitor efficiency are shown in Table-1. As observed, the rate of corrosion decreases similarly the efficiency of the inhibitor increases by the addition of inhibitor concentration at different temperatures. Among the three investigated temperature, the inhibitor at 303 K shows the better efficiency of 96.89% in 1 N HCl medium.

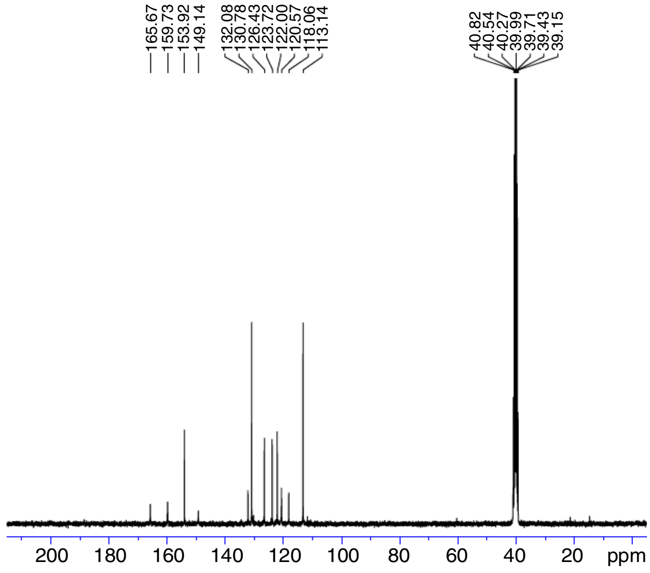

Fig. 3. ^{13}C NMR spectrum of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide)

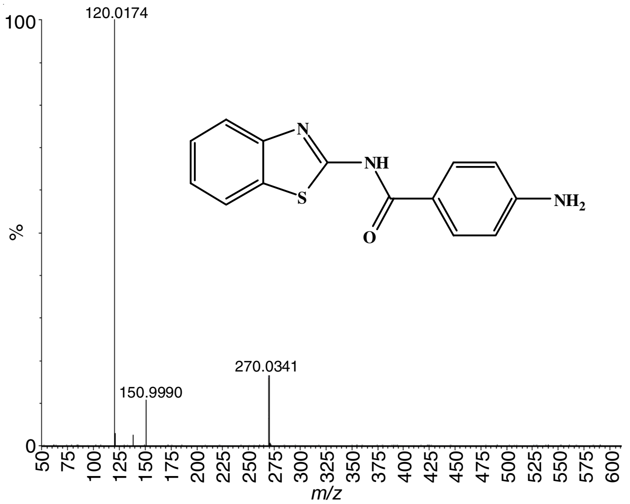

Fig. 4. Mass spectrum of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide)

TABLE-1
CORROSION INHIBITION BEHAVIOUR OF MILD STEEL IN 1 N HCl SOLUTION IN ABSENCE AND PRESENCE *N*-(1,3-BENZOTHIAZOL-2-YL)-4-AMINOBENZAMIDE INHIBITOR

Conc. of inhibitor (%)	303 K		318 K		333 K	
	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
Blank	27.5642	-	29.6324	–	27.8965	–
10	26.1524	88.8	26.5423	88.61	25.6415	80.10
20	25.3289	93.31	23.1254	90.7	23.1874	84.74
40	23.9874	94.23	22.0325	91.02	21.9875	86.80
60	21.5698	95.23	17.8954	92.23	20.9687	91.01
80	20.6789	96.16	16.6214	93.51	18.9863	92.13
100	20.2547	96.89	15.4231	94.01	18.0231	92.87

CR = Corrosion rate; IE = Inhibition efficiency

Potentiodynamic polarization studies: Corrosion on mild steel in 1 N HCl with inhibitory effect of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide at three different temperature was studied using potentiodynamic polarization studies and depicted in Fig. 5. Using polarization values various potentiodynamic parameters were calculated (Table-2). It is observed that the E_{corr} values were slightly shifted towards cathodic region, which infers that the inhibitor controlled the corroding reaction in mild steel in acidic medium, where it represent the blocking active sites on the metal surface effectively protected by the inhibitor [17]. This evidence explains that there is a considerable polarization access at cathode. The inhibitive action of *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide on mild steel in acidic medium at different temperatures is a cathodic type of inhibitor. Corrosion reaction which shows the variability on Tafel slopes reveals that inhibitor at all concentration at different temperature shows the corrosion mechanism process at cathode. At three different temperatures on comparison shows that I_{corr} values were decreased.

On comparing the mass loss data and polarization parameter show a related inhibition values. *N*-(1,3-Benzothiazol-2-yl)-4-aminobenzamide shows the maximum efficiency of 96.06% in 1 N HCl at 303 K (Table-2). This can be explains due to the involvement of nitrogen atoms present in the inhibitor retards the hydrogen evolution from the metal [18]. Inhibitor contains (-NH group) in the inhibitor shows an electrostatic attraction of the inhibitor and metal surface.

Electrochemical impedance spectroscopy (EIS): EIS measurement at OCP-open circuit potential was performed for *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide inhibitor on mild steel corrosion in 1 N HCl. Fig. 6a-c show a Nyquist plots for interface of mild steel electrode and electrolyte in the absence and presence of various concentration of inhibitors at different temperatures. It is seen that the diameter of the semicircle increases on the increasing the concentration of the inhibitor, which implies that electrostatic attraction of inhibitor form a strong film over the metal surface.

From Table-3, it is concluded that on the addition of the inhibitor in 1 N HCl at different concentration, the C_{dl} value decreases indicating the formation of homogenous layer on the surface of the metal, which is roughened due to corrosion [19]. Efficiency of the inhibitor indicated the action of inhibitor due to the adsorption of inhibitor molecule on surface of the

TABLE-2
POLARIZATION PARAMETERS OF MILD STEEL ELECTRODE IMMERSED IN THE ABSENCE AND PRESENCE OF THE OF THE INHIBITORS AT THREE DIFFERENT TEMPERATURES

Temperature (K)	Inhibitor concentration	β_c (V dec^{-1})	β_a (V dec^{-1})	E_{corr} (V)	$I_{corr} \times 10^{-4}$ (A)	Corrosion rate (mmpy)	Inhibition efficiency (%)
303	Blank	96.0	138.1	-603	825.2	9.5721	–
	10	116.2	235.0	- 628	392.1	4.54798	52.48
	20	120.0	271.5	-647	255.6	2.96528	72.57
	40	128.7	358.0	-655	125.8	1.45977	86.49
	60	132.5	305.3	-654	84.3	0.97809	90.95
	80	142.8	285.2	-668	57.3	0.66516	93.85
	100	147.9	325.8	-657	36.8	0.42631	96.06
318	Blank	107.6	220.3	-618	1235.6	14.33346	–
	10	131.5	216.3	-623	636.4	7.38261	48.49
	20	135.2	242.3	-620	377.9	4.38395	69.41
	40	127.8	210.7	-622	236.4	2.74227	80.87
	60	141.6	280.7	-647	169.7	1.96806	86.27
	80	127.8	285.2	-668	120.4	1.39656	90.26
	100	136.0	258.4	-679	96.4	1.11847	92.20
333	Blank	107.6	293.3	-652	1892.5	21.95	–
	10	131.5	195.4	-662	1131.2	13.12	40.23
	20	135.2	240.9	-609	783.3	9.09	58.61
	40	127.8	226.4	-615	550.5	6.39	70.91
	60	141.6	248.9	-624	440.8	5.11	76.71
	80	127.8	197.5	-645	345.0	4.00	81.77
	100	136.0	231.9	-653	277.4	3.22	85.34

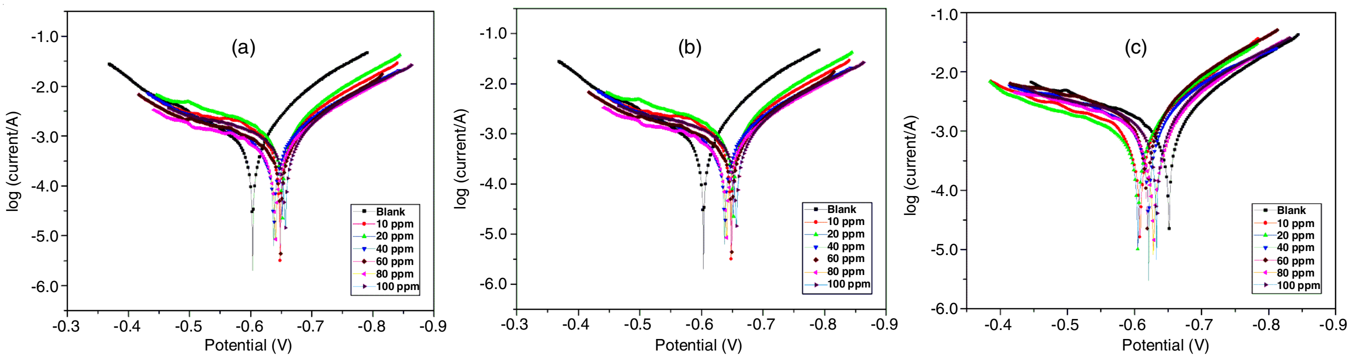

Fig. 5. Potentiodynamic polarization curves of mild steel in 1 N HCl in the absence and presence of the inhibitor at (a) 303 K, (b) 318 K and (c) 333 K

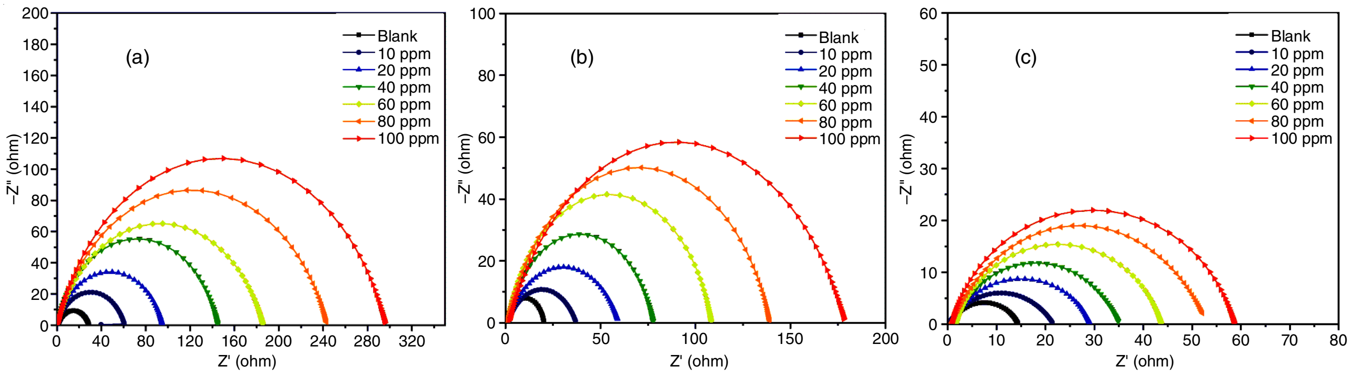

Fig. 6. AC impedance curves of mild steel electrode immersed in 1 N HCl in the absence and presence of the inhibitor at (a) 303 K, (b) 318 K and (c) 333 K

TABLE-3
AC IMPEDANCE PARAMETERS OF MILD STEEL ELECTRODE IMMERSED IN 1 N HCl IN THE ABSENCE AND PRESENCE OF THE INHIBITOR AT DIFFERENT TEMPERATURES

Inhibitor concentration	303 K			318 K			333 K		
	R_{ct} (ohm cm^2)	Cdl (μF × 10^{-5})	Inhibition efficiency (%)	R_{ct} (ohm cm^2)	Cdl (μF × 10^{-5})	Inhibition efficiency (%)	R_{ct} (ohm cm^2)	Cdl (μF × 10^{-5})	Inhibition efficiency (%)
Blank	27.9	83.9	–	19.65	207.8	–	13.78	390.9	–
10	60.9	60.6	54.13	35.99	145.2	45.40	19.58	213.8	29.62
20	95.2	33.8	70.70	58.46	125.1	66.39	28.19	154.2	51.12
40	144.9	18.3	80.74	76.71	37.9	74.38	34.18	80.6	59.68
60	186.1	10.0	85.00	107.2	33.1	81.67	42.14	56.9	67.30
80	243.8	8.1	88.55	138.3	13.6	85.79	52.37	28.8	73.69
100	296.0	7.8	90.57	177	9.4	88.90	57.92	14.8	76.21

metal. Due to presence of -NH group in *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide inhibitor shows a better inhibitive effect.

Conclusion

Synthesis of the organic compound *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide was characteried successfully by the spectral studies. On controlling of corrosion on mild steel, the present study reveals that synthesized *N*-(1,3-benzothiazol-2-yl)-4-aminobenzamide in 1 N HCl found to be an effective inhibitor exhibiting an inhibition efficiency of maximum 96.89 % in 1 N HCl at 303 K. Based on the polarization studies synthesized inhibitor shows a cathodic shift indicated that inhibitor is a cathodic type inhibitor.

CONFLICT OF INTEREST

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

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