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Corrosion inhibition studies on Schiff bases derived from 2-amino-6-methoxy-benzothiazole

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ABSTRACT

The present investigation deals with corrosion of mild steel in 1M HCl and the inhibitive effect of Schiff base ligands [N-(p-anisalidene)- 6-methoxy-1,3-benzothiazol-2-amine (AMBTA) and N-(2-hydroxy-1-naphthalidene)-6-methoxy-1,3-benzothiazol-2-amine (HNMBTA)] derived from 2-amino-6-methoxy-benzothiazole (AMBT) by weight loss method and electrochemical studies. The surface morphology of the mild steel plates in the presence and absence of the inhibitors have been examined by the study of the SEM.

Key words: AMBT (2-amino-6-methoxy-benzothiazole), AMBTA (N-(p-anisalidene)-6-methoxy-1,3-benzothiazol-2-amine) and HNMBTA (N-(2-hydroxy-1-naphthalidene)-6-methoxy-1, 3-benzothiazol-2-amine)

INTRODUCTION

Corrosion studies have become important due to increasing awareness, to conserve the world's metal resources. Inhibitors are substances which when added in small quantities to the aqueous corrosive environment, decreases the rate of corrosion of the metal. They produce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathode and/or anodic process **[1], [2]**.

The condensation product of an amine and aldehyde with general formula of RC=NR' are well known organic inhibitor **[3]**. So Schiff bases act as inhibitor in acid environments. Acid solutions are widely used for removal of undesirable scale and rust in many industrial processes. Inhibitors are generally used in these processes to control metal dissolution as well as consumption of acid **[4]**.Today, organic inhibitors perform this role well and new series of them are developing to replace the inorganic ones.

In the present study AMBT and their Schiff bases are used as corrosion inhibitor of mild steel in 1M HCl. Inhibition efficiency of Schiff bases is much greater than that of corresponding amine and aldehyde and this is attributed due to the presence of a –CH=N– group in these molecules. The size, orientation, shape, and electric charge on the molecule determine the degree of adsorption and hence the effectiveness of the inhibitor **[5], [6]**.

EXPERIMENTAL SECTION

Metal Composition of mild steel: C-0.084%, Mn-0.369%, Si-0.129%, P-0.025%, S-0.027%, Cr-0.022%, Mo-0.011%, Ni-0.013%, Iron-Rest (%)

2.1. Specimen preparation

Rectangular mild steel of size 3cm x 2cm x 0.01cm containing a small hole of 2mm diameter were taken. The specimens are thoroughly cleaned, buffed, rubbed with 1/0, 2/0, 3/0 and 4/0 grades of emery sheets to obtain mirror like spotless surface. They are then washed with double distilled water and finally degreased using acetone. The specimens are then dried using hot air drier weighed and kept in a desiccators to avoid absorption or moisture.

2.2. Weight loss method:

The initial weight of the polished plate was taken. The 1M HCl solutions were taken in100ml beakers and the specimens were suspended in triplicates into the solution using glass hooks. Care was taken to ensure the complete immersion of the specimen. After a period of 3 hours the specimens were removed, washed with running water, dried and weighed using chemical balance. From the initial and final masses of the specimen the loss in weight was calculated. The experiment was repeated by varying inhibitor concentrations in 1M HCl.

The effect of temperature is studied by the weight loss procedure. This was carried out at different temperature ranges i.e. 30^0C, 40^0C, 50^0C and 60^0C using thermostat.

$$\text{Efficiency of inibitor}(\%) = \frac{(\text{Weight loss without inhibitor - Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Weight loss in mgms}}{\text{Density} \times \text{Area in sq.inch} \times \text{Time in hours}}$$

Where, Density of mild steel = 7.86 g/cc

$$\text{Surface coverage } (\theta) = \frac{(\text{Weight loss without inhibitor - Weight loss with inhibitor})}{\text{Weight loss without inhibitor}}$$

From this, a graph was plotted between C/θ Vs C and log C Vs log (θ/ (1–θ)).It helps to know whether the adsorption of inhibitors follows Langmuir adsorption isotherm and to obtain a linear relationship. Temkin adsorption plot of θ Vs log C was found to be linear.

The activation energy was calculated by graphical method by plotting log (corrosion rate) Vs 1000/T (K) for a temperature range of 30-60^0C in 1M HCl with and without inhibitor at an inhibitor concentration of 0.001M. The inhibition efficiency was found to decrease with increasing temperature. $E_a = 2.303 \times 8.314 \times$ Slope (KJ)

The free energy of adsorption ΔG^o_{ads} has been calculated from the equilibrium constant of adsorption using the equation **[7]**.

$$k = \frac{1}{55.5} \exp\left[-\frac{\Delta G^o_{ads}}{RT}\right]$$

Where,

$$k = \frac{\theta}{C(1-\theta)}$$ (From Langmuir equation)

θ - Surface coverage of the inhibitor
C – Concentration of inhibitor in Mol/ 50ml

$\therefore \Delta G^o_{ads}$ = RT ln (55.5 k)

2.3. Electrochemical studies

Electrochemical measurements were carried out in a glass cell with a capacity of 50ml. A platinum electrode and a saturated calomel electrode (SEC) were used as counter electrode and a reference electrode respectively. The mild steel electrode was then placed in the test solution for 10-15 minutes before electrochemical measurement.

Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit (Potentiodynamic model PGSTAT 12). The EIS measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01 Hz with signals amplitude of 10mV. The Tafel polarization measurements were made after EIS for a potential range of -200mV to +200mV with respect to open circuit potential, at a scan rate of 1mV/sec. The I_{corr}, E_{corr}, R_t and C_{dl} values were obtained from the data using the corresponding “corr view” and “Z view” software.

$$\text{Inhibition efficiency (\%)} = \frac{R_{t(inh)} - R_{t(blank)}}{R_{t(inh)}} \times 100$$

Where,
$R_{t(inh)}$ – charge transfer resistance in the presence of inhibitor

$R_{t(blank)}$ – charge transfer resistance in the absence of inhibitor

$$\text{Inhibition efficiency (\%)} = \frac{I_{corr(blank)} - I_{corr(inh)}}{I_{corr(blank)}} \times 100$$

Where,
$I_{corr\ (blank)}$ – corrosion current in the absence of inhibitor
$I_{corr\ (inh)}$ – corrosion current in the presence of inhibitor

2.4. Surface examination study of mild steel specimen by SEM

The surface morphology of the present work was carried out by using HITACHI MODEL-S 3400 Scanning Electron Microscope. The surface examination of mild steel specimens were made in order to understand the surface morphology of the mild steel in 1M HCl in the presence and absence of inhibitors.

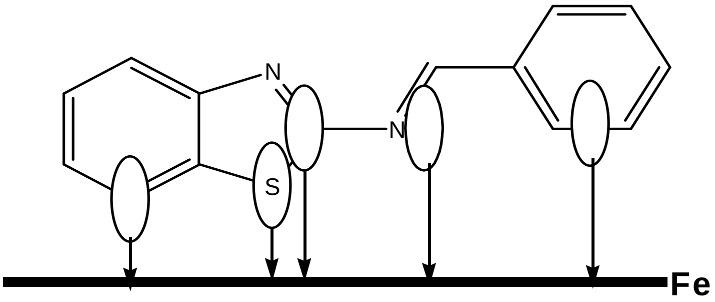
RESULTS AND DISCUSSION

3.1. Weight loss method

Table (1) gives the values of the inhibition efficiency obtained from the weight loss method for different concentrations of AMBT and its Schiff bases in 1M HCl. Using this data, the parameters like inhibition efficiency, corrosion rate and surface coverage were calculated.

Analysis of table (1) clearly indicates that the parent compound AMBT exhibits lowest inhibition efficiency (71.48%) even at a concentration of 0.001M. On the other hand, AMBT derived Schiff bases (HNMBTA &AMBTA) exhibit a high inhibition efficiency of (97.35% & 94.96%) at 0.001M concentration of the inhibitors. Table (1) revealed the fact that metal loss progressively decreased with increasing inhibitor concentration, the inhibition efficiency of all the compounds was found to increase with increase in concentration of the inhibitor and the corrosion rate decreases with increase in concentration of all the tested inhibitors. The surface coverage (θ) for different concentrations of the inhibitor were calculated. The observation of figures (1), (2) & (3) shows that a plot of C/θ Vs C , log C Vs log (θ/(1-θ)) and θ Vs log C gives a straight line confirming that the adsorption of these compounds on mild steel surface obeys Langmuir adsorption isotherm and Temkin adsorption isotherm.

Very high inhibition efficiency of these compounds is understandable from the electron donating properties of the atom like different nitrogen and sulfur present in the molecule. From the structure of the Schiff bases, an extensively delocalized orbital covers all the molecular atoms and the orbital is filled up with a number of π-electrons, being contributed from the differing anchoring atoms of the molecule. It is apparent from the molecular structure that these molecules are able to adsorb on the metal surface through nitrogen, sulfur, $>C=N$ group,-CH=N- group and aromatic rings **[8]**.



The order of inhibition efficiency of the tested compound is,

HNMBTA > AMBTA > AMBT

The number of anchoring sites in AMBT is less the extent to which it gets adsorbed on the metal surface is less and this accounts for its minimum inhibition efficiency.

HNMBTA compounds have high inhibition efficiency i.e.97.35% at 0.001M due to presence of three aromatic rings, $>C=N-$ group,-CH=N-group nitrogen, sulfur and –OH group. Therefore number of these anchoring sites in these compounds increases, inhibition efficiency also increases. The inhibition efficiency of AMBTA is 94.96%, at 0.001M

The weight loss data obtained at higher temperature range of 30°C-60°C are presented in table (2). The data clearly reveal that inhibition efficiency decreases with increase in temperature, weight loss increases with increase in temperature and corrosion rate increases with increase in temperature. The plot of log (corrosion rate / T) Vs 1000/ T (K) give a straight line. It is a transition state graph as shown in figure 4. The logarithm of the corrosion rate of mild steel is represented as a straight line function of 1000/T where T is the temperature in Kelvin (fig.5- Arrhenius plot). Using the Arrhenius plots, the free energy of adsorption ΔG_{ads} and activation energy E_a were calculated and presented in table (3). For uninhibited acid solution, the calculated value of E_a is 79.11KJ/mole. The calculated values of Ea for the inhibited acid solution of tested compounds are 89.3, 122.17 & 106.01 KJ/mole. This result indicates that the presence of inhibitor in the acid solution has affected the value of the activation energy of the corrosion reaction. The negative free energy of adsorption indicates interaction of the inhibitor molecules **[9]** and spontaneous adsorption on the metal surface **[10]-[13]**.

TABLE-1 Inhibition efficiencies for the corrosion of mild steel in 1M HCl at 28±1°C

Name of the inhibitor	Inhibitor concentration (M)	Weight loss (gms)	Inhibition efficiency (%)	Corrosion rate (mpy)	Degree of coverage (θ)
AMBT	Blank	0.0698	-	868.43	-
	0.0001	0.0320	54.15	398.14	.5415
	0.0002	0.0265	62.03	329.71	0.6203
	0.0003	0.0245	64.90	304.82	0.6490
	0.0005	0.0220	68.48	273.72	0.6848
	0.001	0.0199	71.48	247.59	0.7148
AMBTA	Blank	0.0258	-	314.12	-
	0.0001	0.0051	80.25	62.09	0.8025
	0.0002	0.0041	84.10	49.92	0.8410
	0.0003	0.0029	88.75	35.31	0.8875
	0.0005	0.0015	94.19	18.26	0.9419
	0.001	0.0013	94.96	16.17	0.9496
HNMBTA	Blank	0.0339	-	412.74	-
	0.0001	0.0062	81.71	75.49	0.8171
	0.0002	0.0043	87.31	52.35	0.8731
	0.0003	0.0027	92.04	32.87	0.9204
	0.0005	0.0024	92.92	29.22	0.9292
	0.001	0.0009	97.35	11.20	0.9735

TABLE-2 Inhibition efficiencies for the corrosion of mild steel in 1M HCl at higher temperatures

	Name of the inhibitor	Temperature (K)	Weight loss (gms)	Inhibition efficiency (%)	Corrosion rate (mpy)
1.	Blank	303		-	421.78
		313	0.0755	-	939.35
		323	0.2522	-	3137.81
		333	0.5276	-	6564.27
2.	AMBT	303	0.0099	70.79	123.17
		313	0.0260	65.56	323.49
		323	0.1000	60.31	1244.18
		333	0.2200	58.30	2737.19
3	AMBTA	303	0.0017	94.90	21.15
		313	0.0077	89.80	96.18
		323	0.0354	85.96	440.05
		333	0.1313	75.11	1630.42
4.	HNMBTA	303	0.0015	95.57	18.66
		313	0.0067	91.13	82.79
		323	0.0291	88.46	361.91
		333	0.1183	77.58	1469.60

TABLE-3 Activation energies (E_a) and free energy of adsorption ($\Delta G°_{ads}$) for the corrosion of mild steel in 1M HCl at 0.001M concentration of the inhibitors

S. No	Name of the inhibitor	E_a(KJ)	$\Delta G°_{ads}$ at various temperatures (KJ)			
			303 k	313 k	323 k	333 k
1.	Blank	79.11	-	-	-	-
2.	AMBT	89.30	-29.75	-29.59	-29.43	-28.52
3.	AMBTA	122.17	-34.88	-34.20	-34.09	-33.30
4.	HNMBTA	106.01	-35.26	-34.81	-34.49	-33.68

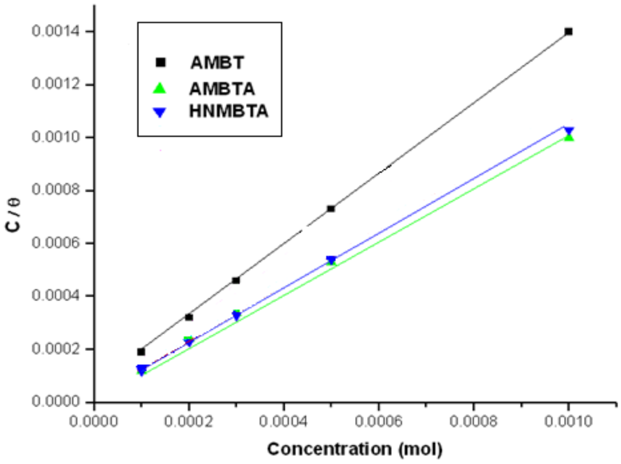


Fig-1 Langmuir adsorption isotherm plot

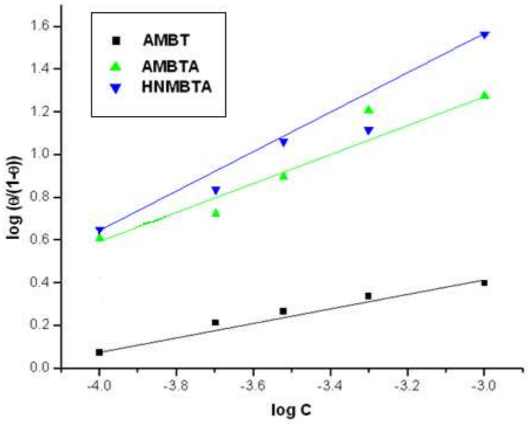


Fig-2 Langmuir adsorption isotherm plot

The adsorption of the inhibitors on the metal surface may be either physisorption or chemisorption. From table (3) it is clear that E_a for inhibited systems are higher than those of uninhibited system. According to R. Rajalakshmi et al **[14]** for the inhibitors which involve in predominant chemisorption, inhibition efficiency decreases with increase in temperature. Hence although the inhibitors taken for study can interact with mild steel surface through physisorption and chemisorption mechanism, it is the chemisorption mechanism which predominates.

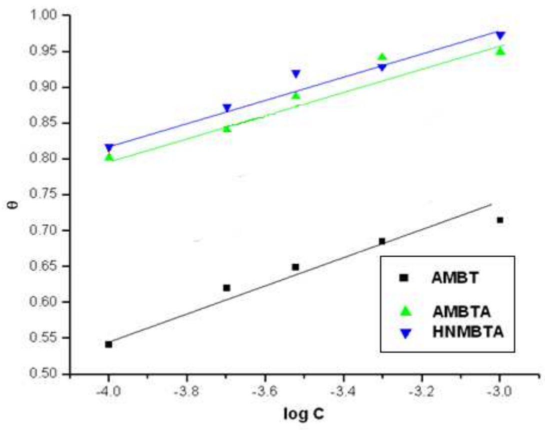


Fig-3 Temkin Adsorption plot

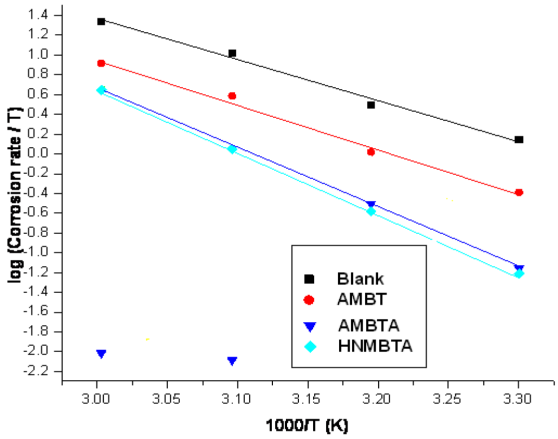


Fig-4 Transition state plot

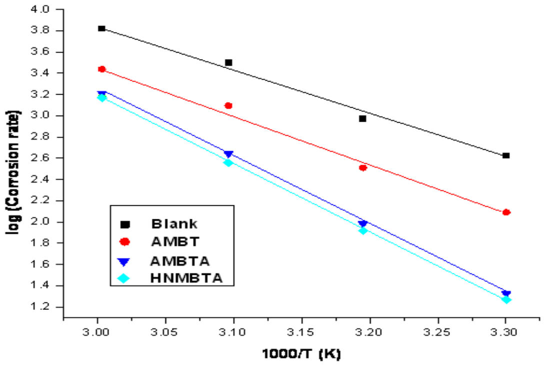


Fig-5-Arrhenius plot

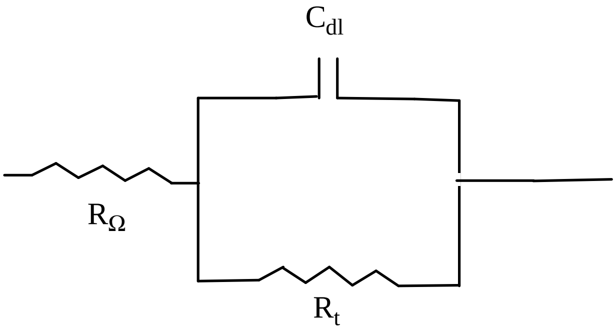
3.2. Electrochemical studies

3.2. 1.AC-impedance measurements

The corrosion behavior of mild steel in acidic solution in the presence and absence of the inhibitors was investigated by EIS method at 28±1°C after immersion for 10 minutes. The impedance diagrams obtained were perfect semi circles figure (6&7). The charge transfer resistance, R_t values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru and Haruyama **[15]**. To obtain the double layer capacitance (C_{dl}) the frequency at which the imaginary component of the impedance is maximum (-z″ max) was found and C_{dl} values were obtained from the equation. The data are presented in table (4).

$$F(-z''\max) = \frac{1}{2\pi C_{dl} R_t}$$

A simple electrode reaction such as metal deposition or metal dissolution can be represented by a modified equivalent circuit.



R_Ω - Series resistance
R_t – Charge transfer resistance
C_{dl} – Double layer capacitance

By adopting complex plane analysis for the total cell impedance Z, Sluyters et al [16], have resolved it into real and imaginary components as,

$$Z' = R_\Omega + \frac{R_t + \sigma\omega^{-1/2}}{\left(\sigma\omega^{-1/2}C_{dl} + 1\right)^2 + \omega^2 C_{dl}^2\left(R_t + \sigma\omega^{-1/2}\right)^2}$$

$$Z'' = \frac{W\,C_{dl}\left(R_t + \sigma\omega^{-1/2}\right)^2 + \sigma^2 C_{dl} + \sigma\omega^{-1/2}}{\left(\sigma\omega^{-1/2}C_{dl} + 1\right)^2 + \omega^2 C_{dl}^2\left(R_t + \sigma\omega^{-1/2}\right)^2}$$

The simplified equation for cell impedance is

$$\left[Z' - R_\Omega - \frac{R_t^2}{2}\right] + [Z'']^2 = \frac{R_t^2}{4}$$

Which is the equation of a semicircle (Z″ vs. Z′ - constant concentration) with its centre on Z′ axis at $Z' = R_\Omega\ T^{1/2}\ R_t$ and radius ½ R_t. The interaction with the Z′ axis are at $Z' = R_\Omega$ for and $\omega = \alpha$ and at $Z' = R_\Omega + R_t$ for $\omega = 0$. These are called Nyquist plots. With an increase in inhibitor concentration, the radius of the semicircle increases and the double layer capacitance C_{dl} decreases. In this investigation for all the tested inhibitors C_{dl} decreases with increase in inhibitor concentration obviously due to increased adsorption as required by theory.

3.2. b. Polarization studies

Both anodic and cathodic polarization curves for mild steel in 1M HCl at selected concentration of the inhibitors are shown in figure (8). Values of corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c) and corrosion inhibition efficiency for selected concentrations of the inhibitors are presented in table (5). It is evident from the table that I_{corr} decreases with increasing inhibitor concentration resulting in an increase in inhibition efficiency.

TABLE-4 Impedance parameters values for corrosion of mild steel in 1M HCl

S.No	Name of the inhibitor	Inhibitor concentration (M)	R_t (ohmcm^2)	Cdl (µF/cm^2)	Inhibition efficiency (%)
1.	AMBTA	Blank	18.20	36.5600	-
		0.0001	183.95	28.4770	90.11
		0.0005	186.01	24.1720	90.22
		0.001	229.00	22.6810	92.05
2.	HNMBTA	0.0001	297.25	17.9880	93.88
		0.0005	308.56	15.3410	94.10
		0.001	367.9	14.1230	95.05

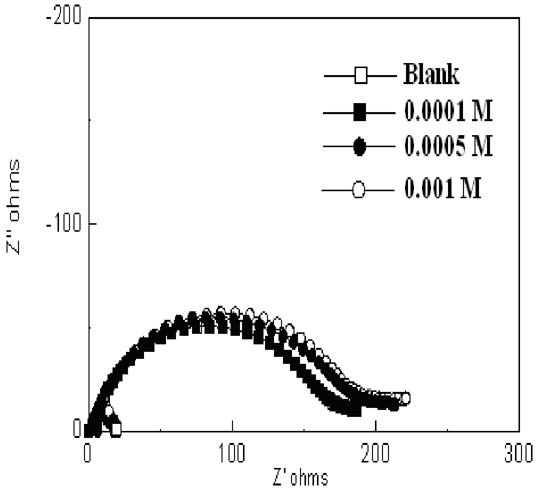


Fig-6

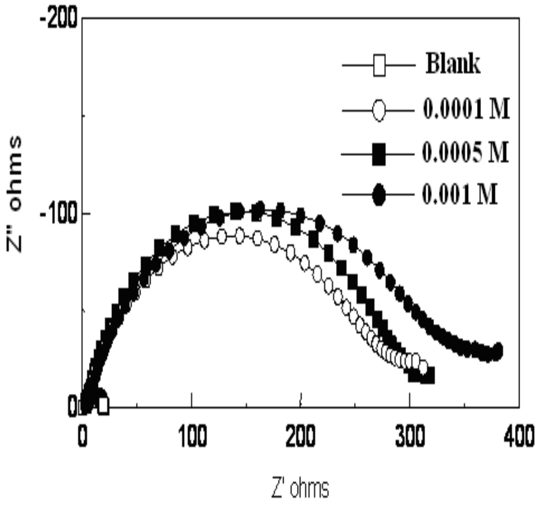


Fig-7

(Fig -6 & 7 Nyquist diagram for mild steel in 1M HCl for selected concentrations of inhibitor)

TABLE-5 Tafel polarization parameters values for the corrosion of mild steel in 1 M HCl

S.No	Name of the inhibitor	Inhibitor concentration (M)	Tafel slopes (mg/dec)		E_{corr} (mV)	I_{corr} (μAmp/cm^2)	Inhibition efficiency (%)
			b_a	b_c			
1.	AMBTA	Blank	33	-31	-650	2.49	-
		0.001	75	-71	-134	0.15	93.98
		0.0001	68	-67	-240	0.40	83.94
		0.00001	59	-56	-243	1.002	59.76
2.	HNMBTA	0.001	78	-75	-114	0.12	95.18
		0.0001	69	-67	-219	0.43	82.73
		0.00001	61	-59	-235	0.91	63.75

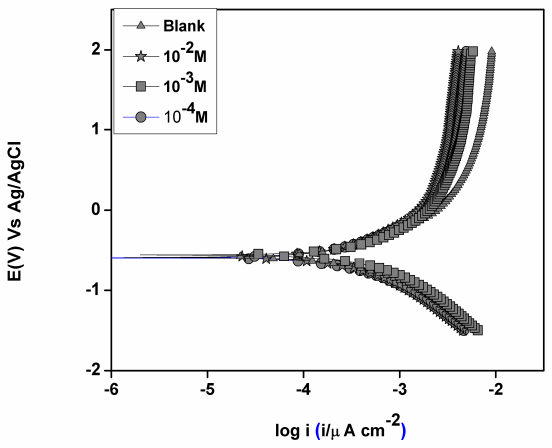


Fig-8 Tafel Polarization curve for mild steel in 1M HCl in HNMBTA

Analysis of the polarization data in table (5) reveals that E_{corr} values are only slightly shifted in the presence of the inhibitors, I_{corr} values decrease with increase in the concentration of the inhibitors. The Tafel constants b_a and b_c are both affected but b_a is affected to a greater extent. Hence it can be concluded that although all the inhibitors behave as mixed type inhibitors they are more anodic in nature.

3.3. Surface examination study of mild steel specimen by SEM

The formation of an adsorbed protective film of inhibitor molecule on the mild steel surface is also confirmed by SEM studies. Figures (9-11) shows the scanning electron micrographs of mild steel specimens exposed to1M HCl containing 0.001M concentration of AMBTA, HNMBTA and AMBT. Uniform corrosion can be observed in figure (11). The metal surface is fully covered with the inhibitor molecules giving it a high degree of protection (fig 9 & 10)

SEM Photographs

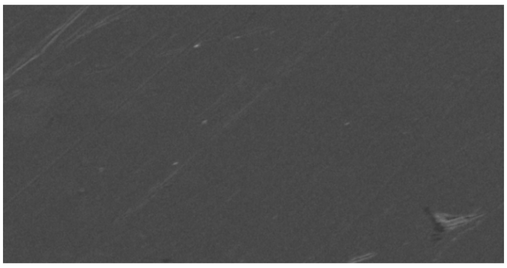


Fig-9 (AMBTA)

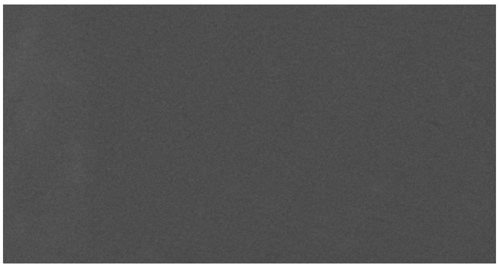


Fig-10 (HNMBTA)

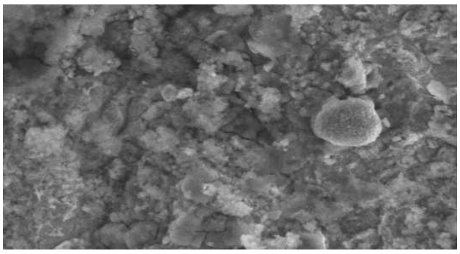


Fig-11(AMBT)

CONCLUSION

The influence of 2-amino-6-methoxy-benzothiazole and its Schiff bases on the corrosion of mild steel in 1M HCl was carried out by weight loss & electrochemical method. The synthesized compounds were good inhibitors because these compounds are able to absorb on the metal surface through the nitrogen atom, sulfur atom, $>C{=}N$ groups, -CH=N- group and aromatic rings that can cause effective adsorption process leading to the formation of an insoluble protective surface which suppresses the metal dissolution reaction.

The parent compound 2-amino-6-methoxy-benzothiazole has very low inhibition efficiency. All the investigated Benzothiazole derived Schiff bases are effective inhibitors for the corrosion of mild steel in 1M HCl. They inhibit corrosion by getting adsorbed on the metal surface. The inhibition efficiency increases with increase in inhibitor concentration. The adsorption of these inhibitors follows Langmuir and Temkin adsorption isotherm.

The effect of temperature indicates that the inhibition efficiency decreases with increasing temperature. The activation energy (E_a) is higher for inhibited acids than for uninhibited acids showing the temperature dependence of inhibition efficiency. The less negative value of ΔG^{o}_{ads} with increase in temperature indicates the spontaneous adsorption of the inhibitors on the metal surface.

Electrochemical impedance spectroscopy experiments have shown that an increase in inhibitor concentration causes an increase in polarization resistance R_t and a decrease in C_{dl} values owing to the increased thickness of the adsorbed layer. Tafel slopes obtained from potentiodynamic polarisation (vide table – 5) curves indicate that they are anodic in nature.

SEM reveals the information of a smooth, dense protective layer in presence of effective inhibitor. (As shown in fig 9 &10)

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