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Heterocyclic Organic Derivative as Corrosion Inhibitor for Mild Steel in 1 N HCl

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ABSTRACT

The inhibition effect of heterocyclic organic derivative viz., 2-(Benzothiazol-2-ylsulfanyl)-1-(5-methyl-thiazol-2-ylamino)-ethanol (BMTE) was evaluated against mild steel corrosion in 1 N HCl solutions using conventional weight loss method, potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy. The results of weight loss method have proved that BMTE was efficient corrosion inhibitor. Electrochemical polarizations such as Tafel Intercept and Linear Polarization Resistance revealed the mixed mode of inhibition. The results of electrochemical impedance spectroscopy have shown the changes in the impedance parameters like charge transfer resistance and double layer capacitance to confirm the strong adsorption on the mild steel surface. The increase in the value of inhibition efficiency was due to the adsorption of the molecules evaluated leading to the formation of a protective layer on the surface of mild steel. The inhibition action of these compounds was, assumed to occur via adsorption on the steel surface through the active centres contained in the molecules.

Keywords: Acid corrosion inhibitor of mild steel, electrochemical impedance spectroscopy, Tafel and Polarization methods.

INTRODUCTION

The use of corrosion inhibitor is one of the most effective measures for protecting metal surfaces against corrosion in acid environments. The corrosion of iron and mild steel (MS) is a fundamental academic and industrial concern that has received a considerable amount of attention [1]. A study of the mechanism of the action of corrosion inhibitors has relevance both from the point of view of the search for new inhibitors and also for their effective use [2]. Acid solutions are very commonly used for removal of undesired scales and rust in many industries. To control corrosion of metals, organic inhibitors are used since many years. In recent times, organic inhibitors are generally used to protect the metal from corrosion by forming a barrier film on the metal surface. Their effectiveness is related to the chemical composition, their molecular structure, and their affinities to get adsorbed on the metal surface. The addition of corrosion inhibitors effectively secures the metal against an acid attack. Inhibitors are used in these processes to control metal dissolution [3-5] and, during past decade many organic inhibitors have been studied in different media [6-9]. The mechanism of their action can be different, depending on the metal, the medium and the structure of the inhibitor. One possible mechanism is the adsorption of the inhibitor, which blocks the metal surface and thus do not permit the corrosion process to take place. Organic compounds containing electronegative functional groups and π-electrons in conjugated double or triple bonds generally exhibit good inhibitive properties by supplying electrons via π orbitals. Specific interaction between functional groups and the metal surface and heteroatoms like N, O and S [10-12] plays an important role in inhibition due to the free electron pairs they possess. When both these features combine, increased inhibition can be observed [13-17].

MATERIALS AND METHODS

Preparation of inhibitor

This compound was synthesized by stirring the mixture of 2-chloro-1-(5-methyl-thaizole-2-yl-amino)-ethanol (0.005 mol) and 2-marceptobenzothaizole (0.005 mol) in ethanol with catalytic amount of triethylamine and heated to reflux for 6-7 hrs. After conclusion of the reaction (TLC), the reaction mixture was poured onto crushed ice; the solid mass thus separated out was filtered, washed with water and dried to give the desired compound (BMTE) [24-25].

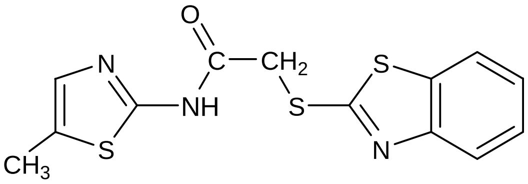

Figure 5: 2-(Benzothiazol-2-ylsulfanyl)-1-(5-methyl-thiazol-2-ylamino)-ethanol (BMTE)

Specimen preparation

MS specimens having compositions of 0.09 % P, 0.37 % Si, 0.01 % Al, 0.05 % Mn, 0.19 % C, 0.06 % S and the remainder Fe, were used for the electrochemical polarizations and impedance measurements. The samples of 1 cm × 1 cm area were polished with different emery papers of grades 120, 320, 400, 800, 1,000 and 2,000 degreased with acetone dried at room temperature and then stored in desiccators before use. The acid solutions were made from analytical grade 37% HCl by diluting with double-distilled water.

Weight loss method

The weight loss (WL) measurements were carried out by weighing the prepared specimens before and after immersion for 4 h in 100 ml stagnant test solutions in the presence and absence of various concentrations of the BMTE in 1 N HCl. From the weight loss data, percent inhibition efficiency (*IE %*) was calculated at different concentration at 30°C.

Potentiodynamic polarization measurements

All of the electrochemical studies were carried out using three electrodes cell with a platinum counter electrode (CE) and a saturated calomel reference electrode (SCE) and MS sample as working electrode (WE). The electrolytes used were acidic solutions maintained at 30°C. The AC impedance measurements are shown as Nyquist plots and polarization data as Tafel plots. Recently imported CH Electrochemical analyzer model 608 C (USA) was used for this purpose. Polarization resistance measurements were first carried out with a scan rate of 0.01 V/s at −10mV to +10mV vs. corrosion potential (E_{corr}) of the working electrode. Polarization curves were also obtained at the scan rate of 0.01 V s^{-1} in the range of −250 mV to +250 mV vs. E_{corr}. The MS electrodes were immersed for 2 h in the test solution for the impedance measurements which were carried out at the E_{corr}.

Electrochemical impedance spectroscopy (EIS)

EIS is now a sophisticated and established laboratory technique, with the relevant software to determine important parameters like the charge transfer (corrosion) resistance (R_t) rate and double-layer capacitance (C_{dl}) [26-29]. The AC impedance measurements were carried out in the range of 0.1 Hz to 1000 Hz. The A.C. signal was 5 mV peak-to-peak with 12 data points per decade. The same cell and system as in the polarization method were used. The double layer capacitance (C_{dl}) and the charge transfer resistance (R_t) were calculated from Nyquist plots.

Scanning electron microscopy (SEM)

The surface morphology of the MS specimens immersed in 1 N HCl in presence and absence of the BMTE was studied by using scanning electron microscopy. The immersion time of the electrodes for the SEM analysis was 4 h.

RESULTS AND DISCUSSION

Weight loss measurements

Corrosion of MS in 1 N HCl in the absence and presence of various concentrations (20-100 ppm) of BMTE was studied by weight loss experiments. The corrosion rate (W_{corr}) and the values of related inhibition efficiency (E_w %) were calculated according to following equation.

$$E_w\% = 100 \times \frac{W_0 - W_{corr}}{W_0} \qquad \text{(Eq 1)}$$

where W_{corr} and W_0 are the corrosion rates of MS with and without inhibitor respectively.

The values of E_w %, W_0 and W_{corr} were obtained from weight loss measurements with the addition of various concentrations of BMTE after 4 h of immersion in 1 N HCl solutions.

Table 1 Inhibition Efficiency of MS in 1 N HCl in the presence and absence of different concentrations of BMTE

Inhibitor	IC^a (mg kg^{-1})	W (µg cm^{-2} h^{-1})	E_W %
BMTE	1 N HCl	17.789	-
	20	10.981	38
	40	7.425	58
	60	4.913	72
	80	2.995	83
	100	1.413	92

a) IC is the inhibitor concentration

From the Table 1, it was found that the value of E_w % was increased with an increase in the concentration of the additives, suggesting that the number of molecules adsorbed were increased over the MS surface, blocking the active sites of acid attack and thereby protecting the metal from corrosion. At highest concentration of 100 ppm of the additive studied, the E_w% attained was 92 % for BMTE which confirmed that the additives was very effective as inhibitor.

Potentiodynamic (Tafel) polarization measurements

To evaluate the effect of BMTE on the electrochemical behavior of MS, cathodic as well as anodic polarization studies were carried out as shown in Tafel plots in Figure 1. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) were derived from these curves and are given in Table 2. The values of inhibition efficiency (E_I %) were calculated using the following equation.

$$E_I\% = 100 \times \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \qquad \text{(Eq 2)}$$

where I_{corr} and $I_{corr(inh)}$ were the values of corrosion current densities without and with the additives, respectively, which were determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential E_{corr}. It was found in Table 2 that the values of E_I % was increased with increase in the concentration of the additive. At the highest concentration of 100 ppm, the values of E_I % was 97.62 % BMTE respectively, which confirmed the strong adsorption on the MS surface to control corrosion rates [18].

The inhibiting property of the tested BMTE has also been evaluated by determining the polarisation resistance R_p (Ωcm^2). The corresponding polarisation resistance (R_p) values for MS in 1 N HCl in the absence and presence of different concentrations of the additive is also given in Table 2. The values of inhibition efficiency (E_{Rp} %) were calculated as follows:

$$E_{RP}\% = 100 \times \frac{R_{p(inh)} - R_p}{R_{p(inh)}} \qquad \text{(Eq 3)}$$

where R_p and $R_{p(inh)}$ were the polarisation resistance in the absence and in the presence of the additives, respectively.

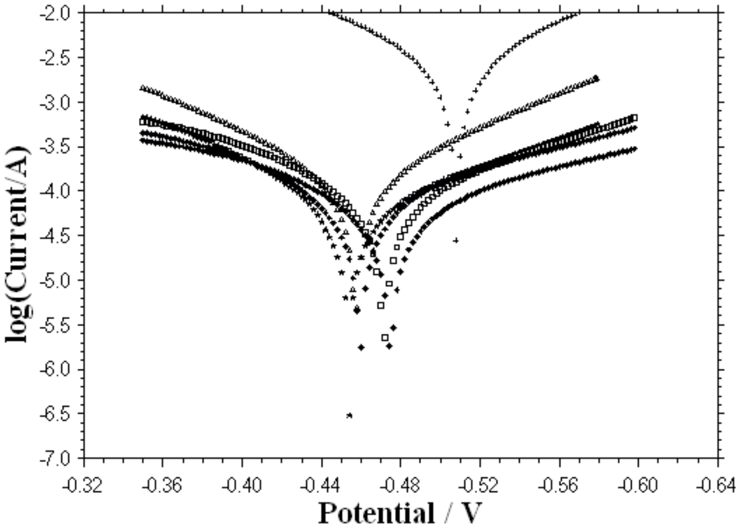

Figure 1: Tafel plots showing the effect of BMTE on the corrosion of MS in a HCl medium (+ 1 N HCl, ♣ 100 mg kg−1, □ 80 mg kg−1, ♦ 60 mg kg−1, △ 40 mg kg−1 and, ★ 20 mg kg−1).

Corrosion currents obtained with the additive was lower than corrosion current obtained for MS in 1 N HCl solution without inhibitors. Table 2 has shown that the *IE %* was increased with an increased the concentration of BMTE. BMTE has acted as an effective corrosion inhibitor suppressing both in anodic and cathodic reactions due to their adsorption on the MS surface blocking the active sites. Moreover, there was an anodic shift in E_{corr} values to show that the compounds might have retarded anodic reaction of the acid corrosion of MS more in comparison of the cathodic one.

Table 2 Electrochemical parameters obtained from anodic and cathodic polarization cures of MS in 1 N HCl and different concentrations of BMTE at 30^0C

Inhibitor	IC^a (mgkg^{-1})	-E$_{corr}$ (mV)	k^b/ (mV par decade)		I$_{corr}$ (mA cm^{-2})	R$_p$ (Ωcm^2)	E$_I$ %	E$_{Rp}$ %
			ba	bc				
BMTE	1 N HCl	508	145	135	4.080	7	-	-
	20	485	103	106	0.185	153	95.46	95.42
	40	483	176	123	0.158	199	96.12	96.48
	60	467	164	171	0.113	322	97.23	97.82
	80	458	175	163	0.107	342	97.37	97.95
	100	453	192	180	0.097	415	97.62	98.13

a) *IC is the inhibitor concentration*
b) *K is the Tafel constant*

Electrochemical impedance spectroscopy (EIS)

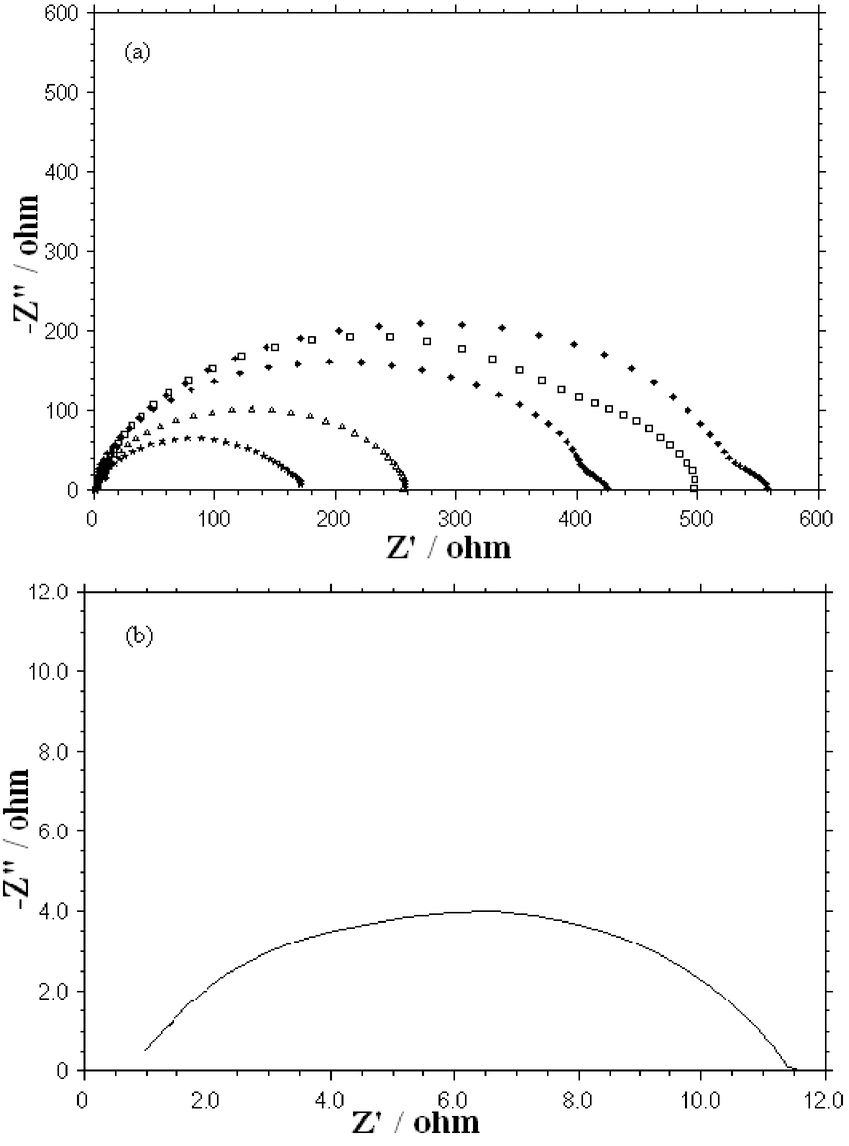

Figure 2: Nyquist plots showing: (a) the effect of BMTE on the corrosion of MS in 1 N HCl solution (✦ 100 mg kg−1, □ 80 mg kg−1, ◆ 60 mg kg−1, △ 40 mg kg−1 and ★ 20 mg kg−1) which (b) 1 N HCl blank system.

The R_p values of MS in 1 N HCl in the absence and presence of different concentrations of the tested additive is also given in Table 2. From the results, it was found that the R_p values were gradually increased with increase in the concentration of the additive. The values of inhibition efficiency (E_{Rp} %) of BMTE obtained by electrochemical methods were in good agreement with those of E_I (%).

Nyquist plots of electrochemical impedance spectroscopy for MS in 1 N HCl containing different concentration of BMTE is presented in Figure 2.

The values of inhibition efficiency (E_R %) were calculated by following the equation.

$$E_R\% = 100 \times \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \qquad \text{(Eq 4)}$$

where R_t and $R_{t(inh)}$ were the charge-transfer resistance (Ω cm^2) values in absence and the presence of the additives, respectively.

To obtain the values of double layer capacitance (C_{dl}), the values of frequency at which the maximum imaginary component of the impedance $-Z_{im(max)}$ were found and were used in the following equation with corresponding R_t values:

$$C_{dl} = \frac{1}{2\pi f_{\max} R_t} \qquad \text{(Eq 5)}$$

Nyquist plots in Figure 2(a) contained depressed semi-circles with the centre under the real axis, whose size were increased with the increase in concentration of the additive, confirming that the charge transfer processes were mainly controlling the corrosion of MS. An isolated Nyquist plot for MS the blank system is shown in Figure 2(b) and the value of real impedance (Z') was minimum only 12 Ω cm^2 which indicated that there was least charge transfer resistance (R_t) of the acid corrosion reactions. There was a gradual increase in the diameter of each of the semicircles of the Nyquist plots when the concentrations were raised from 20 to 100 ppm in Figure 2(a). This gradual increase of the diameters corroborated that the R_t values were increased up to highest concentration of 100 ppm due to formation and gradual improvement of the barrier layer of the inhibitive molecules added, and as a result the acid corrosion rates of MS were gradually decreased.

Table 3 Data from electrochemical impedance measurements of mild steel in 1 N HCl for various concentrations of BMTE

Inhibitor	IC^a (mg kg^{-1})	R_t (Ω cm^2)	Cdl (µF cm^2)	E (%)
BMTE	1 N HCl	12	168	-
	20	175	137	93.14
	40	255	114	95.29
	60	425	80	97.17
	80	500	39	97.60
	100	560	35	97.85

Table 3 presents the values of R_t and C_{dl}. There was a gradual decrease in value of C_{dl} with an increase in the concentration of both BMTE. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of the BMTE on the MS electrode lead to decrease its electrical capacity because they might have displaced the water molecules and other ions originally adsorbed on the MS surface. The decrease of this capacity with increasing concentrations of BMTE was associated with the formation of a protective layer on the MS electrode surface [19]. Inhibition efficiency E_I (%) was found to increase an increase in concentration with BMTE. The results obtained from EIS have shown the similar trend as those obtained from electrochemical polarisations and weight loss measurements.

The results have suggested that the corrosion rate of MS was significantly decreased due to adsorption mechanism affecting both the anodic and cathodic processes. The nature of interaction between MS surface and inhibitor can be established by isotherm which describe adsorption behaviour of the inhibitor on metal surface.

Adsorption isotherm

The results have suggested that the corrosion rate of MS was significantly decreased due to adsorption mechanism affecting both the anodic and cathodic processes. The nature of interaction between MS surface and inhibitor can be established by isotherm which describe adsorption behaviour of the inhibitor on metal surface.

The surface coverage *(θ)* of different concentrations of BMTE in 1 N HCl solution was calculated from the corrosion rates obtained by weight loss measurements, using following the equation.

$$\theta = \frac{W_0 - W}{W_0} \qquad \text{(Eq 6)}$$

where W_0 and W were the corrosion rates in the absence and presence of the inhibitors, respectively.

The adsorption behaviour was described by using the Langmuir adsorption isotherm expressed as:

$$K_{ads} = \frac{\theta}{C_{ing}}(1-\theta) \qquad \text{(Eq 7)}$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process, C is the inhibitor concentration.

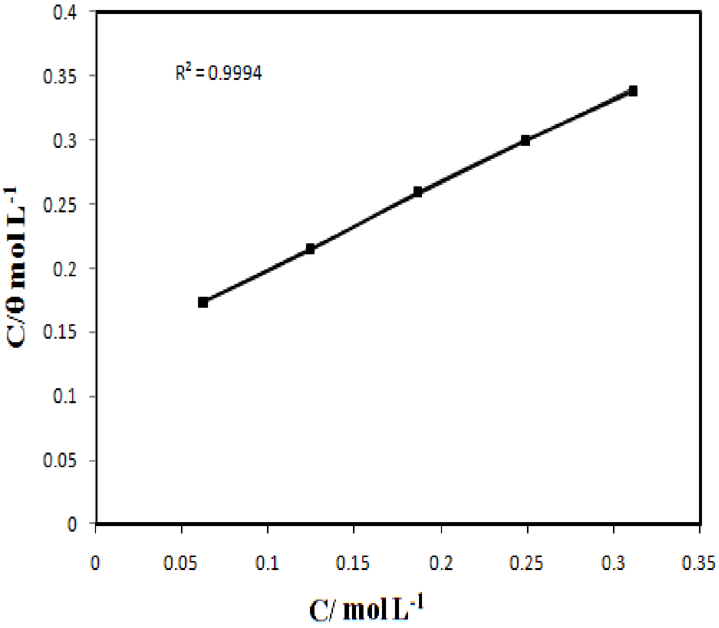

Figure 3: Langmuir isotherm adsorption of BMTE on mild steel in 1 M HCl at room temperature

Plots of C/θ versus C yield a straight line shown in Figure 3. In this case the linear regression coefficients (R^2) were almost equal to 1 and the slopes were very close to 1, indicating that the adsorption of BMTE obeys the Langmuir isotherm.

K_{ads} values can be calculated from the intercepts of the straight lines on the C/θ-axis, and the constant of adsorption, K_{ads} is related to the standard free energy of adsorption, ΔG^0_{ads}, with following equation.

$$\Delta G_{ads} = -2.303RT\log(55.5K_{ads}) \qquad \text{(Eq 8)}$$

where K_{ads} is the equilibrium constant of adsorption, R is the gas constant and T, absolute temperature, the value 55.5 is the molar concentration of water solution in mol L^{-1}.

The addition of inhibitors causes negative values of ΔG^0_{ads}, indicated that adsorption of studied BMTE was a spontaneous process. It is generally accepted that the values of ΔG^0_{ads} up to -20 kJ mol^{-1}, the types of adsorption were regarded as *physisorption*, the inhibition acts due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1}, were seen as *chemisorption* [20-21], which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond. The values of ΔG^0_{ads} in our measurement was found to be -31.10 KJ mol^{-1}, it may suggested that the adsorption of BMTE involves two types of interaction, chemisorption and physisorption. [22-23].

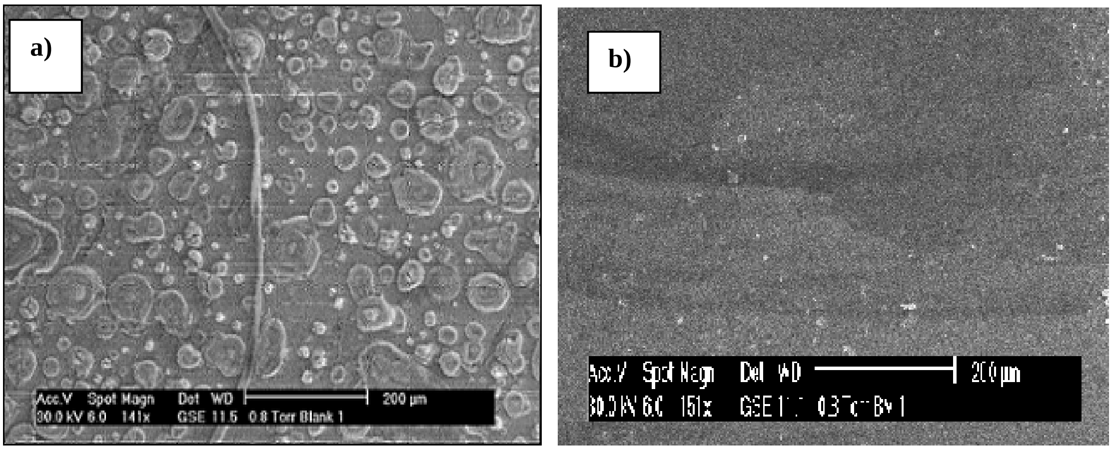

Figure 4: SEM images of MS (a) in 1 N HCl solution and (b) with 100 ppm of BMTE

The SEM photograph in Figure 4(a) has shown that the surface of MS was extremely damaged in the absence of the inhibitor while Figure 4(b) have clearly shown the formation of a film by the adsorption of BMTE on the MS surface which was responsible for the corrosion inhibition.

CONCLUSION

- The protection efficiency of BMTE inhibitor increases with the increase of the inhibitor concentration.
- Polarization curves showed that BMTE is mixed type of corrosion inhibitor.
- The results of the weight loss, electrochemical polarizations and EIS were all in very good agreement to support the above conclusions.

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