



Preparation, characterization, and evaluation of polymeric resin (BHMET) from the reaction of malic anhydride with recycled PET as a corrosion inhibitor for C-steel in HCl

Preparación, caracterización y evaluación de resina polimérica (AHMET) a partir de la reacción de anhídrido maleico con PET reciclado como inhibidor de corrosión para acero-C en HCl

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ABSTRACT

Introduction: The plastic soft drink bottle from polyethylene terephthalate (PET) was introduced to consumers in 1970s. Because PET have ester group its chemical recycling is preferred. To control and reduce the environmental pollution recycling and reusing of PET has turned into an imperative procedure from the ecological perspective and it has given business opportunity because of far reaching use and accessibility of PET polymer. Also another source of pollution to the environment was the corrosion of materials. Corrosion is the deterioration and loss of a material and its critical properties due to chemical, electrochemical and other reactions of the exposed material surface with the surrounding environment. Understanding corrosion mechanisms allow to use corrosion-resistant materials and altering designs. Organic inhibitors are very efficient to protect the metals from corrosion in all chemicals (acidic, basic and salt) media. There were many types of corrosion inhibitors and the organic inhibitor are being applied widely to protect metals from corrosion in many aggressive media. The aim of this study is to utilize waste PET-bottles will be depolymerized by 2,2-dithioethanol to produce (Bis(2-((2-hydroxyethyl) thio) ethyl) terephthalate (BHTE), then by reacting of (BHTE) with maleic anhydride to produce Bis (2-((6-Mono malic acid –hydroxyethyl ester) sulfanyl) ethyl terephthalate(BHMET). The prepared (BHMET) will be used as corrosion inhibitor and its efficiency to protect the carbon steel in acidic will be assessed. **Materials and Methods:** Depolymerization of PET waste done with 2,2-dithioethanol. The weight proportion of PET to 2,2-dithioethanol 1:8 (wt%) and zinc acetate (0.5 wt% based on PET) was added as catalyst. Temperature of the reaction mixture was between 160-180 °C for 12 h, then the reaction mixture was kept at 140 °C for 3 h, then allowed to cool to room temperature. With vigorous agitation distilled water in excess to the reaction mixture to allow the black liquid viscous compound oligomer of Bis(2-((2-hydroxyethyl) thio) ethyl terephthalate (BHET) to precipitate. In a three neck round bottom (250 ml) attached with mechanical stirrer and thermometer (5.7gm) of (BHET) compound was added and heated for (15 min.) at (60 °C). Then (2.5gm) of malic anhydride and (1%) sulfuric acid was added. By the mechanical stirrer the mixture was mixed for (50 min.) at temperature (80°C). After the reaction the mixture was washed with distilled water to avoid the acid residue. Scheme (1) shows the mechanism for the prepared (BHMET) corrosion inhibitor.

SCIENTIFIC RESEARCH

How to cite this paper:

Yasir A , Khalaf A and Khalaf M . Preparation, characterization and evaluation of polymeric resin (BHMET) from reaction of malic anhydride with recycled PET as a corrosion inhibitor for C- steel in HCl *Innovaciencia*. 2019;7 (1): 1-12.
<http://dx.doi.org/10.15649/2346075X.510>

Reception date:

Received: 20 February 2019
Accepted: 29 April 2019
Published: 25 October 2019

Keywords:

Waste polymer, Glycolysis, Corrosion inhibitor

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Results and Discussion: Polarization Tafel plot in presence and absence of different concentrations of BHMET show that the Tafel factors, inhibition efficiency (% IE), surface coverage (θ), corrosion rate and charge transfer resistance was measure. It is apparently that the shapes of the Tafel plots for the inhibited and uninhibited carbon steel are different. The current density of the inhibited carbon steel decreases, while the other parameters behavior does not change. A negative shift was observed for the corrosion potential (E_{corr}) due to adsorption of the inhibitor. Tafel slopes (β_a and β_c), the anodic and cathodic both decreases with the addition of BHMET. This reveals that BHMET is a mixed-type inhibitor influencing the iron dissolution and hydrogen evolution. The decrease of the positive and negative currents in the with using the corrosion inhibitor BHMET due to passivation the active sites on the surface of the electrode. At inhibitor (BHMTE) concentration of 50PPM at 298k the surface coverage and inhibition efficiency reached its maximum. **Conclusions:** Bis [2-((6-Mono malic acid –hydroxyethyl ester)sulfanyl)ethyl terephthalate (BHMET) prepared and used as corrosion inhibitors of carbon steel in 0.1M HCl solution. Two parameters effects were studied, The concentration of the inhibitor (BHMET) and the temperature. From the data, the higher (%IE) was for the 10ppm at 298 and at 313 the 10ppm was the higher inhibitor efficiency. The adsorption of the BHMET inhibitor onto the surface of the carbon steel follows the Langmuir's adsorption isotherm. The prepared compound was mixed type inhibitor and the ΔG_{ads}° indicates that the adsorption of (BHMET) inhibitor involves chemisorption.

INTRODUCTION

The plastic soft drink bottle from polyethylene terephthalate (PET) was introduced to consumers in 1970's (1-3). Because PET have ester group its chemical recycling is preferred. To control and reduce the environmental pollution recycling and reusing of PET has turned into an imperative procedure from the ecological perspective and it has given business opportunity because of far reaching use and accessibility of PET polymer (4-7). Also another source of pollution to the environment was the corrosion of materials (8). Corrosion is the deterioration and loss of a material and its critical properties due to chemical, electrochemical and other reactions of the exposed material surface with

the surrounding environment (9-11). Understanding corrosion mechanisms allow to use corrosion-resistant materials and altering designs (12). Organic inhibitors are very efficient to protect the metals from corrosion in all chemicals (acidic, basic and salt) media. There are many types of corrosion inhibitors and the organic inhibitor being applied widely to protect metals from corrosion in many aggressive media. The aim of this study is to utilize waste PET-bottles will be depolarized by 2,2-dithioethanol to produce (Bis(2-((2-hydroxyethyl thio) ethyl) terephthalate (BHTE), then by reacting of (BHTE) with maleic anhydride to produce Bis (2-((6-Mono malic acid –hydroxyethyl ester)sulfanyl) ethyl terephthalate(BHMET).The prepared (BHMET) will be used as corrosion inhibitor and its efficiency to protect the carbon steel in acidic will be assessed .

MATERIALS AND METHODS

Materials

Carbon steel (C1010) obtained from Metal Samples (USA) its composition was: C=0.13, Mn=0.3, Si=0.37, P=0.04, S=0.05, Cr=0.1, Ni=0.3, Cu=0.3, AS=0.08 and the reminder was Fe. PET waste bottle was collected and grinded. 2,2-dithioethanol, Zinc acetate, malic anhydride and HCl were obtained from Aldrich Chemical Co.

Instruments

Fourier transforminfrared (FT-IR) spectroscopic measurements were made using Jasco 4200 spectrometer. NMR spectra was obtained by Bruker -400 MHZ using DMSO as solvent while the thermal analysis was measured using TGA-DTA from Netzsch (STA 449).

Corrosion Inhibition Measurements

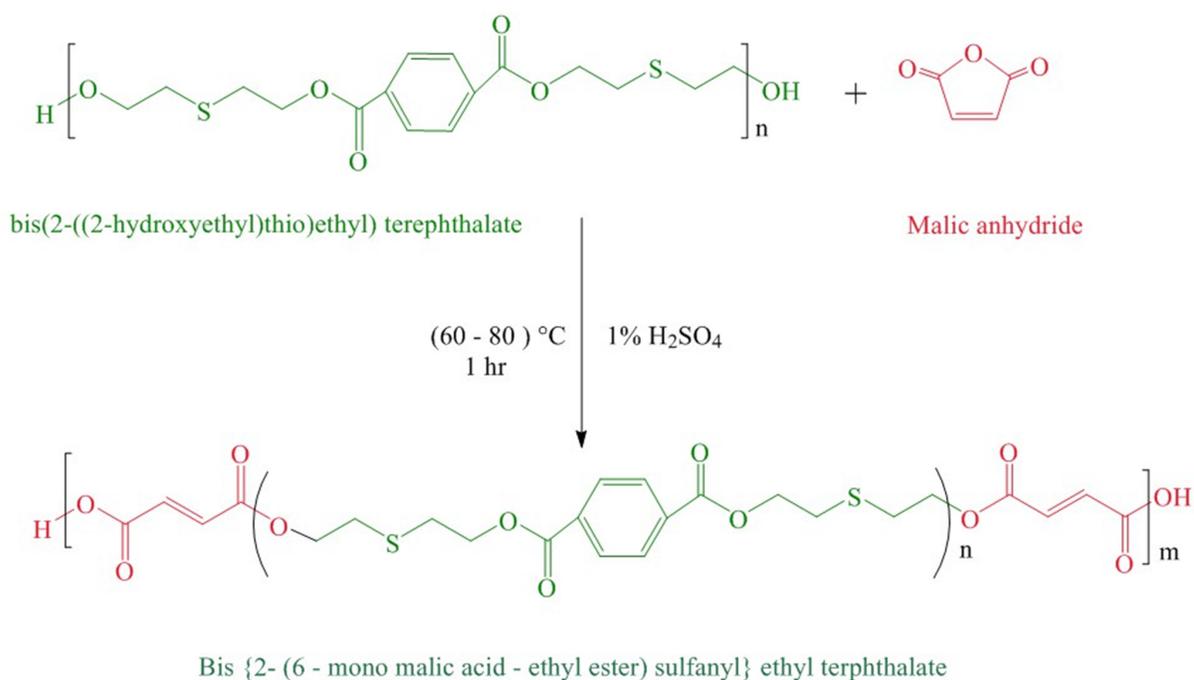
The corrosion inhibition measurements were performed utilizing a potentiostat/ galvanostat DY2300 Series Potentiostat/Bipotentiostat supplied by Digi-lvy company. A three electrode cell gathering, comprising of a platinum as the counter electrode (CE), a saturated calomel electrode as the reference electrode (RE) and C-steel rod as the working electrode (WE). A water bath was used to maintain the temperature at the required temperature of the

electrolyte. From the polarization data, the following parameters were achieved the degree of surface coverage (θ), the percentage inhibition efficiency (% IE), corrosion rate and charge transfer resistance. ⁽¹³⁾

Chemical recycling of PET

Depolymerization of PET waste done with 2,2-dithioethanol. The weight proportion of PET to 2,2-dithioethanol 1:8 (wt%) and zinc acetate (0.5 wt% based on PET) was added as catalyst. Temperature of the reaction mixture was between 160-180 °C for 12 h, then the reaction mixture was kept at 140 °C for 3 h, then allowed to cool to room temperature. With vigorous agitation distilled water

in excess to the reaction mixture to allow the black liquid viscous compound oligomer of Bis(2-((2-hydroxyethyl) thio)ethyl terephthalate (BHET) to precipitate ⁽¹⁴⁾. In a three neck round bottom (250 ml) attached with mechanical stirrer and thermometer (5.7gm) of (BHET) compound was added and heated for (15 min.) at (60 °C). Then (2.5gm) of malic anhydride and (1%) sulfuric acid was added. By the mechanical stirrer the mixture was mixed for (50 min.) at temperature (80°C). After the reaction the mixture was washed with distilled water to avoid the acid residue. Scheme (1) shows the mechanism for the prepared (BHMET) corrosion inhibitor.



Scheme (1). Mechanism of BHMET preparation

Characterization for inhibitor

The FTIR spectrum of the corrosion inhibitor (BHMET) is presented in Fig. 1. Fig.1 shows the band at (1717) cm^{-1} which is assigned for the ester carbonyl group, while the strong band at (3416 cm^{-1}) assigned to carboxyl group (COOH). A weak aliphatic band at (1641 cm^{-1}) assigned to (C=C) and (C-S) band appear at (1050 cm^{-1}) and the band at (1221 cm^{-1}) is attributed to stretching vibrations C-O in the cyclic anhydride ⁽¹⁵⁾. The ¹HNMR of the (BHMET) is shown in Fig. 2. From the Figure the singlet weak wide peak (a) at

(13.15ppm) was attributed to the terminated proton of the carboxyl group (-COOH) and another strong multiples (b) at (8.17ppm) is assigned to the proton of the benzene group and a doublet peak (c) at (6.47ppm) is attributed to the proton of the double bond. A triplet peak(d) is attributed to the methylene group next to the carbonyl ester at (4.54 ppm) due to the proton which is affected by the nearest proton of the (CH_2).

A strong triplet peak (e) at (4.31ppm) is attributed to the methylene group near the oxygen atom. Strong triplet peak (f) at (3.62) was assigned to the symmetric methylene groups near the sulfur atom and a (g)

peak appeared at (3.01ppm) for the asymmetric methylene groups near the sulfur group. While the

strong multiple (h) at (2.59ppm) is attributed to the used solvent d_6 -DMSO (16-18).

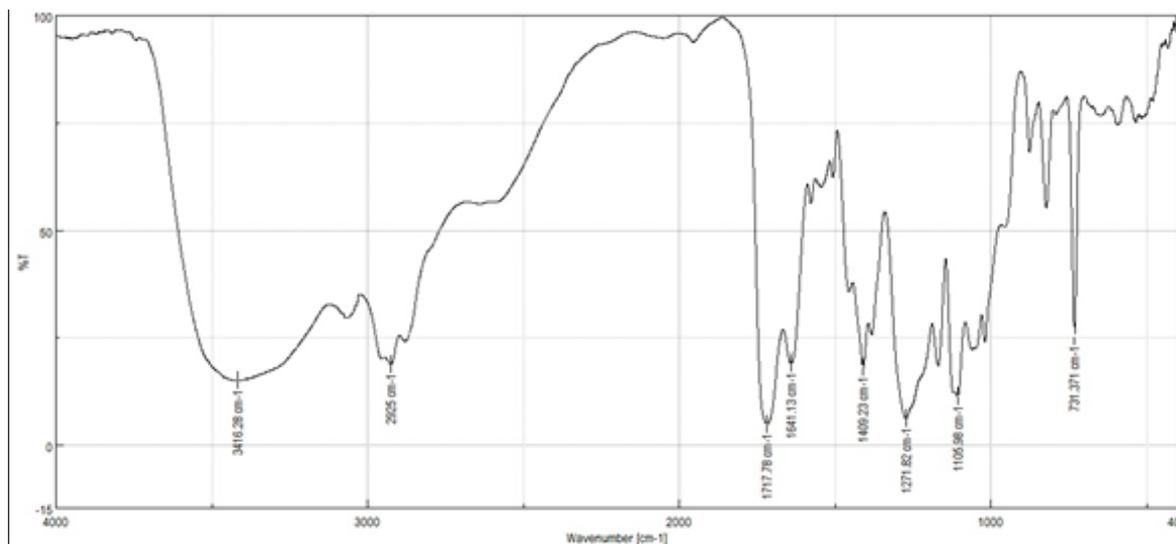


Figure 1. FTIR spectra of BHMET

RESULTS AND DISCUSSION

Electrochemical Measurements

Polarization Measurements (Tafel method)

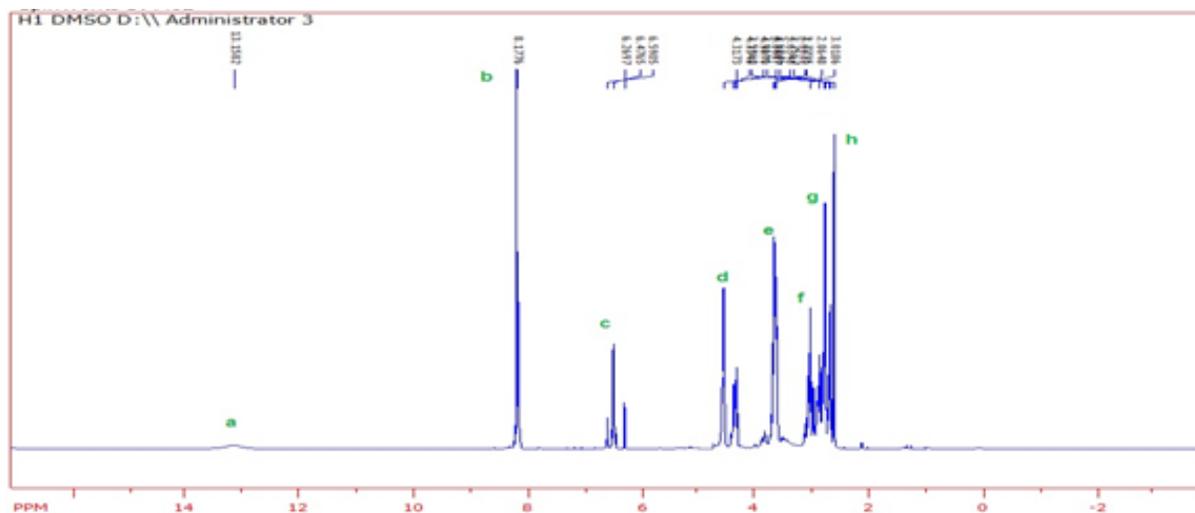


Figure 2. HNMR spectra of BHMET. a= 13.15ppm, b= 8.17ppm, c= 6.47ppm, d= 4.54 ppm, e= 4.31ppm, f= 3.62, g= 3.01ppm, h= 2.59ppm.

Polarization Tafel plot in presence and absence of different concentrations of BHMET are shown in Figs. (3-6). The Tafel factors, inhibition efficiency (% IE), surface coverage (θ), corrosion rate and charge transfer resistance was given in Table 1. It

is apparently that the shapes of the Tafel plots for the inhibited and uninhibited carbon steel are different. The current density of the inhibited carbon steel decreases, while the other parameters behavior does not change. A negative shift was observed for the corrosion potential (E_{corr}) due to adsorption of

the inhibitor. Tafel slopes (β_a and β_c), the anodic and cathodic both decreases with the addition of BHMET. This reveals that BHMET is a mixed-type inhibitor influencing the iron dissolution and hydrogen evolution (19,20). The decrease of the positive and negative currents in the with using the corrosion inhibitor BHMET due to passivation the active sites on the surface of the electrode (21,22). At inhibitor (BHMTE) concentration of 50PPM at 298k the surface coverage and inhibition efficiency reached its maximum. As can be seen from Table 1, BHMET inhibitor greatly reduce corrosion current with a slight shift in the corrosion potential.

Table (1) shows the values of (R_{ct}) increases with inhibitor concentration, which indicates that the efficiency inhibitor to preventing the corrosion of carbon – steel and indicating that the amount of inhibitor adsorbs on the surface of the carbon-steel increasing. The highest resistance to charge transfer ($R_{ct(inh)}$) value at (298 K) was (497.1 Ω) at concentration (50 ppm) of the inhibitor BHMET at (328K),while for the uninhibited was (18.69 Ω) at the same temperature (23)

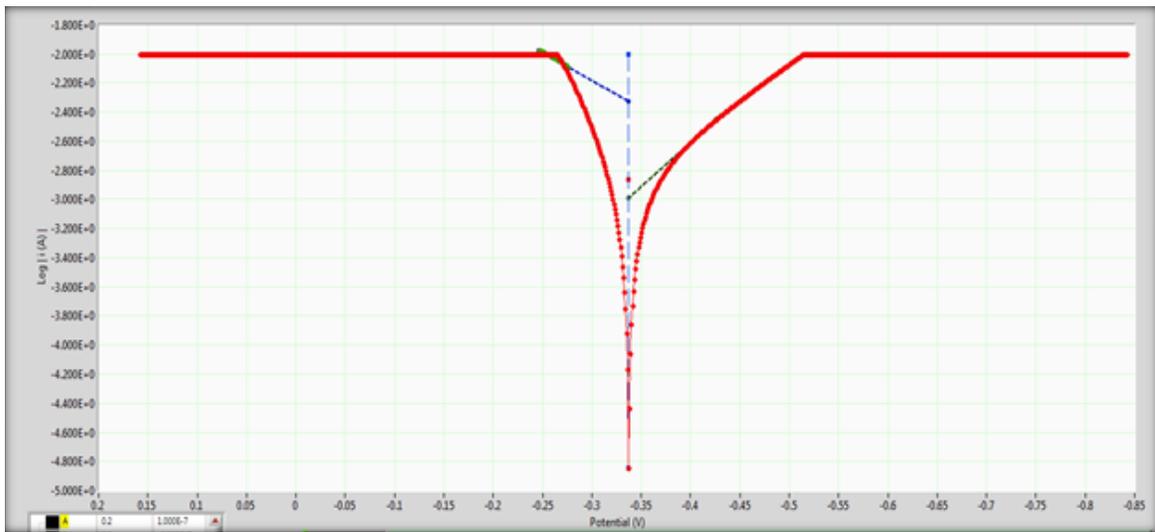


Figure 3. Potentiodynamic polarization curves for carbon steel corrosion in 0.1 M HCl 303K(blank)

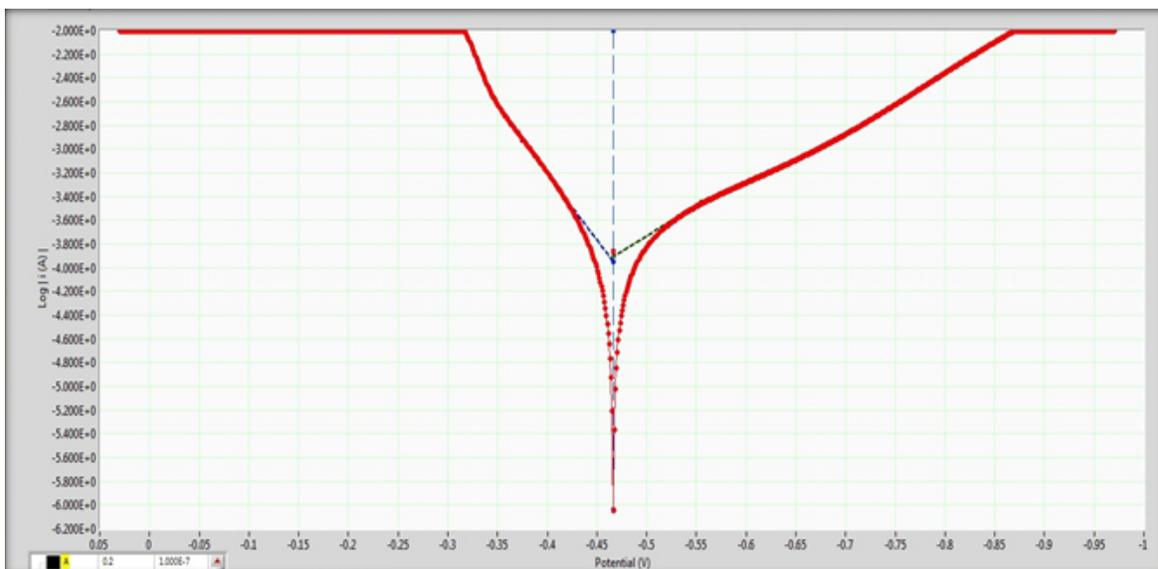


Figure 4. Potentiodynamic polarization curves for carbon steel corrosion in 0.1 M HCl in presence of 50ppm BHMET at 303K.

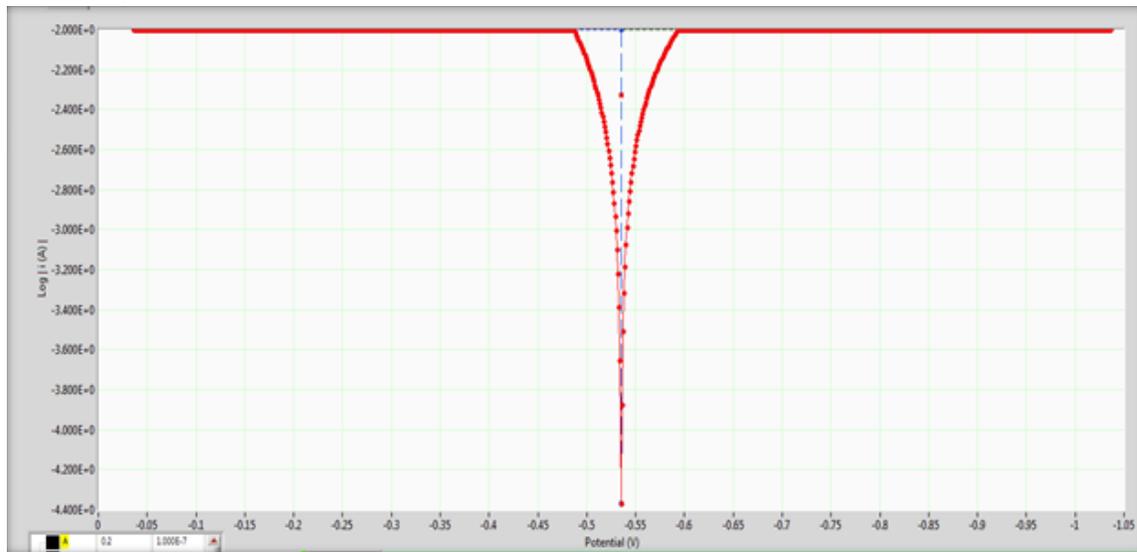


Figure 5. Potentiodynamic polarization curves for carbon steel corrosion in 0.1 M HCl at 333K (blank)

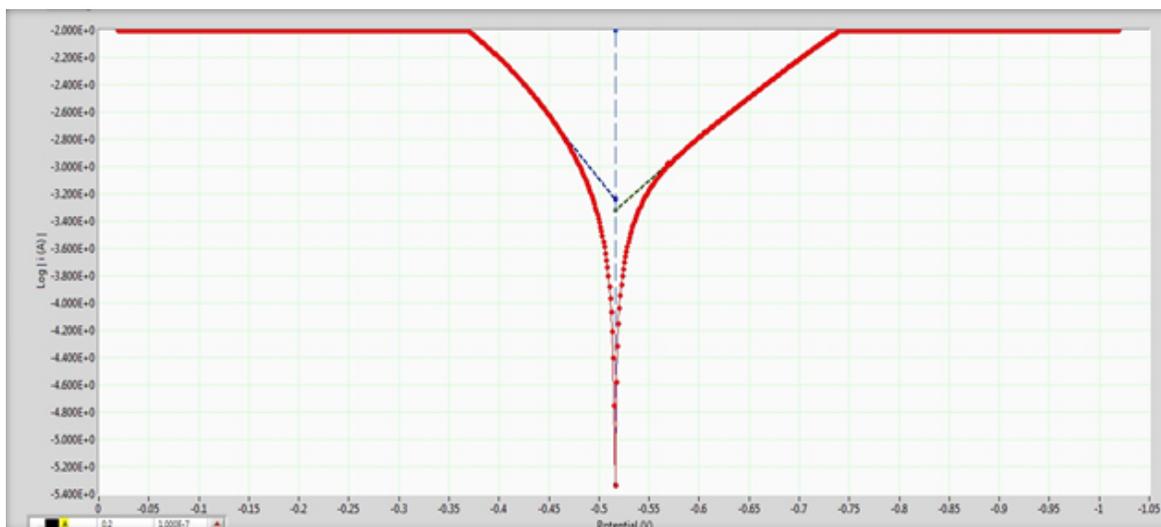


Figure 6. Potentiodynamic polarization curves for carbon steel corrosion in 0.1 M HCl in presence of 10 ppm BHMET at 333K

Table 1. The effect of inhibitor(BHMET) concentrations at different temperatures on the Tafel parameters for C-steel in 0.1M HCl

Conc. ppm	T. K	E _{corr} mv	β_a A/V	B _c A/V	I _{corr} mA/cm ²	R _{ct} Ω	CR mpy	%IE	η
Blank		- 517	3.934	- 6.073	1.375	18.69	74.3	-	-
10	298	- 482	11.23	- 6.080	6.510×10 ⁻²	394.7	3.51	95.2	0.952
20		- 479	10.85	- 6.072	5.789×10 ⁻²	443.9	3.12	95.7	0.957
30		- 482	10.88	- 6.162	5.745×10 ⁻²	447.2	3.10	95.8	0.958
40		- 486	9.155	- 6.322	5.287×10 ⁻²	485.9	2.85	96.1	0.961
50		- 483	9.207	- 6.199	5.168×10 ⁻²	497.1	2.79	96.2	0.962
Blank		- 523	4.574	- 5.954	2.117	12.14	114.41	-	-
10	308	- 470	1.150	- 5.247	1.481×10 ⁻¹	173.5	8.0	93.0	0.930
20		- 466	12.64	- 4.934	1.538×10 ⁻¹	167.1	8.31	92.7	0.927
30		- 474	11.49	- 5.245	2.088×10 ⁻¹	123	11.28	90.1	0.901
40		- 475	10.95	- 5.203	1.798×10 ⁻¹	142.9	9.71	91.5	0.915
50		- 466	11.4	- 5.134	1.380×10 ⁻¹	186.1	7.46	93.5	0.935
Blank		- 527	8.233	- 5.606	3.344	7.684	180.72	-	-
10	318	- 367	10.29	- 6.104	3.783×10 ⁻¹	67.91	20.44	88.6	0.886
20		- 509	10.43	- 6.313	4.421×10 ⁻¹	58.12	23.89	86.7	0.867
30		- 371	10.43	- 5.649	3.850×10 ⁻¹	66.74	20.81	88.4	0.884
40		- 392	9.558	- 6.938	6.40×10 ⁻¹	40.15	34.58	80.8	0.808
50		- 384	9.760	- 6.776	5.280×10 ⁻¹	49.34	28.14	84.4	0.844
Blank		- 535	8.233	-5.668	4.709	5.456	254.52	-	-
10	328	- 516	9.370	- 6.458	5.816×10 ⁻¹	44.18	31.43	87.6	0.876
20		- 391	8.857	- 7.475	8.249×10 ⁻¹	31.15	44.6	82.4	0.824
30		- 401	9.075	- 7.168	8.420×10 ⁻¹	30.51	45.5	82.1	0.821
40		- 387	9.025	- 7.460	7.790×10 ⁻¹	32.98	42.11	83.4	0.834
50		- 389	9.492	- 6.697	7.317×10 ⁻¹	35.12	39.55	84.4	0.844

Effect of Temperature

Temperature was highly affected by the action of inhibitor. The reaction between the acid media and the metal was affected by the temperature. In the acidic media the corrosion rate increase with increase temperature due to decreases of hydrogen evolution (24,25). Table 1 shows the decrease of the efficiency of the (BHMET) inhibitor with increasing temperature from(298-328K) via the decreasing of the corrosion rate C-steel in 0.1 M HCl, the inhibitor efficiency (% IE) decreased from 96.2% at 308K to 84.4 % at 328K for 50 ppm concentration of (BHMET) inhibitor. Arrhenius equation used to calculate the activation energy Ea of the corrosion process in 0.1M HCl in the presence and absence of inhibitor (BHMET): (26)

$$\ln W = \ln A - \frac{E_a}{RT} \text{----- (1)}$$

Where Ea is the activation energy, A is the Arrhenius constant, W is the corrosion rate (mpy) , R is the gas constant and T is the absolute temperature, and equation 2

$$\ln \frac{W}{T} = \ln \frac{R}{Nh} + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{----- (2)}$$

Where N, h was Avogadro number and Plank constant.

From Fig. 12 the straight lines was obtained and from equations (1,2) values of Ea found to be 0.0337 kJ.mol⁻¹ and 0.0619 kJ.mol⁻¹ in the absence and pres-

ence of 50 ppm of inhibitor (BHMET), respectively. Results of E_a indicates a strong inhibition action which increase the energy barrier for the corrosion

process in the presence of inhibitor (BHMET) than the situation without inhibitor (27).

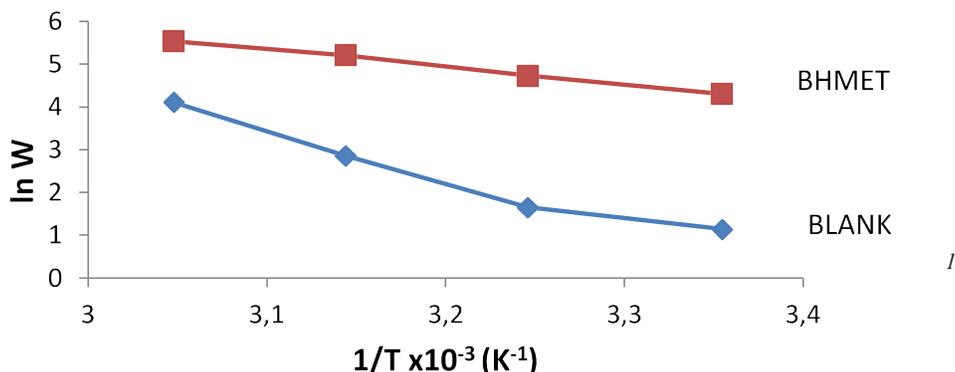


Figure 7. Plot of $\ln w$ and $1/t$ for the blank and 50 ppm (BHMET) inhibitor

And other parameters were calculated from Fig.7 using equation 2 the enthalpies (ΔH), which had positive sign indicates that its endothermic nature of dissolution process (28-29). While the negative values of entropies (ΔS) show that the activated complex

in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

Table 3. Thermodynamic parameters for mild steel in 0.1M HCl in absence and presence of 50ppm BHMET.

Inhibitor con.(ppm)	E_a (kJmol-1)	ΔH (kJmol-1)	ΔS (KJmol-1 K-1)
0 (BLANK)	0.0337	0.0705	- 0.19685
30	0.0706	0.2088	- 0.19646

Adsorption isotherm

Adsorption isotherms related to the mechanism of inhibition corrosion reactions. The adsorption isotherm depends on the chemical structures of the inhibitor, and the electrochemical processes on the metal surface related to the adsorption of the inhibitor (30). Based on the functional groups in the structure of the inhibitor the adsorption of the inhibitor molecules on the surface of the metal. The degree of surface coverage (θ) ($\theta = E (\%)/100$) and the K_{ads} was calculated using (eq. 4).

$$\theta = E (\%)/100 \dots \dots \dots (3)$$

$$K_{ads} = \frac{\theta}{(1-\theta) C} \dots \dots \dots (4)$$

Where C is the concentration of inhibitor, K_{ads} the adsorptive equilibrium constant, and θ is the fraction of the surface covered. While the standard free energy of adsorption reaction (ΔG_{ads}^0) related to the (K_{ads}) shown by following equation (34):

$$\Delta G_{ads}^0 = - RT \ln 55.5 K_{ads} \dots \dots \dots (5)$$

K_{ads} the adsorptive equilibrium constant, T is the absolute temperature (K), R is the universal gas constant and the value of 55.5 is the concentration of water in the solution in mol/L and the data shown in table (4).

Table 4. The adsorption free energy (ΔG°_{ads}) and equilibrium constant (K_{ads}), for the adsorption of inhibitors on C-steel in 0.1 M HCl at (298 k).

Conc. ppm	T. k	θ	ΔG°_{ads} (KJ/mol)	Kads L/g
10	298	0.952	-28.713	1983
20		0.957	-27.282	1112
30		0.958	-26.340	760
40		0.961	-25.821	616
50		0.962	-25.334	506

The high values of K_{ads} mean good inhibition efficiency of the inhibitor and strong electrical interaction between the absorber and the adsorbent. The negative values of ΔG°_{ads} indicate that the adsorption of inhibitor molecule on steel surface is spontaneous and also the strong interaction between inhibitor molecules and the metal surface (35-37). Generally, an adsorption process suggests either physisorption or chemisorption. ΔG°_{ads} value lower than (-40 kJ/mol) are related to the chemisorption between charged molecule and charged metal (38-39). In the present work, the value of ΔG°_{ads} is found to be lower than (-40 kJ/mol); means that the adsorption mechanism of BHMET on carbon steel surface

is mainly the chemisorption.

Thermal analysis study of BHMET

Thermal analysis curve TGA & DTA was shown in Fig.8 and table (5). The inhibitor (BHMET) was stable thermally up to a temperature (220 °C), and also the (T_{max}) (temperature of decomposition) was (345 °C) which is indicate that the inhibitor was stable, and the char residue at (600 °C) was 7 %. The initial decomposition temperature of inhibitor ($T_i = 230$ °C) and the final decomposition temperature was ($T_f = 400$ °C). From Fig.8 the DTA curve indicate that decomposition of the inhibitor was Endothermic. (41)

Table 5. Thermal analysis TGA and DTA parameters of BHMET

Decomposition temperature (T_{max})	345 °C
Rate of Decomposition % / min	3.30 °C
50 % wt. loss ($T_{1/2}$)	315 °C
Char yield 7 % at	600 °C
$\Delta T = T_f - T_i = (400 - 230)$ °C	170 °C

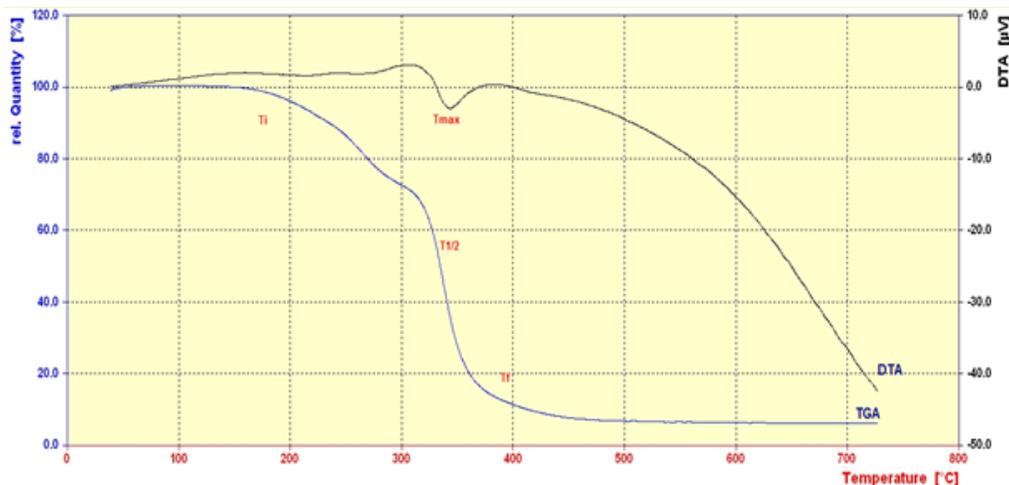


Figure 8. Thermal analysis, TGA and DTA curve of BHMET

CONCLUSIONS

Bis[2-{{(6-Mono malic acid –hydroxyethyl ester} sulfanyl)ethyl terephthalate (BHMET) prepared and used as corrosion inhibitors of carbon steel in 0.1M HCl solution. Two parameters effect was studied, The concentration of the inhibitor (BHMET) and the temperature. From the data the higher (%IE) was for the 10ppm at 298 and at 313 the 10ppm was

the higher inhibitor efficiency. The adsorption of the BHMET inhibitor onto the surface of the carbon steel follows the Langmuir's adsorption isotherm. The prepared compound was mixed type inhibitor and the ΔG°_{ads} indicates that the adsorption of (BHMET) inhibitor involves chemisorption.

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