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Corrosion Inhibitors for Carbon Steel using some Amide Resins derived from Waste Water drink Bottles

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Abstract

Two amide resins, *(bis-(2-hydroxy ethylene) terephthalamide) BHETA*, and *N1,N1,N4,N4 -tetra -(2-hydroxyethyl)-terephthalamide) THETA* were prepared from reaction of waste water bottles (PET) with Monoethanolamine (MEA) and diethanolamine (DEA) respectively using microwave oven, (power less or equal to 600 w) for 20 minutes. The products were characterized by FTIR spectroscopy then evaluated as corrosion Inhibitors for Carbon steel in 0.1 M HCl at different temperatures using Taffel plots and Electrochemical *Impedance Spectroscopy (EIS)* techniques. The obtained results showed that the Inhibition Efficiency (%E) increased up to 76% and 83% for BHETA and THETA respectively. The adsorption isotherm was investigated using Langmuir equation, and the obtained results confirmed the occurrence of physico adsorption that occurs between the Inhibitor and surface of the metal, and the thermodynamic functions were calculated : *Activation energy (Ea), Enthalpy ($\Delta \mathring{H}_{ads.}$), Free energy ($\Delta \mathring{G}_{ads.}$) and entropy $\Delta \mathring{S}_{ads.}$* .
The coating properties of 25% w\w of each BHETA and THETA with commercial acrylic paint were evaluated using EIS technique and showed that the efficiency of coating increased up to 89% and 93.6% when adding BHETA and THETA respectively.

Keywords: PET waste. Aminolysis. PDP. EIS. BHETA. THETA

1. **Introduction**

At various periods of time, attempts were made to prepare compounds that could be used as inhibitors to prevent corrosion on metal. This field has received great attention. The inhibition of corrosion is influenced by several factors such as the nature and condition of the metal surface, the type of corrosive medium, and the structure of the chemical compound used as an inhibitor is directly related to its efficiency in adsorption to the metal surface. [1,2]. *Poly Ethylene Terephthalate* (PET) waste is battening over time owing its use in many fields such as textiles, single use soft drink bottles and envelopments as well as ribbons and bags. PET possesses excellent chemical stability, mechanical properties, and inactivity and is nontoxic, light weight, translucent, and moldable. [3]. Therefore, from the principle of preserving resources and the environment the recycling of PET can be used in various methods such as mechanical and chemical recycling [4]. Chemical recycling processes "sustainable development" of PET waste use different methods, such as

hydrolysis, Alcoholysis, aminolysi, hydrolysis, and glycolysis. These different processes give useful by-products [5,6]. Regarding the aminolysis process, different types of amines are often used in the depolymerization process such as mon-ethanolamine, di-ethanolamine, tri-ethanolamine and the use of Zn $(CH_3COO)_2$ salts as a catalyst in the depolymerization reaction. The quantity and purity of the product is high, and it can also be used in the manufacture of useful products through several chemical reactions [7,8]. Organic synthesis with the help of microwave oven has revolutionized chemical research as it provides many advantages, including time control as well as better temperature control. [10]

2.Material

Carbon steel with a composition of (C = *0.083%, Mn = 0.50%, Si = 0.011%, P = 0.03%, S = 0.002%)* and the residue Fe. PET wastes were acquired from the local market, cut into Small lots size 4 × 4 mm, were washed with distilled water to remove dirt, rewashed with ethanol, and then dried in an oven at (80Ċ) for 1 hour.

3. Chemicals.

Chemical materials were obtained from different sources and as follows: Zinc acetate (FLUKA-UK), di-ethanolamine(DEA), Mono-ethanolamine (MEA) (Aldrich - Germany), ethanol (Hi Media - INDIA), and HCl (alpha - UK).

4. EXPERIMENTAL

Synthesis of *(bis-(2-hydroxy ethylene) terephthalamide), (BHETA)* and *N1,N1,N4,N4-tetra -(2-hydroxyethyl) terephthalamide), (THETA).*

Using microwave oven (EGS-TURKY, 900W, 25 L), the PET waste was reacted with Diethanolamine (DEA) and Mono-ethanolamine (MEA) as separate as the molar ratio (1: 1) of PET: amine; zinc acetate (% 1 w / w) was added as a catalyst. Finally, the microwave oven had been started for 20 min.

5. PHYSCO - CHEMICAL TESTS

5.1 Water Resistance

A dry wood piece (W1) was weighed, coated with mixture from (acrylic resin and amide resin), left to dry at room temperature, and was later immersed in water for 30 minutes. Then, the coating layer was removed from wood and weighed (W2) .The same above procedures were applied using concrete cube.

The coating efficiency IE% was calculated according to equation (1). (11). The obtained results were listed in table (1).

$$\%IE = \frac{W2}{W1} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

5.2. Chemical Resistance test

Using glass foil on which test samples was different mediums, 0.1 M of KOH, 0.1 M HCl, (10% w / w NaCl) and distilled water separately. After 30 minutes, it was removed and tested for chemical resistance. [13]

6. Electrochemical measurements

Electrochemical measurements were probed using Potentiodynamic Polarization (PDP) and Electrochemical Impedance Spectroscopy (EIS) Techniques with a computer–controlled potentiostat (model Corr Test –CS350). Three-electrode cells (saturated calomel electrode (SCE) with a hiber-loggin capillary as a reference electrode (RE), platinum counter electrode (CE) and (Carbon steel) as working electrode (WE) were used in PDP technique, and EIS measurement was performed using (model Corr Test –CS350). 10 mV was used in the frequency range of (10 Hz - 105 Hz) at room temperature. [13]

7. Characterization of products

Using infrared spectroscopy (FTIR-8400S SHIMADZU-Japan)

8. Results and discussion

Fig. 1. Represents the aminolysis of PET using ethanolamine, diethanolamine get respective *terephthalamides* (*BHETA, THETA)*

Figs .2and 3. Represents the FTIR spectrums for BHETA and THETA respectively, and showed that the (O - H) primary alcohol was absorbed at wave length 3290 , 1053 cm^{-1} for BHETA, and 1045 cm^{-1}, 3414 cm^{-1} for THETA, the secondary amide stretching are observed at 3363, 1554 and 1315 cm^{-1} for BHETA , while the tertiary amide functional group were appearing at Frequencies at 1373 cm^{-1} , 1593 cm^{-1} for THETA. Other peaks were observed at 2939 and 2827 cm^{-1}, corresponding to aromatic –CH and aliphatic $–CH_2$, consecutively.[14]

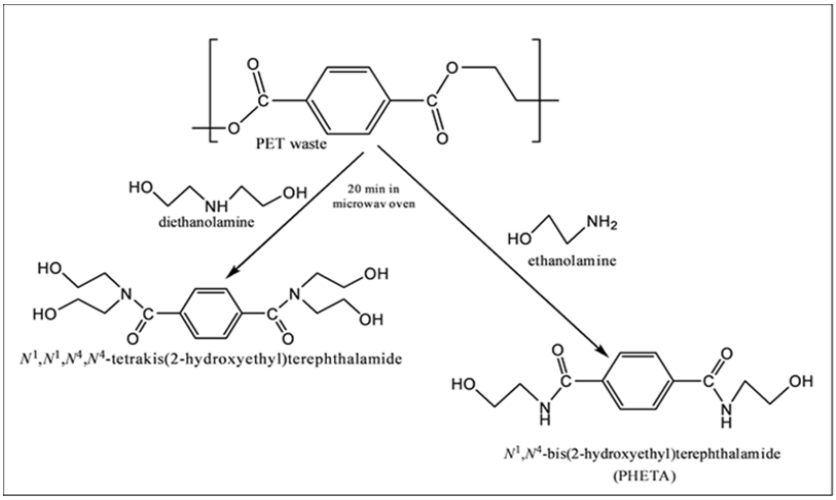

fig. 1, Aminolysis of PET waste

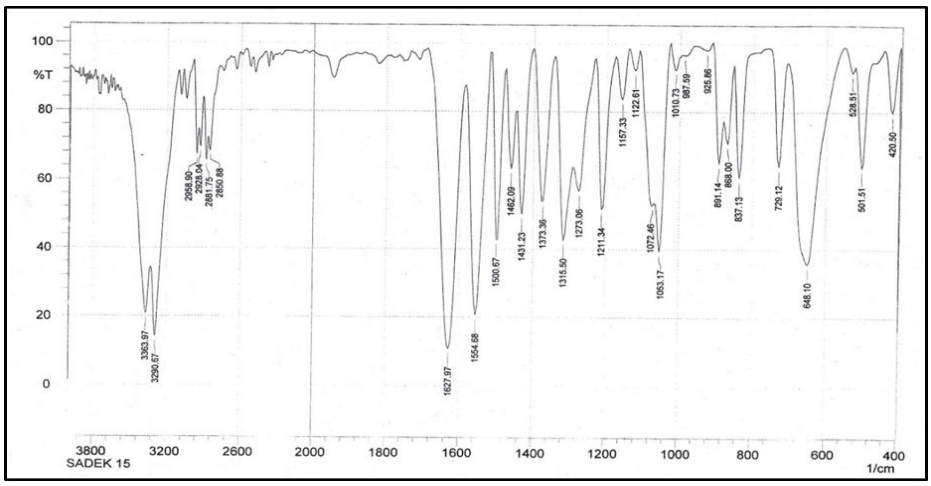

Fig .2. FTIR Spectra for BHETA

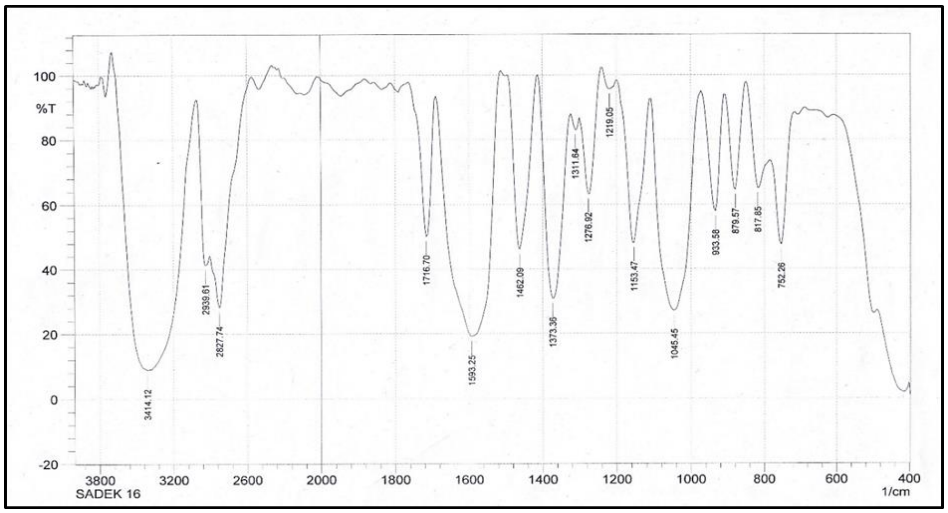

Fig .3 FTIR spectra for THETA.

Water resistance test

The water resistance of acrylic paint with and without BHETA and THETA were tested, and the results were listed in table (1) and showed good water resistance of paints for wood and concrete materials

Table (1) indicates the percentage of water resistance efficiency of the compounds PHETA and THETA.

Tests	%IE Water resistance Wood	%IE Water resistance concrete
PHETA*	89.21	81.34
THETA*	75.82	81.1

*Commercial acrylic paint used in a 2: 1 ratio with amide resins

Chemical Resistance

The chemical resistance of acrylic paint containing amide resins BHETA and THETA were evaluated by different media table (2) and showed that they were not affected by H_2O, NaCl and HCl, while 0.1 M KOH was affected by paint after a long time.

Table (2) indicates chemical resistance to compounds PHETA and THETA.

Sample	DI H_2O	NaCl 10% w/w	HCl 0.1M	KOH0.1 M
PHETA*	NO, Effect	NO, Effect	NO, Effect	**The Effect is after a Longer time**
THETA*	NO, Effect	NO, Effect	NO, Effect	**The Effect is after a Longer time**

* Commercial acrylic paint used in a 2: 1 ratio with amide resins

[15 -16] Corrosion Study

The corrosion inhibition of carbon Steel in 0.1M HCl was studied by Tafel plots potentiodynamic polarization at different temperatures (293 , 298, 303, 308 , 313,and 318) K , were represented figs. (4 and 5) and tables (3 and 4). The result showed that the BHETA and THETA acts as both anodic and cathodic Inhibitors. The inhibition efficiency (EIS) was calculate according to the equation (2) and its found that the %IE reacted up to 76% and 80% for (BHETA and THETA) respectively.

$$\%\,IE = \frac{I°corr - Icorr}{I°corr} \times 100 = \theta \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where İcorr and Icorr are the corrosion current densities in the uninhibited and inhibited solutions, Consecutive , and(θ) The degree of surface coverage.

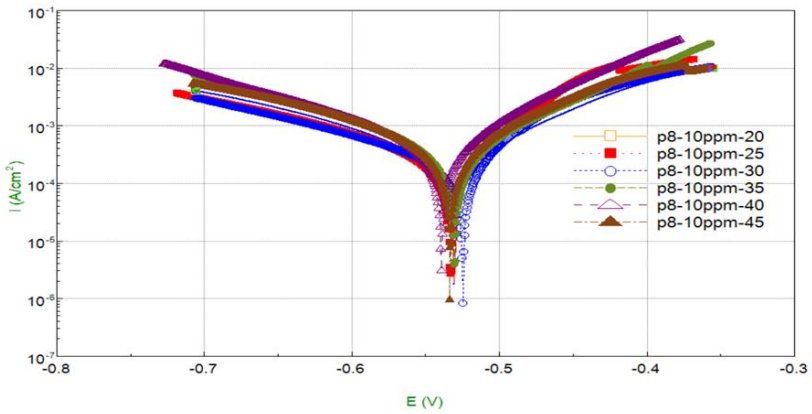

fig . 4 , tafel plot For carbon steel in 10 ppm concentrated with BHETA with different Temperatures (range 293 – 318 k).

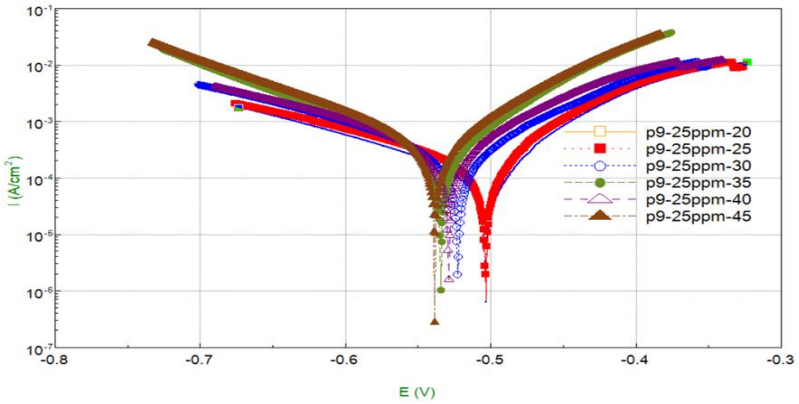

Fig. (5) .Tafel plot for carbon steel in 25 ppm concentrated with THETA with different Temperatures (range 293 – 318 k)

Table 3. Showing the corrosion Inhibition parameters of Carbon Steel in the acid medium And the exist from the optimal concentration of the inhibitor (PHETA)

TEMP.(K)		E_{CORR} (mv)	I_{CORR} (mA/cm^2)	R_{CT} Ω/cm^2	CR (mpy)	% IE	Θ
293	blank	-532	0.90	39.40	420.04	.....	
	PHETA	-530	0.32	82.367	149.5	64	0.64
298	blank	-535	0.95	43.97	440.26		
	PHETA	-533	0.359	77.786	166.36	62	0.62
303	blank	-537	1.53	29.37	709.15		
	PHETA	-524	0.367	85.916	169.91	76	0.76
308	blank	-530	1.57	36.51	728.1		
	PHETA	-521	0.417	59.845	193.23	73	0.73
313	blank	-539	1.65	26.089	762.86		
	PHETA	-538	0.482	48.52	223.18	71	0.71
318	blank	-533	1.85	19.25	857.41		
	PHETA	-530	0.526	55.362	243.75	72	0.72

Table, 4. Showing the corrosion Inhibition Parameters for the Corrosion of carbon Steel in the acid medium and the exist from the optimal concentration of the inhibitor (THETA).

TEMP.(K)		E_{CORR} (mv)	I_{CORR} (mA/cm^2)	R_{CT} Ω/cm^2	CR (mpy)	% IE	Θ
293	blank	-532	0.90	39.40	420.04	.....	
	THETA	-503	0.157	162.16	72.911	83	0.83
298	blank	-535	0.95	43.97	440.26		
	THETA	-504	0.258	108.72	119.54	73	0.73
303	blank	-537	1.53	29.37	709.15		
	THETA	-522	0.306	83.203	141.99	80	0.80
308	blank	-530	1.57	36.51	728.1		
	THETA	-525	0.319	58.366	148.15	80	0.80
313	blank	-539	1.65	26.089	762.86		
	THETA	-529	0.421	66.227	195.04	75	0.75
318	blank	-533	1.85	19.25	857.41		
	THETA	-530	0.464	44.198	214.58	75	0.75

Adsorption isotherm

The adsorption isotherm was investigated using the Langmuir isotherm equations. *activation Energy Ea.* were computed from the arrhenius equation (3) and Its the Transition state equation to calculate the activation energy . a straight line was drawn from ln CR versus 1 / T, and were represented in Fgs 6 and 7, The activation energy was calculated according to Equation 3.

$$\text{Ln CR} = -\frac{Ea}{RT} + \text{Ln A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

A, Arrhenius constants.

The obtained data showed the activation energy in the exist from Inhibitors are greater Than the activation energy In the Absence of Inhibitors, this meen the physco adsorption mechanism was acted for amide inhibitors [17].

Adsorption equilibrium constants $K_{ads,}$ was calculated according to equation (4)

$$K_{ads} = \frac{\theta}{(1-\theta).C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

C, concentration inhibitors

The standard free energy of adsorption, $\Delta\mathring{G}$ ads were calculated according to equation (5)

$$\Delta\mathring{G}_{ads} = -RT \text{ Ln } (55.5\ K_{ads}) \quad \ldots\ldots\ldots\ldots \quad (5)$$

Where R is the gas constant, J mol^{-1} K^{-1}, the value of 55.5 is the concentration of water in acid solution in mol/L and T is the absolute temperature

The enthalpy adsorption ΔH_{ads} calculated the Van't Hoff equation expressed by Eq. (6).

Ln CR = $\frac{\Delta \mathring{H}}{RT}$ + C …… (6)

As in Equation (6) were evaluated from the slope plot of Ln (K ads) versus 1/T (Figure 6). The values of $\Delta \mathring{H}$ ads.

The entropy adsorption $\Delta \mathring{S}_{ads}$ calculated as in eq. (7).

$\Delta \mathring{G}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads}$..... (7)

The obtained results were listed in tables (5 and 6), and showed that the negative values of the $\Delta \mathring{G}$ads are less than 20 kJ / mol. This means that the adsorption of the inhibitors on the metal surface can be considered as physical adsorption [18]

The $\Delta \mathring{H}$ ads were calculated according to equation 2 as shown in figs (8 and 9), the negative values indicate that the inhibitory adsorption process on the metal surface is an exothermic process and this confirms the occurrence of physico adsorption which happens between the inhibitor and surface of the metal. [19]

The negative values of the adsorption entropy represented in tables (5 and 6) indicate that the system is heading to a less random state on the surface of the metal, and this state is associated with the exothermic reactions. [20]

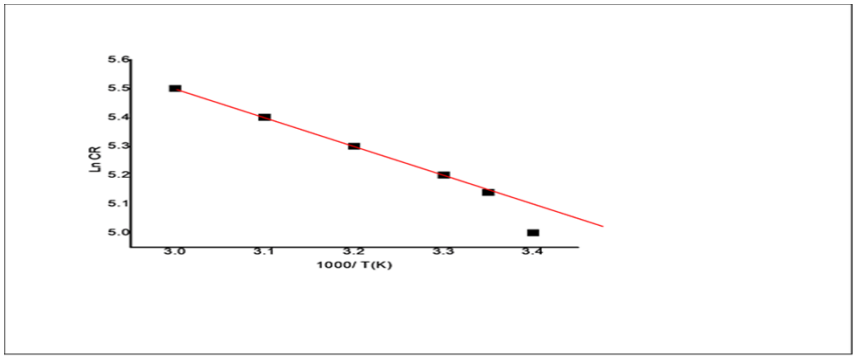

Fig.6. Arrhenius plot to calculate Ea. of corrosion of carbon steel in a 0.1 M HCl solution, in the Presence of 10ppm of the PHETA

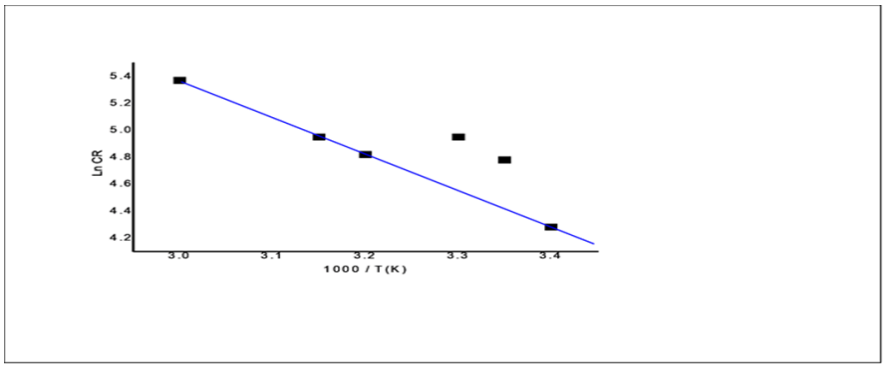

Fig.7. Arrhenius plot to calculate Ea. of corrosion of carbon steel in a 0.1 M HCl solution in the presence of 10ppm of the THETA

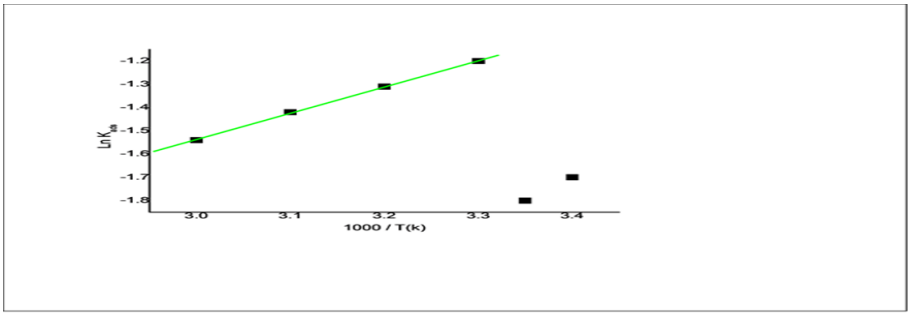

Fig. (8) Van't Hoff plot equation for calculating $\Delta\mathring{H}_{ads}$ of PHETA at different temperatures

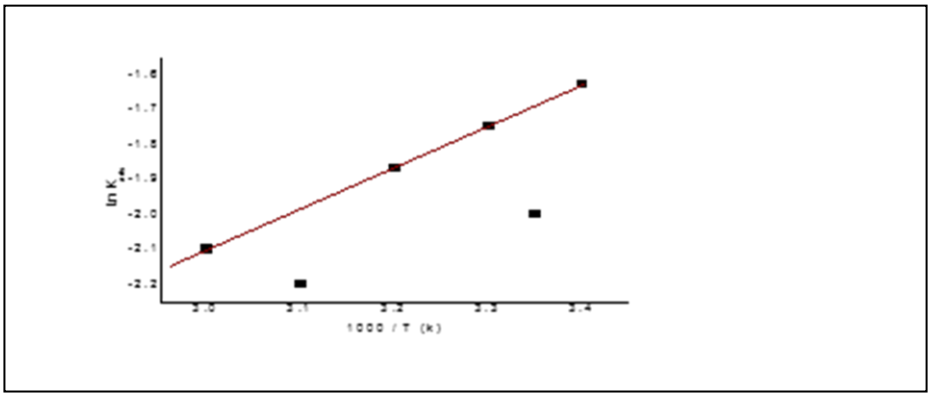

Fig. (9) Van't Hoff plot equation for calculating ΔĤads of THETA at different temperatures

Table (5) shows the variables computed from the Langmuir isotherm equations and the free compression energy for adsorption and adsorption entropy for the optimal concentration of the inhibitor (10 ppm) of the compound BHETA.

T(K)	$\Delta\mathring{G}_{ads}$ **KJ/mol**	$\Delta\mathring{S}_{ads}$ **J .K^{-1} . mol^{-1}**
293	-55.2	-175.3
298	-53.36	-166.3
303	-71.53	-223.3
308	-68.38	-209.6
313	-65.43	-196.6
293	-69.55	-191.04

Table (6) shows the variables computed from the Langmuir isotherm equations and the free compression energy for adsorption and adsorption entropy for the optimal concentration of the inhibitor (25 ppm) of the compound THETA.

T(K)	$\Delta\mathring{G}_{ads}$ **KJ/mol**	$\Delta\mathring{S}_{ads}$ **J .K^{-1} . mol^{-1}**
293	-56.2	-162.6
298	-44.2	-118.6
303	-59.8	-168.2
308	-55.2	-150.5
313	-48.7	-127.3
293	-49.2	-126.9

Electrochemical impedance spectroscopy

The values of the inhibition efficiency (% IE) were calculated according to equation 8, and the results were listed in table.

The capacity of the double layer Cdl, which represents the coating layer formed from the coating in the presence and absence of the damper measured in unit (μF.cm^{-2}) is calculated as in equation (9)

$$\%IE = \frac{Rp(inhib) - Rp(uninhib)}{Rp(inhi)} \times 100 \quad \ldots\ldots\ldots\ldots (8)$$

$$Cdl = \frac{1}{2\pi\, fmax} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where Rp (inhibit) and Rp (uninhib) polarization resistance of presence and absence inhibitor, $fmax$ the frequency maximum (Hz)

The results obtained from impedance spectra as shown by the Nyquist plots in Figures (11) and (12). Using the simple model describing the corrosion process Figure (10). The obtained complex plane diagrams are low semicircles, indicating that the Imperfect capacitive behavior of mineral solution interface. Capacitance dispersion on solid surfaces can be attributed to surface roughness, degree of crystallinity, chemical heterogeneity.

Table (7). EIS parameters values for the corrosion of carbon steel in 0.1 M HCl solutions in the presence and absence of inhibitor.

Inhi.	%Wt of inhi.	R_P(KΩ.cm^2)	C_{dl} µF.cm^{-2}	F_{max} Hz)(	%IE
Acrylic paint	.....	617	5.5E-7	469	.....
BHETA	25w\w	7547	1.15E-7	183	89
THETA	25w\w	9672	2.5E-8	72	93.6

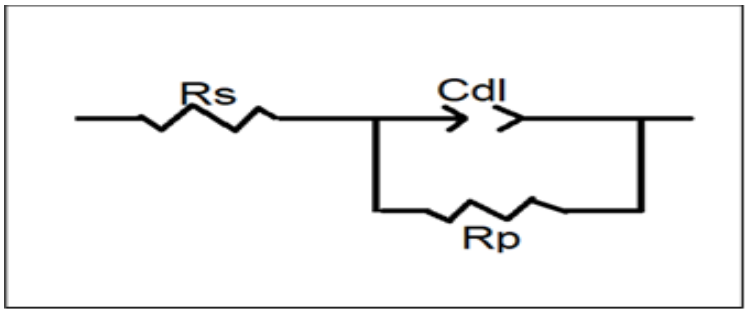

Figure 10. Equivalent circuit for the carbon steel surface/corrosive media

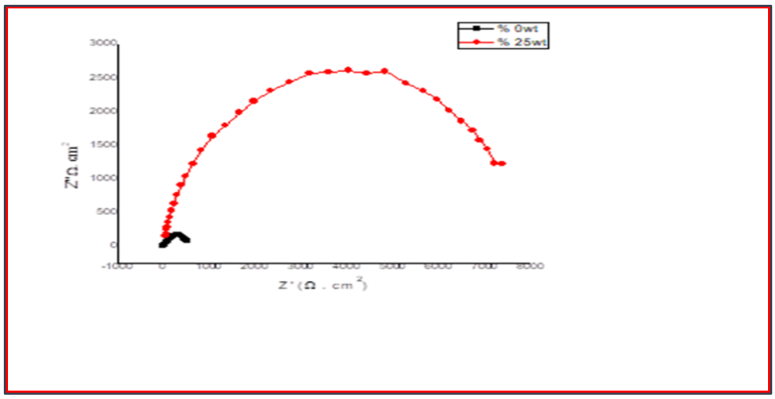

Fig. 11. The Nyquist plots for obtained in 0.1 M HCl solutions in the absence and presence of (%25 w\w) BHETA.

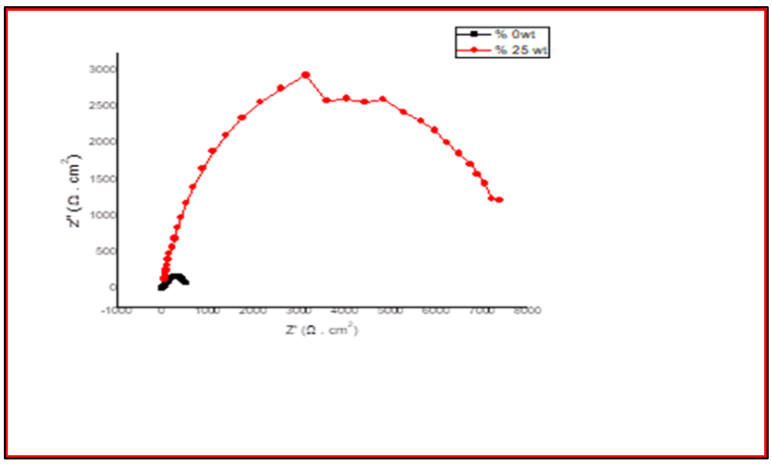

Fig. 12. The Nyquist plots for obtained in 0.1 M HCl solutions in the absence and presence of (%25 w\w) THETA.

Conclusion

The degradation of PET waste by monoethanolmine and diethanolamine using microwave oven are given high yield in stubbier reaction Time. This Kind of recycling Shows a overgrown Industrial Prospect In The Efficient Recycling of PET waste due to Easy Preparation, Low Price, And Relatively milder Degradation Conditions. The degradation products were improved the corrosion inhibition for carbon steel in 0.1 HCl. Resins act as inhibitors of the mixed type. The results were indicated that THETA is strongly absorbed on The Surface of The metal, from The Results obtained from EIS are indicated improve the protection of carbon steel.

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