STUDIES ON CORROSION INHIBITION OF C-STEEL IN 1M ACETIC ACID SOLUTIONS BY ETHOXYLATED POLY (ETHYLENE TERPHTHALATE) DERIVED FROM PLASTIC WASTE

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Abstract

The inhibition of three ethoxylated poly (ethylene terphthalate), derived from plastic waste by reacting of PET with triethanol amine followed by reacting with polyethylene glycol, (PEG), which has different molecular weights 400, 1000 and 4000. On the corrosion of steel in 1M acetic acid solutions have been studied at different temperatures (30-60°C) by weigh loss. The inhibition efficiency for the three compounds increased with increasing of the inhibitors concentrations and temperatures. The inhibition efficiency for the three inhibitors decrease in the order (Tn= 9< 22< 90). The polarization curves indicate that these compounds act as mixed-type inhibitors. The inhibition occurs through adsorption of the inhibitor molecules on the metal surface without modifying the mechanism of corrosion process. Langmuir adsorption isotherms fit well the experimental data of dissolution and adsorption were calculated and discussed.

Key words: *corrosion inhibitor, ethoxylation, plastic waste.*

Introduction

Carbon steel is frequently used in the manufacture of the pipelines due to the aggressiveness of the liquids which carried by them. These liquids may be petroleum containing water, nitrogen and sulfur. All kinds of water passed through these lines contain chlorides, nitrate and sulfate anions. For this reason, the injection of corrosion inhibitors through different sites of pipe is very important.

Poly (ethyleneterphthalate), PET, is widely used in the manufacture of high-strength fibers, photographic films, and soft drink bottles **[1]**. The disposal of a large number of PET bottles caused serious environmental problem. There are various methods used to recycling PET bottles **[2-4]**. Study of organic corrosion inhibitor is an attractive field of research due to its usefulness in various industries. Acid solutions are generally used for the removal of undesirable rust in several industrial processes. Inhibitors are usually used in these processes to control the corrosion of metal. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulpher and oxygen **[5-11].** Many organic acids or their salts are used to inhibit the corrosion rate of metal in aqueous media **[12, 13]**.Steel is used in fabrication of reaction vessels, storage tanks, etc. by industries, which either manufacture or use acetic acid as reactant.

In the previous works **[14-16]**, PET plastic waste was used as cheap and safe corrosion inhibitors for C-steel in hydrochloric acid, sulfuric acid and nitric acid corrosive media**.**

The present work is one from a series aimed to alleviate of environmental pollution by converting PET waste into useful products, and to evaluate the inhibition action of plastic waste on the corrosion of some metals and alloys, in different aqueous media.

In the present work, Triethanolamine (TEA) were used to convert PET waste to water soluble oligomers, followed by the reaction of the obtained oligomers with PEG, which have different molecular weights, 400, 1000 and 4000 to give three different non ionic surfactants. The prepared materials (oligomers) as corrosion inhibitors for C-steel in 1 M acetic acid at different temperatures were evaluated.

Experimental

PET waste was collected from beverage bottles. Triethanolamine (TEA) were purchased from Aldrich Chemical Co., Ltd. (UK), were used as catalysts for depolymerization of PET used in this work.

PET waste is converted to glycolyzed product (T_2). The reaction of PET with TEA was discussed in previous articles **[17].** Also ethoxylation of T_2 using ß, ß\ -dichlorodiethylether (DCDE) and polyethyleneglyol (PEG) was discussed. The aggressive 1M AcOH solution was prepared by dilution of analytical grade AcOH with bidistilled water.

Techniques:

Gravimetric and Polarization Measurements:

The steel samples were polished with different emery papers up to 1200 grade, and washed thoroughly with bidistilled water and then dried with acetone. The composition of the C-steel(X_{46}) used: C, Mn, P, S, Cr, Mo and Si are 0.29, 1.25, 0.03, 0.03, 0.04, 0.04 and 0.27 respectively

Steel specimens, having dimensions 2cm x 2cm x 0.05cm, were suspended from glass hooks in containers for 7days at different temperatures ranged from 303-333±1 K.

Electrochemical measurements were carried out in conventional three electrode electrolysis cylindrical Pyrex glass cell. A saturated calomel electrode (SCE) and a disc platinum electrode were used as a reference and auxiliary electrodes, respectively. The area exposed to the corrosive solution was $1cm^2$. The temperature was controlled at 303±1°K. Electrochemical experiments were recorded using of a radiometer analytical, voltamaster (PGZ301, DYNAMIC ELS VOLTAMMETRY).

Results And Discussions

The three ethoxylated products coded as Tn_9, Tn_{22} and Tn_{90}, were obtained from depolymerization of PET with TEA using 1:2 wt % of PET to TEA followed by etherfication of the glycolyzed product with PEG in the presence of DCDE. In this respect, three different molecular weights of PEG, namely, PEG400, 1000 and 4000 gm/mol to preduce the surfactants, Tn9, Tn22 and Tn90. The numbers, 9,22and 90 are referred to number of ethylene oxide groups in PEG **[17]**.

Evaluation of the Prepared Oligomers as Corrosion Inhibitors:

The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media **[18]**. The choice of the inhibitor is based on two considerations:

First: it could be synthesized conveniently from relatively cheep raw materials,

Secondly: it contains the electron cloud on the aromatic ring or the electronegative atoms such as N_2 and O_2 in the relatively long chain compounds **[19]**. In this respect, the present corrosion inhibitors were prepared from recycled PET waste and introducing TEA in their chemical structure to increase their abilities to dissolve in water and to use as corrosion inhibitors for C-steel. The corrosion of C-steel in 1 M AcOH solution at different temperatures was studied by either weight loss and potentiodynamic polarization techniques.

Potentiodynamic Polarization Measurements:

Anodic and cathodic polarization curves for carbon steel in 1 M AcOH with and without various concentrations (50-200 ppm) of inhibitors were represented in **Figures (1-3).** The curves were swept from –1000 to 0 V (SCE) with scan rate of 20 mVs^{-1}. Figures (1-3) illustrate the effect of adding progressive addition (50 – 200 ppm) of selected inhibitors on the cathodic and anodic polarization curves of carbon steel alloy (X_{46}) in 1M AcOH at 30°C. The addition of the inhibitors decreases the corrosion current densities (I_{corr}). Furthermore, it was also found that all inhibitors behave as mixed-type, i.e. both cathodic and anodic polarization curves are affected by the inhibitors **[20]**. The variable values of the cathodic Tafel slopes suggest that the inhibition action of such compounds occurs by simple blocking of the electrode surface area **[20]**. The cathodic current–potential curves give rise to parallel Tafel lines, which indicated that hydrogen evolution reaction was controlled **[21]**. Addition of inhibitors increases both the cathodic and anodic over potential of carbon steel alloy and causes displacement of the cathodic and anodic polarization curves. Therefore, these oligomers could be classified as mixed type (anodic/cathodic) inhibitors. These results indicated that the used ethoxylated products inhibit AcOH corrosion of carbon steel via their adsorption on both anodic and cathodic active sites without modifying the mechanism of corrosion reaction. This means that the adsorbed inhibitor molecules block the surface active sites and decrease the area available for hydrogen evolution and metal dissolution reactions **[21].**

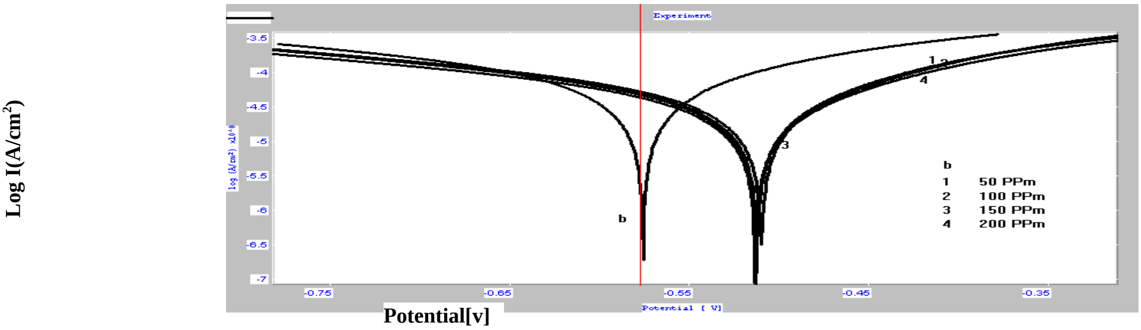

Figure 1: Potentiodynamic polarization curves of C-steel in 1 M AcOH in absence and presence of diffirent concentrations of inhibitorTn_9 at 303 K

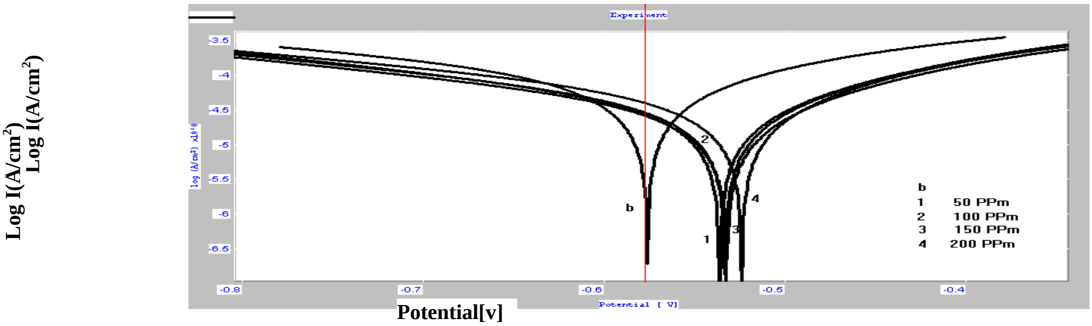

Figure 2: Potentiodynamic polarization curves of C-steel in 1 M AcOH in absence and presence of diffirent concentrations of inhibitor Tn_{22} at 303 K

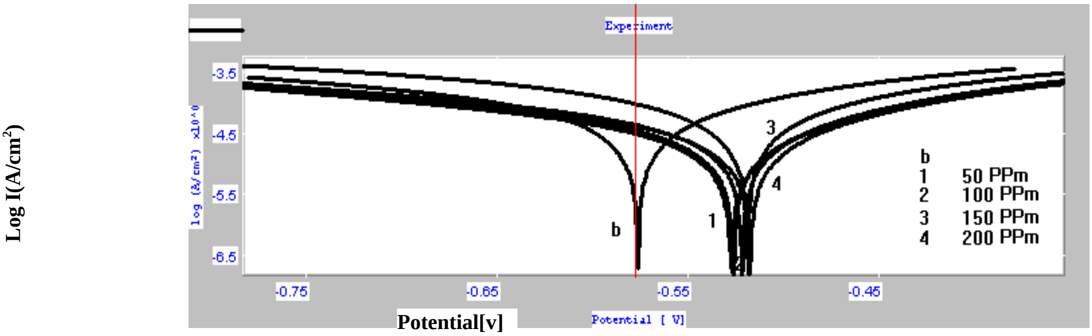

Figure 3: Potentiodynamic polarization curves of C-steel in 1 M AcOH in absence and presence of diffirent concentrations of inhibitor Tn_{90} at 303 K

The corrosion potential (E_{corr}), the corrosion current density (I_{corr}) were determined from extra-pollation of cathodic I_c and anodic Tafel lines. The values of E_{corr}, I_{corr}, R_p, Tafel slopes (b_c, b_a), degree of surface coverage (θ) and inhibition efficiency (IE) were calculated for each sample and listed in Table (1). It is clear that the values of corrosion potentials E_{corr} remain almost unchanged and indicate that the prepared surfactants act mainly as mixed type inhibitors **[22].** Addition of the three prepared inhibitors to AcOH solution decreases the values of I_{corr} and increases the values of R_p for carbon steel alloy.

The inhibition efficiency IE of inhibitors was calculated from polarization measurements by using the following equation:

$$IE = 1 - (I_{inh} / I_{uninh}) \times 100 \qquad (1)$$

Where: I_{uninh} and I_{inh} are the corrosion current densities in the absence and presence of inhibitor respectively. Also, the polarization resistance (R_p) can be calculated using Stren-Geary equation.

$$R_p = (b_a \text{ x } b_c)/\ (2.303\ i_{corr}\ (b_a + b_c)) \qquad (2)$$

The inhibition efficiency calculated from the polarization measurements were listed in Table (1). It is obvious that the inhibition efficiency increases with increasing the concentration of inhibitors. Also the protection efficiency of these surfactants decreases in the order, $Tn_{90} > Tn_{22} > Tn_9$, due to the difference in the chain length of the hydrocarbon chain causes and increase in the bulk of the groups attached to the adsorption center [13], and hence reduce the rate of corrosion.

Table 1: Polarization data of the prepared inhibitors.

Sample	Conc., ppm	$I_{corr.}$, mA/cm^2	$-E_{corr.}$, mV	Rb, ohm.cm^2	ba, mV	-bc, mV	IE	θ
Blank	0	2.165	61.84	37.82	186.9	226.4	0	0
Tn_9	50	0.495	518.2	94.6	146.8	168.2	81.2	0.812
	100	0.446	528.8	84.9	139.6	169.4	83.4	0.834
	150	0.397	561.1	75.3	131.5	179.3	85.6	0.856
	200	0.403	567.6	53.2	135.4	158.3	87.9	0.879
Tn_{22}	50	0.371	493.2	89.5	129.6	169.1	83.6	0.836
	100	0.362	490.3	103.2	118.0	174.2	85.3	0.853
	150	0.423	482.5	136.3	120.1	144.3	88.2	0.882
	200	0.484	481.3	140.2	99.8	153.4	90.1	0.901
Tn_{90}	50	0.256	486.2	198.5	98.4	185.5	85	0.85
	100	0.297	472.1	290.6	69.2	183.2	87	0.87
	150	0.318	468.2	258.8	124.7	378.6	91	0.91
	200	0.389	462.3	241.6	63.3	178.2	92.5	0.925

Adsorption Isotherms:

If one supposes that the adsorption of inhibitor follows the Langmuir adsorption isotherm, the surface coverage could be given by the equation:

$$C_i/\ \theta = (1/\ K_{ads}) + C_i \qquad (3)$$

Where, C_i is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant. The degree of surface coverage (θ) for different concentrations of the inhibitors in acidic media, **[23]** has been evaluated from Potentiodynamic measurements by using the following equation: the surface coverage θ was obtained from the relation:

$$\theta = 1 - (I_{inh}/I_{uninh.}) \qquad (4)$$

Careful inspection of these results showed that, inhibition efficiency increases with increasing inhibitor concentration and surface coverage.

In the present work, it was observed that, all isotherms have slope less than unity the deviation from unity may be explained on the basis of interaction between the adsorption species on metal surface **[23]**. The inhibition of these compounds may be due to their adsorption and formation of adsorbed monolayr at metal surface interface. The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm. The relation between C_i/θ against C_i was illustrated in **Figure (4)**.

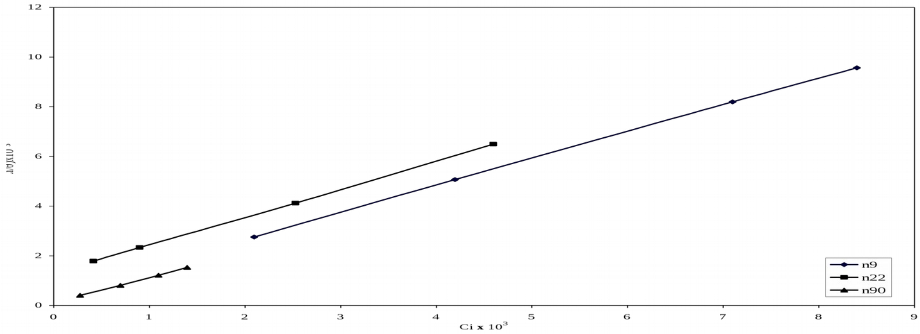

Figure 4: Langmuir adsorption isotherm for Tn_9, $T\ n_{22}$ and Tn_{90} Inhibitors

Weight Loss Measurements:

Effect of Temperature:

Effect of temperatures on the corrosion behavior of carbon steel in 1 M acetic acid was studied by the weight loss method over temperature range (303–333 K). The data display that the rate of corrosion increases with an increase in temperature from 303 to 333K as represented in Table (2). Also, Figures (5-7) indicated that the weight losses of carbon steel in 1 M AcOH increase with increase with immersion time. The results of carbon steel inhibition efficiency of 200 ppm of the prepared oligomers at different temperatures show that the weight losses decrease (corrosion rate) with increasing temperature from 303 – 333K which indicate chemical adsorption **[22].**

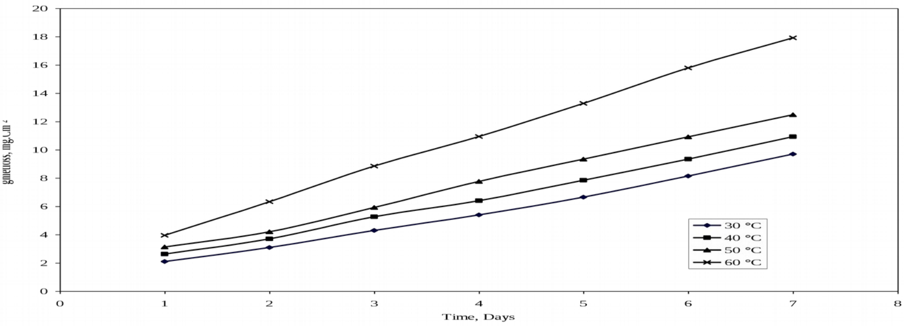

Figure 5: **Weight loss-time curves of C-steel alloy in 1 M A_COH in the presence of 200 ppm of inhibitor Tn_{90} at different temperatures.**

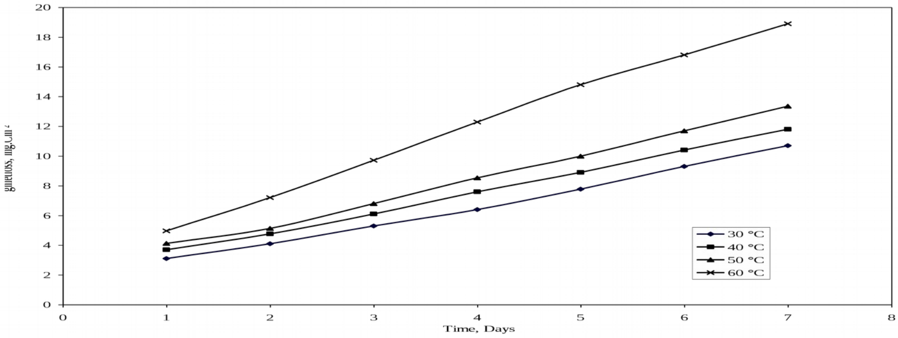

Figure 6: **Weight loss-time curves of C-steel alloy in 1 M A_COH in the presence of 200 ppm of inhibitor Tn_{22} at different temperatures.**

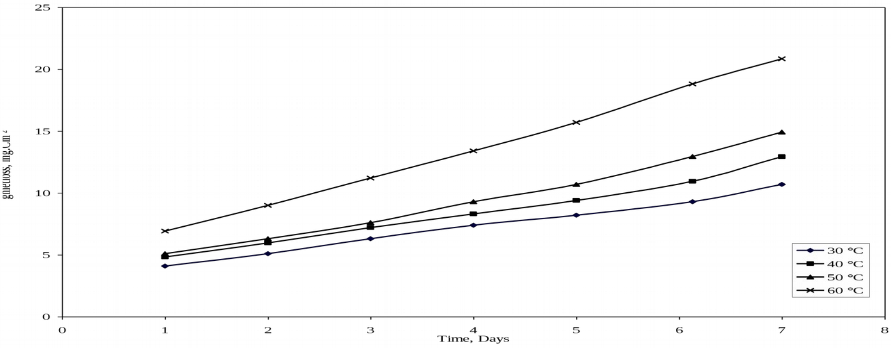

Figure 7: **Weight loss-time curves of C-steel alloy in 1 M A_COH in the presence of 200 ppm of inhibitor Tn_9 at different temperatures**

Activation Energy of corrosion:

Corrosion is an electrochemical phenomenon and consequently follows the laws in chemical kinetics. The corrosion rate increases with temperature as a result of decreasing the apparent activation energy, E_a of the charge transfer reactions. Increasing temperature also enhances the rate of H^+ ion diffusion to the metal surface beside the ionic mobility, which increases the conductivity of the electrolyte. The effect of temperature on the inhibition efficiency of corrosion inhibitors is important in elucidation of the mechanism and kinetics of their action. Moreover, at lower temperature, adsorbed hydrogen atoms (exothermic process) blocked the cathodic area.

The activation energy (Ea) can be calculated from Arrhenius equation [**22].**

$$\text{Log } R_{corr} = \log A - Ea/2.303RT \qquad (5)$$

A is pre-exponentional factor related to concentration, steric effect and metal surface characteristics, etc. Plotting of log R_{corr} against 1/T for the free acid solution (blank) and 200 ppm of the used inhibitors were represented in Figure (8). The activation energies were calculated and listed in Table (2). The results showed that, the values of activation energy (Ea) increase in the same order of increasing the inhibition efficiency of the inhibitors. It is also indicated that the whole process is controlled by surface reaction **[24].**

Table 2: Degree of surface coverage (θ) and percentage of inhibition efficiency (IE) of the Used inhibitors in 1M AcOH at different temperatures calculated from weight loss data.

Compound	T, ºK	(1/T)x10^{-3}	R_{corr} mg.cm^2.day^{-1}	Log R_{corr}	IE	θ	E_{active}, k.J.mol^{-1}
Tn_9	303	3.3	1.042	0.01787	86	0.86	154
	313	3.19	0.96	0.0177-	87	0.87	
	323	3.09	0.81	0.0915-	88	0.88	
	333	2.91	0.76	0.1192-	90	0.9	
Tn_{22}	303	3.3	0.88	0.0555-	88	0.88	163
	313	3.19	0.79	0.1024-	89	0.89	
	323	3.09	0.69	0.1612-	9.5	0.905	
	333	2.91	0.62	0.2076-	91.6	0.916	
Tn_{90}	303	3.3	0.74	0.1308-	90	0.9	182
	313	3.19	0.69	0.1612-	91.5	0.915	
	323	3.09	0.59	0.2291-	93	0.93	

	333	2.91	0.41	0.3872-	94.2	0.942	

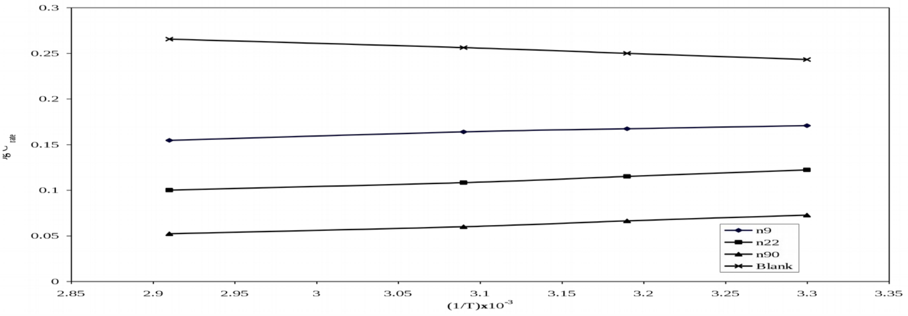

Figure 8: Rrelation between log R_{corr} against 1/T at different temperature in presence and absence of 200 ppm of Tn_9, Tn_{22} and Tn_{90}.

Thermodynamic Functions of adsorption

The free energy of adsorption (ΔG_{ads}*) at different temperatures was calculated from the following equation:

$$\Delta G_{ads}^{*} = RT\,(\log R_{corr} - \log KT/h) \qquad (6)$$

K, is equilibrium constant, which given by

$$K = \theta / C_i\,(1- \theta) \qquad (7)$$

The values of E_a* and ΔG_{ads}* were listed in Table (3). The negative values of ΔG_{ads}* indicate that the spontaneous adsorption of inhibitors on the surface of carbon steel. The negative values of ΔG_{ads}* also suggest the strong interaction of the inhibitor molecules onto the steel surface **[25].** The thermodynamic functions of inhibitors adsorption, entropy, ΔS_{ads}*, enthalpy, ΔH_{ads}* and free energy, ΔG_{ads}* are calculated from the equations:

$$\Delta H_{ads}^{*} = Ea^{*} + RT \qquad (8)$$

Where, R is the universal gas constant. Entropy of inhibitor adsorption (ΔS_{ads}*) can be calculated using the following equation:

$$\Delta S_{ads}^{*} = (\Delta H_{ads}^{*} - \Delta G_{ads}^{*})/T \qquad (9)$$

The calculated ΔS_{ads}* data were listed in Table (3**).** All obtained data show that ΔS_{ads} values are positive and increased by increasing temperature which indicate that the inhibitors more oriented and more ordered on the surface of the metal. Table (3) showed being that ΔH_{ads}* has negative values, indicating that, the reaction is exothermic. On the other hand, the negative value of ΔH_{ads} indicated that the adsorption of inhibitors is a chemical one and the surfactant forms stable layer at the surface of steel. This behavior protects steel form the environmental conditions (AcOH) and decreased the corrosion rate.

The chemical adsorption can be explained on the basis of the effect of chemical structure of inhibitor on its inhibition efficiency. In this respect, the benzene ring and the C=O group of the used oligomers can form a big π bond. Accordingly, not only the π electron of the benzene and carbonyl enter unoccupied orbital of iron, but also the π*orbital can accept the electrons of d orbital of iron to form feed back bonds, which produce more than one center of chemical adsorption on the steel surfaces [**14,22**]. On the other hand, the presence of the electron donating groups in the structure of the used inhibitors such as (CH_2 –CH_2), increases the electron density on the nitrogen of the NH group and increases inhibition efficiency by increasing the chain length of the inhibitor. At low inhibitor concentrations, the corrosion of steel was inhibited due to the adsorption of surfactant molecules on the surface by the hydrophilic head groups. The hydrophobic chain may be oriented towards the aqueous medium and may also be arranged horizontally to the steel surface **[14, 23].**

Table 3. Thermodynamic activation parameters of adsorption for C-steel in 1 M AcOH in absence and presence of 200 ppm of the inhibitors at different temperatures.

Compound	Temp., °K	E*	-ΔG*, k.J.mol^{-1}	ΔH*, k.J.mol	ΔS, k.J.mol.k^{-1}
Blank	303	94	36.14	26.2	0.178
	313		37.21	26.8	0.186
	323		40.1	27.3	0.196
	333		42.2	28.1	0.198
Tn_9	303	154	56.6	29.3	0.142
	313		59.8	29.9	0.148
	323		62.7	31.1	0.152
	333		64.9	32.8	0.159
Tn_{22}	303	163	65.8	32.9	0.149
	313		68.1	34.2	0.153
	323		69.8	34.8	0.159
	333		72.3	35.6	0.163
Tn_{90}	303	182	73.2	35.8	0.172
	313		74.5	36.9	0.173
	323		75.4	37.6	0.179
	333		76.8	38.2	0.186

Conclusions:

Based on the obtained results, the following conclusions are drawn: -

1- All studied oligomers are excellent inhibitors and act as a mixed type inhibitors for carbon steel corrosion in acetic acid solution.

2- Inhibition efficiencies increased by increasing inhibitor concentration and by increasing temperatures up to 333 K.

3- All entropy parameters for adsorption of inhibitors molecules on steel are positive and increase by increasing the temperature which indicates that the inhibitors being more oriented and more ordered on the surface of the metal.

4- The activation parameters of the adsorption (E*****, ΔH***** and ΔS*****) were calculated and showed that the used inhibitors decrease the rate of corrosion.

5- The adsorption of these inhibitors on steel surface obeys Langmuir's adsorption isotherm.

6- The increase in the ethylene oxide unites in the molecular structure leads to more inhibition efficiency.

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