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REDA ABDEL HAMEED
Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt., mredars2@yahoo.com

H. ISMAIL
Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt.

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CORROSION OF CARBON-STEEL ALLOY IN 0.1M NITRIC ACID IN PRESENCE OF PLASTIC WASTE AS CORROSION INHIBITORS

REDA-ABDEL HAMEED A.S., *H. AL SHAFEY ISMAIL, S.A. SOLIMAN AND M. S. METWALLY

Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt.
** Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt.*

Abstract

Recyclization of poly (ethyleneterphthalate), (PET), with Diethanolamine and Triethanolamine having 1:2 wt% of PET: wt% of DEA or wt% TEA, in presence of manganese acetate as a catalyst.

The inhibition action of the prepared compounds (D_2 & T_2) on the corrosion of carbon-steel which used in the manufacture of petroleum pipelines in nitric acid was evaluated, at different concentrations of inhibitors from (50-250 ppm) at different temperatures, ranged from (303-333 K).

The polarization curves indicate that these compounds may act as mixed-type inhibitors.

The adsorption of the prepared compounds on C-steel was found to follow the Langmuir adsorption isotherm,they also obey El-Awady isotherm.

The values of activation energies (E_a*) and all thermodynamic activation parameters which determined, indicating that the type of adsorption was chemical adsorption.

Key words: Recycling, Nitric acid, Corrosion, Inhibitor, Carbon Steel.

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, protons, 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].

Inhibition of C-steel corrosion in aqueous solutions occurred by organic [5-8] and inorganic [9] compounds as well as synergetic inhibitors was studied [10-12]. The inhibition of steel corrosion in acidic solutions was studied in considerable detail [13]. In the previous works [14, 15], PET plastic waste was used as a cheap and safe corrosion inhibitors for C-steel in both hydrochloric acid (1M HCL) and sulfuric corrosive media [27].

The present work is the 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, Diethanolamine and Triethanolamine (DEA and TEA) were used to convent PET waste to water soluble oligomers, and evaluation of the prepared materials (oligomers) as corrosion inhibitors for C-steel in 0.1 M nitric acid at different temperatures.

Experimental

PET waste was collected from beverage bottles. Diethanolamine (DEA) and 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 products (D_2 and T_2). The reaction of PET with DEA and TEA was discussed in previous articles [16, 17]. The aggressive 0.1M HNO_3 solution was prepared by dilution of analytical grade HNO_3 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 ^{o}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^{o}K. Electrochemical experiments were recorded using of a radiometer analytical, voltamaster (PGZ301, DYNAMIC ELS VOLTAMMETRY).

Results and Discussions

The two glycolyzed products, signified as D_2 and T_2, were obtained from depolymerization of PET with DEA and TEA respectively, using 1:2 (wt% of PET to either DEA or TEA).

All depolymerization reactions of PET were carried out in nitrogen atmosphere and in presence of 0.5% manganese acetate as a catalyst. The glycolysis consists of trans-etherification of PET and the depolymerization of PET polymer chain to lower molecular weight oligomers. The temperatures of glycolysis reaction of PET with either DEA or TEA must be fixed at 210 ^{o}C throughout the reaction to prevent the formation of alicyclic derivatives between hydroxyl groups of the produced poly-hydroxy glycolyzed PET [16, 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 DEA and 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 0.1 M HNO_3 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 0.1 M HNO_3 with and without various concentrations (50-300 ppm) of inhibitors were represented in Figures (1, 2). The curves were swept from –0.75 to 0.30 V (SCE) with scan rate of 20 mVs^{-1}. Figures (1,2) illustrate the effect of adding progressive addition (50 – 300 ppm) of selected inhibitors on the cathodic and anodic polarization curves of carbon steel alloy (X_{46}) in 0.1M HNO_3 at 30^{o}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 D_2 and T_2 products inhibit HNO_3 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].

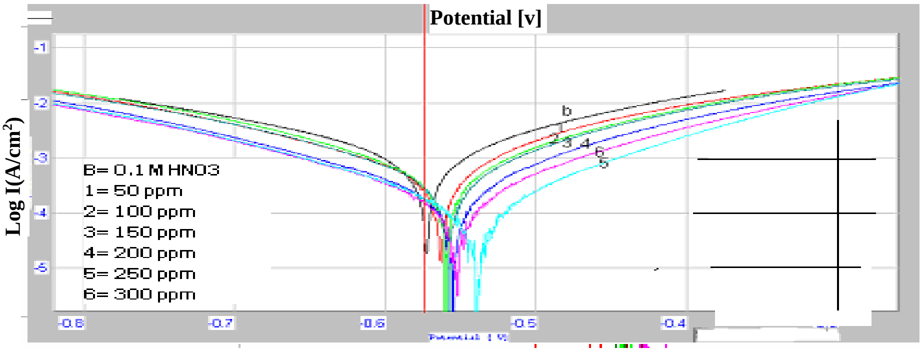

Figure 1: Potentiodynamic polarization curves of C-steel in 0.1 M HNO_3 in absence and presence of diffirent concentrations of inhibitorT_2 at 303 K

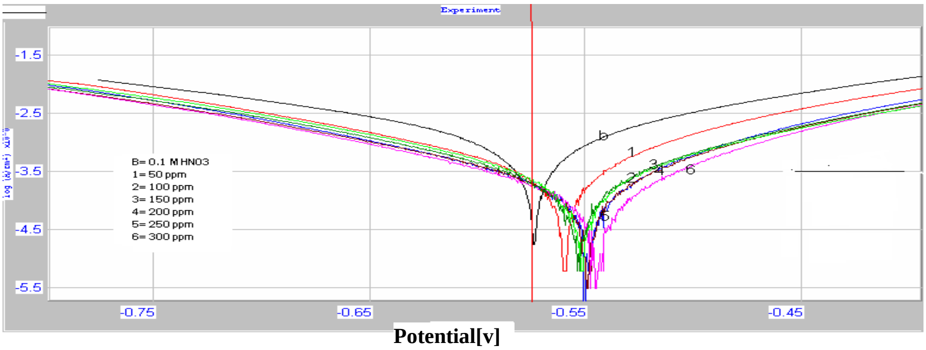

Figure 2: Potentiodynamic polarization curves of C-steel in 0.1 M HNO_3 in absence and presence of diffirent concentrations of inhibitor D_2 at 303 K

The corrosion potential (E_{corr}), the corrosion current density (I_{corr}) were determined from extra-pollation of cathode 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 (P%) 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 two prepared inhibitors to HNO_3 solution decreases the values of I_{corr} and increases the values of R_p for carbon steel alloy. The inhibition efficiency P% of inhibitors was calculated from polarization measurements by using the following equation:

$$P\% = 1 - (I_{inh} / I_{uninh}) \times 100 \quad (1)$$

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.

$$R_p = (b_a \times b_c) / (2.303\, i_{corr}\, (b_a + b_c)) \quad (2)$$

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.

Adsorption Isotherms

The relation between the calculated efficiency and concentrations of the selected surfactants were represented in Figure (3). S-shaped adsorption mode, indicated from Figure (3), proved that the mechanism of inhibition involves the formation of monolayer at the metal-solution interface.

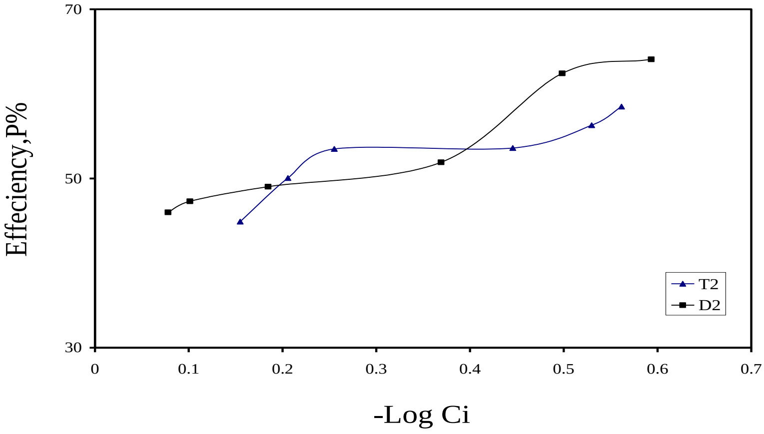

Figure 3: S-curve for the prepared inhibitors.

Table 1: Polarization data of the prepared inhibitors.

Sample	**Conc., ppm**	**$I_{corr.}$, mA/cm2**	**-$E_{corr.}$, mV**	**Rp, ohm.cm^{-2}**	**b_a, mV/decade**	**-b_c, mV/decade**	**P%**	**θ**	**C_i x10^4, mol/L**
Blank	0	0.925	41.38	19.84	126.65	148.54	0	0	0
T2	50	0.316	386.24	62.72	105.68	128.96	47.68	0.4768	0.7
	100	0.272	380.66	61.13	99.79	123.91	50.06	0.5006	0.9
	150	0.236	376.48	43.81	96.91	130.83	53.496	0.53496	1.8
	200	0.243	379.15	46.29	87.77	119.52	53.604	0.53604	2.79
	250	0.301	371.16	39.60	95.68	132.41	56.30	0.5630	3.69
	300	0.288	368.96	38.80	90.08	126.56	58.50	0.5850	3.97
D2	50	0.337	370.08	30.88	106.88	172.96	45.92	0.45.92	0.68
	100	0.316	365,33	35.88	102.74	169.04	47.31	0.473	0.792
	150	0.295	356.47	37.84	99.72	166.61	49.03	0.4903	1.53
	200	0.255	354.31	48.54	94.10	155.52	51.91	0.5191	2.34
	250	0.122	382.46	68.76	97.28	120.96	62.42	0.6242	3.15
	300	0.121	350,56	54.64	95.37	119.44	64.08	0.6408	3.92

The shape of isotherm seems to reflect two modes of adsorption. At very low concentration, the polymer is adsorbed either at the vertical mode or the all active sites on the surface are not fully occupied. The plateau form may be explained by the formation of a monolayer of polymer. Further increase of inhibitor concentration leads to the formation of multilayer generally at horizontal mode. The presence of amide and ester groups reinforces the adsorption phenomenon by inducing the anodic action. 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 Potentiostatic 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 the inhibitors also 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 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 $C_i/\ \theta$ against C_i illustrated in Figure (4).

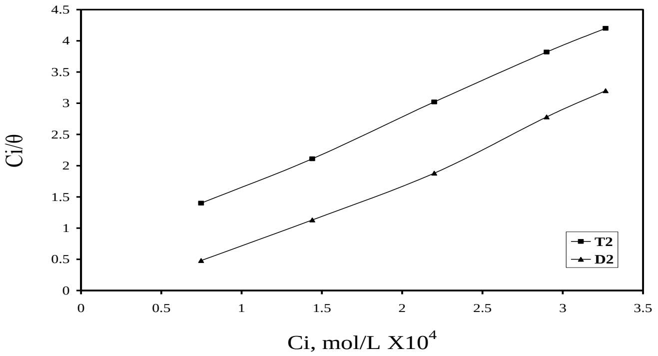

Figure 4: Langmuir adsorption isotherm for T_2 and D_2 Inhibitors

El-Awady isotherm: El-Awady equation was modified to the following one [27]

$$\text{Log } \theta /1- \theta = \quad x\log K +1/x \log Ci \qquad (5)$$

Where K is the equilibrium binding constant, and " x" = number of sites on the metal surface which can be occupied by one molecule of the inhibitor the slop near unity indicating a strong adsorption of inhibitor molecule on the metal surface .Straight lines of plotting θ /1- θ against log Ci as shown in Figure (5), indicate the validity of modified El – Awady isotherm.

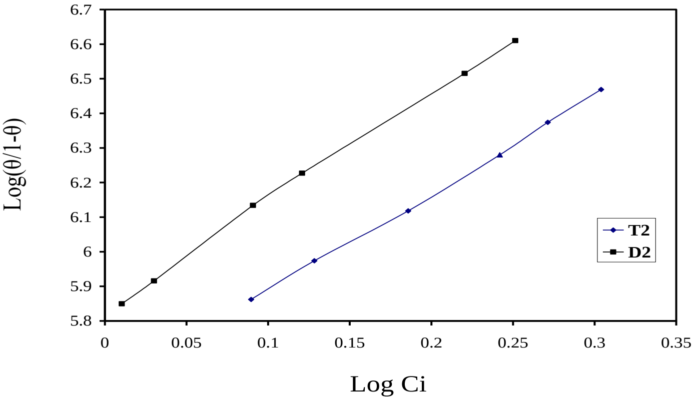

Figure 5: El – Awady isotherm.

Weight Loss Measurements:

Effect of Temperature:

Effect of temperatures on the corrosion behavior of carbon steel in 0.1 M nitric 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 (6, 7) indicated that the weight losses of carbon steel in 0.1 M HNO_3 increase with increase with immersion time. The results of carbon steel inhibition efficiency of 250 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].

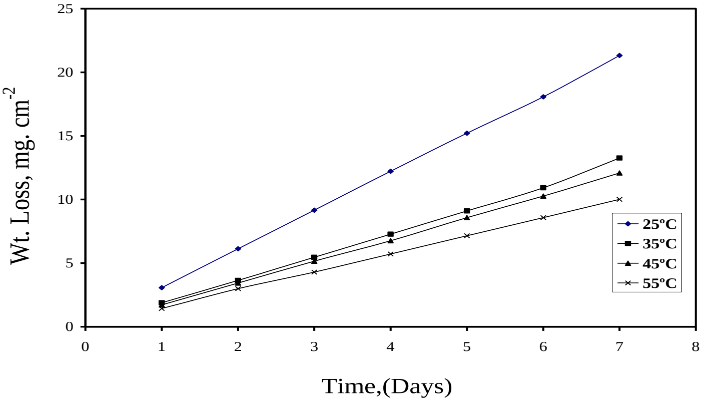

Figure 6: Weight loss-time curves of C-steel alloy in 0.1 M HNO_3 in the presence of 250 ppm of inhibitor T_2 at different temperatures

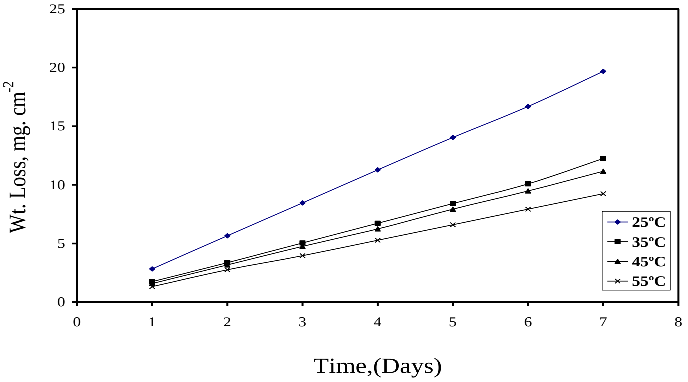

Figure 7: Weight loss-time curves of C-steel alloy in 0.1 M HNO_3 in the presence of 250 ppm of inhibitor D_2 at different temperatures.

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].

$$\text{Log } k_{rate} = \log A - Ea/2.303RT \qquad (6)$$

A is pre-exponentional factor related to concentration, steric effect and metal surface characteristics, etc. Plotting of log K_{rate} against 1/T for the free acid solution (blank) and 250 ppm of the D_2 and T_2 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 (P %) of the inhibitors T_2 and D_2 in 0.1M HNO_3 at different temperatures calculated from weight loss data.

Compound	T, ºK	(1/T)x10^{-3}	K_{rate}, mg.cm^2.day^{-1}	Log K_{rate}	P%	θ	E *$_{active}$, k.J.mol^{-1}
T_2	303	3.30	0.544	-0.1339	56.96	0.5696	103.12
	313	3.19	0.488	-0.1717	59.04	0.5904	
	323	3.18	0.411	-0.2014	63.84	0.6384	
	333	3.01	0.392	-02478	66.08	0.6608	
D_2	303	3.30	0.384	-0.255	60.56	0.6056	105.28
	313	3.19	0.328	-0.3097	63.68	0.6368	
	323	3.18	0.304	-0.3316	65.92	0.6592	
	333	3.01	0.248	-0.4069	68.48	0.6848	

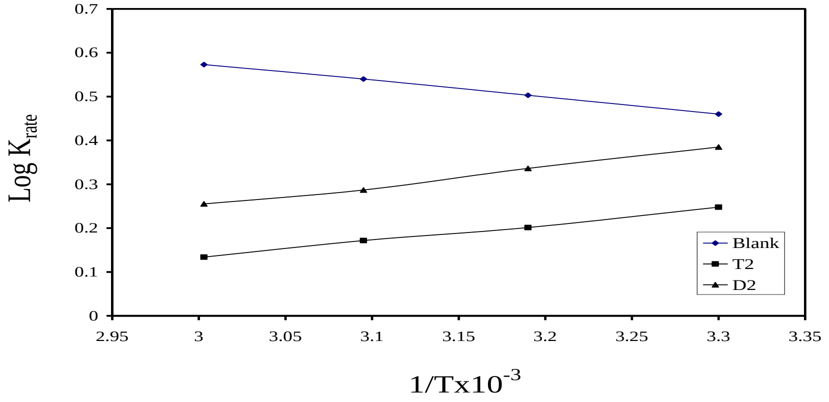

Figure 8: relation between log k_{rate} against 1/T at different temperature in presence and absence of 250 ppm of D_2 and T_2.

Thermodynamic Functions of adsorption

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

$$\Delta G_{ads}{*}=RT\ (\log k_{rate} - \log KT/h) \tag{7}$$

K, is equilibrium constant, which given by

$$K = \theta / Ci\ (1- \theta) \tag{8}$$

The values of E_a and ΔG_{ads}* were listed in Table (3). The negative values of ΔG_{ads}* indicate that the adsorption of these inhibitors on the metal surface taks place spontaneously .that the spontaneous . The high negative values of ΔG_{ads}* also suggest strong interaction of the inhibitor molecules onto the steel surface [25]. The thermodynamic functions of inhibitors adsorption, entropy ΔS_{ads}*and enthalpy, ΔH_{ads}* were calculated from the equations[26,27]:

$$\Delta H_{ads}{*} = Ea + RT \tag{9}$$

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

$$\Delta S_{ads}{*}= (\Delta H_{ads}{*}-\Delta G_{ads}{*})/T \tag{10}$$

The calculated ΔS_{ads}* data are 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 that ΔH_{ads}* has negative values, indicating that, the adsorrption is exothermic. On the other hand, the high negative value of ΔH_{ads} indicate that the adsorption of inhibitors is a chemical one and the surfactant forms stable layer at the surface of steel. This adsorbed layer protects steel form the environmental conditions (HNO_3) 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 D_2 or T_2 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 DEA or TEA such as (CH_2 –CH_2), increases the electron density on the nitrogen of the NH group and increases inhibition efficiency. On the other hand, the corrosion inhibition efficiency of the prepared oligomer of D_2 is greater than T_2 at lower surfactant concentrations, 100-200 ppm, as listed in Table (1). This can be attributed to the presence of trisubstituted ethylene group attached to nitrogen group of TEA which decreases the basicity of amine groups of T_2 due to steric effect [14].

Consequently, the nitrogen groups of T_2 cannot easily interacts with steel and the inhibition efficiency data show that, 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 0.1 M HNO_3 in absence and presence of 250 ppm of the inhibitors at different temperatures.

Compound	Temp., °K	E*	$-\Delta G^*$, $k.J.mol^{-1}$	$-\Delta H^*$, $k.J.mol^{-1}$	ΔS, $k.J.mol^{-1}.k^{-1}$
Blank	303	56.18	31.232	16.88	0.1496
	313		31.256	17.20	0.1568
	323		32.08	17.68	0.1552
	333		33.44	18.24	0.1536
T_2	303	103.12	44.48	18.72	0.104
	313		46.96	19.68	0.106
	323		49.28	20.16	0.107
	333		51.12	21.44	0.109
D_2	303	105.28	51.36	18.24	0.112
	313		57.84	19.36	0.120
	323		59.04	21.04	0.123
	333		60.16	22.08	0.131

Conclusions:

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

1- All studied oligomers are excellent inhibitors and act as a mixed type inhibitors for carbon steel corrosion in nitric 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***, ΔG_{ads}^* 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 and El-Awady adsorption isotherm.
6- The corrosion inhibition efficiency of the prepared oligomer of D_2 is greater than T_2. These results are comparable with those obtained from weight loss measurements.

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