Poly (Oxyethylene)Terphthylamine As Corrosion Inhibitors For Carbon Steel In Methanoic Acid.

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ABSTRACT
Ethoxylation of poly(ethyleneterphthaliamine) derived from Plastic waste by different ethyleneoxide units, namely 22, 90, 1094, 1103. In this respect polyethylene terphthalate waste depolymerized with diethanolamine to gives the corresponding amine, etherification of the produced hydroxyle amine with different molecular weight of polyethylene glycol, (PEG1000, PEG4000) to gives the corresponding poly(oxyethylene) terphthalalime which were separated, identified and evaluted as corrosion inhibitors for Carbon steel in 1 M methanoic acid, the corrosion inhibition efficiency were determined at different concentrations of the used inhibitors by chemical techniquest (weight loss) and electrochemical techniques (potentiodynamic Polarization and open circuits potential). The corrosion inhibition efficiency depends on the inhibitor concentration and type. The protection efficiency increase with increasing the concentration and the number of ethylene oxide units in order of (Dn12 and Dn90). The inhibition was assumed to occur via the adsorption of the inhibitors on the metal surface. And obey Langmuir adsorption isotherm. The polarization curves indicate that these compounds at as mixed-type inhibitors, addition of inhibitors molecules to the corrosive medium produces a negative shift in the open circuit potential. Effects of temperatures on the inhibition efficiency were studied, thermodynamic parameters were computed and discussed, the data obtained from different techniques are in good agreement.

Key words: corrosion inhibitor, ethoxylation, recycling of plastic waste, methanoic acid, polarization, open circuit.

I. INTRODUCTION

The disposal of a large number of Poly (ethylene terphthalate), PET bottles caused serious environmental problem. There are various methods used to recycle PET bottles [1-3]. Carbon steel is frequently used in manufacturer of the pipelines due to the aggressiveness of the liquids which carried by them. These liquids may be petroleum containing water and corrosive ions. All kind 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. Steel is used in fabrication of reaction vessels, storage tanks, etc., by industries, which either manufacture or use formic acid as reactants.

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 undesireable rust in several industrial processes. Inhibitors are usually used in these processes to control the corrosion of metal [4].

Inhibition of C-steel corrosion in aqueous solutions by organic [5-7] and inorganic [8] compounds as well as synergetic inhibition [9-11]. The inhibition of steel corrosion in acidic solution was studied in considerable detail [35-39]. In the previous works [12-14], PET plastic waste was used as a cheap and safe corrosion inhibitors for C-steel in sodium chloride, hydrochloric acid, sulphuric acid, nitric acid and acetic acid corrosive media [28-34]. The present work is one from a series aimed to alleviate of environmental pollution by converting PET waste into useful products, and to evaluation the inhibitive action of plastic waste on the corrosion of some metals and alloys, in different aqueous medium. In this respect polyethylene terphthalate was subjected to depolymerization with diethanolamine (wt % 1:1) to give the corresponding amide which was ethoxalated with different molecular weight of poly ethylene glycol, PEG1000, PEG4000, both of them was evaluated as corrosion inhibitors for carbon steel in 1 M methanoic acid by weight loss, potentiodynamic polarization, and open circuit potential, the effect of concentration and temperature were studied, the thermodynamic parameters were calculated and discussed.

II. EXPERIMENTAL

2.1. Materials and Preparation
PET waste was collected from beverage bottles. Diethanolamine (DEA) were purchased from...
Aldrich Chemical Co., Ltd. (UK), was used for depolymerization of PET used in this work. PET waste is converted to glycolyzed product (the . The reaction of PET with DEA was discussed in previous articles [14, 15]. In the present work, Diethanolamine (DEA ) was used to convert PET waste to water soluble oligomers, followed by ethoxylation with polyethyleneglycol (PEG), which has different molecular weights 1000 and 4000 to give two different nonionic surfactants. The prepared materials (oligomers) used as corrosion inhibitors for steel in IN HCOOH at different temperatures.

2.2. 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 (X46) 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).

III. RESULTS AND DISCUSSIONS
The two different molecular weights of PEG, namely, PEG 1000 and 4000 gm/mol to produce the surfactants, which coded as D$_{n22}$ and D$_{n90}$. The numbers, 22 and 90 are referred to number of ethylene oxide groups in PEG [15].

3.1. Evaluation of the Prepared Surfactants as Corrosion Inhibitors:
The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [16]. The choice of the inhibitor is based on two considerations:
First: it could be synthesized conveniently from relatively cheap 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 [17]. In this respect, the present corrosion inhibitors were designed to prepare from recycled PET waste and introducing DEA in their chemical structure to increase their abilities to soluble in water and to use as corrosion inhibitors for C-steel. The corrosion of C-steel in 1N formic acid solution at different temperatures was studied by weight loss, open circuit potential and by potentiodynamic polarization techniques.

3.2. Weight Loss Measurements:
In the present work, two samples, D$_{n22}$ and D$_{n90}$, were applied as corrosion inhibitors for C-steel (X46). The 1M HCOOH was used as a blank solution for the weight loss measurements. For different concentrations from the prepared oligomers, 50, 100, 150, and 200 ppm are prepared by dilution the required volume of each compound. Weight loss (mg/ cm$^2$) of the surface area was determined in an open system at various time intervals. Weight loss of the steel sample versus time of immersion was plotted in Figures (1, 2). It is evident from these figures that in the blank, weight loss increases with increasing of the time of immersion. On the other hand, the figures obtained in the presence of additives fall significantly below that of free acid in all cases. In this respect, the increase of the additive concentration was accompanied by a decrease of weight loss and an increase of the percentage of inhibition [17].

Figure (1): Weight loss-time curves of C-steel alloy in 1 N HCOOH in absence and presence of different concentration of inhibitor D$_{n22}$ at 303 K.
The corrosion inhibition efficiency (IE %) was calculated by the following equation:

\[ \text{IE} \% = \left( \frac{\Delta w - \Delta w_i}{\Delta w} \right) \times 100 \]  

(1)

Where, \( \Delta w \) and \( \Delta w_i \) are the weight loss per unit area in absence and presence of the inhibitor respectively. \( \Delta w \) can be calculated from the following equation:

\[ \Delta w = w_b - w_a \]  

(2)

Where, \( w_b \) and \( w_a \) are the weight of the specimen before and after reaction, respectively. The obtained data of (IE %) and rate of corrosion (K) of the used surfactants were summarized and listed in Table (1).

The data in Table (1) show increase of the inhibition efficiency (IE %) with increasing number of ethylene oxide in the prepared inhibitors.

The data show that the K values were decreased with increase of inhibitors concentrations and increase with time. On the other hand, the inhibition efficiency was increased with increasing of inhibitors concentration. So that the inhibitors compounds may be chemically adsorbed on the steel surface and cover some sites of the electrode surface.

The chemical adsorption can be explained on the basis of the effect of chemical structure of inhibitors on its inhibition efficiency. In this respect, the benzene ring and the carbonyl group (C=O) of the used oligomers can form a big (\( \pi \)) bond accordingly, not only the (\( \pi \)) of benzene and carbonyl enter unoccupied orbital of iron, but also, the \( \pi^* \) orbital can accept the electron of d orbital of iron to form feed back bonds, which produce more than one center of chemical adsorption on the steel surfaces [18]. On the other hand, the presence of the electron donating groups in the structure of the used inhibitors such as (CH\textsubscript{2}-CH\textsubscript{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 [4, 19].

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

\[ \frac{C_i}{\Delta} = \left( \frac{1}{K_{ads}} \right) + C_i \]  

(3)

Where, \( C_i \) is the inhibitor concentration and \( K_{ads} \) is the adsorption equilibrium constant. The degree of surface coverage (\( \theta \)) for different concentration of the inhibitors in acidic media, [20] has been evaluated from weight loss measurements by using the following equation:

\[ \theta = 1 - \left( \frac{\Delta w_i}{\Delta w} \right) \]  

(4)

Careful inspection of these results showed also that, inhibition efficiency increases with increasement of both inhibitor concentration and surface coverage (\( \theta \)).
Table 1. Degree of surface coverage (θ) and percentage inhibition efficiency (IE %) of the inhibitors \( D_{n22} \) and \( D_{n90} \) in 1 N HCOOH at 303 K, obtained from weight loss measurements after 7 days.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Conc., ppm</th>
<th>Conc., M/Lx10(^4)</th>
<th>Wt. loss, mg.cm</th>
<th>Corrosion rate, (k), mg.cm(^2) day(^{-1})</th>
<th>□</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK</td>
<td>0</td>
<td>0</td>
<td>55.8</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( D_{n22} )</td>
<td>50</td>
<td>0.37</td>
<td>9.8</td>
<td>1.4</td>
<td>0.82</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.9</td>
<td>8.8</td>
<td>1.25</td>
<td>0.84</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.5</td>
<td>7.6</td>
<td>1.1</td>
<td>0.86</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.8</td>
<td>6.2</td>
<td>0.88</td>
<td>0.88</td>
<td>88</td>
</tr>
<tr>
<td>( D_{n90} )</td>
<td>50</td>
<td>0.34</td>
<td>8.9</td>
<td>1.27</td>
<td>0.84</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.7</td>
<td>7.6</td>
<td>1.08</td>
<td>0.86</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.1</td>
<td>6.8</td>
<td>0.96</td>
<td>0.88</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.4</td>
<td>5.2</td>
<td>0.74</td>
<td>0.905</td>
<td>90.5</td>
</tr>
</tbody>
</table>

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 [21]. The results of dissolution of carbon steel in 1 N HCOOH in presence of inhibitors might to interpret on the basis of interface inhibition mode. The inhibitors are acting effectively at the metal solution interface accordingly the small concentration of inhibitors exhibits an effective corrosion inhibition, this may be due to the formation of adsorbed monolayer at the metal surface interface. The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm and the relation of \( \frac{C_i}{\theta} \) against \( C_i \) illustrated in Figure [4].

Influence of temperature on the corrosion behavior of carbon steel in 1N formic acid was studied by the weight loss method over temperature range (303 – 333 K). The data display that the rate of corrosion decreases with an increase in temperature from 303 to 333 K as represented in Table (2). The data in Table (2) show that the inhibition efficiency (IE) increases with increasing temperature and with increasing number of ethylene oxide in the prepared inhibitors.

Also, the Figures (4, 5) indicate that the weight losses of carbon steel in 1N formic acid increase with increase temperature in case of blank. 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 increase temperature from 303 – 333K which indicate chemical adsorption [22].

![Figure 3: Langmuir adsorption isotherm for \( D_{n22} \) and \( D_{n90} \) inhibitors](image-url)
3.4. Activation Energy of corrosion:

Corrosion is an electrochemical phenomenon and 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 of the 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, absorbed hydrogen atoms (exothermic process) blocked the cathodic area.

The activation energy ($E_a$) can be calculated from Arrhenius equation, which appear as the following [23].

$$\log W = \log A - \frac{E_a}{2.303RT} \quad (5)$$

Where, $A$ is pre-exponentional factor related to concentration, steric effect and metal surface characteristics, etc. Plotting of $\log W$ against $1/T$ for the free acid solution (blank) and 200 ppm of the used inhibitor was represented in Figure (6). The apparent activation energy and pre-exponential factor can be calculated according to the slope and intercept of the regression, respectively. The activation energies were calculated and listed in Table (2). The results showed that, the values of activation energy ($E_a$) 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 inhibitors D$_{n22}$ and D$_{n90}$ in 1N HCOOH at different temperatures

<table>
<thead>
<tr>
<th>Compound</th>
<th>T, °K</th>
<th>(1/T)x10$^{-3}$</th>
<th>$K_{rate}$ mg.cm$^{-2}$.day$^{-1}$</th>
<th>Log $K_{rate}$</th>
<th>IE%</th>
<th>□</th>
<th>$E_{active}$ k.J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_{n22}$</td>
<td>303</td>
<td>3.3</td>
<td>0.7744</td>
<td>-0.04886</td>
<td>77.44</td>
<td>0.7744</td>
<td>143.44</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.19</td>
<td>0.6952</td>
<td>-0.09009</td>
<td>78.32</td>
<td>0.7832</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>3.09</td>
<td>0.6072</td>
<td>-0.14181</td>
<td>83.6</td>
<td>0.7964</td>
<td></td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>2.91</td>
<td>0.5456</td>
<td>-0.1827</td>
<td>80.608</td>
<td>0.80608</td>
<td></td>
</tr>
<tr>
<td>D$_{n90}$</td>
<td>303</td>
<td>3.3</td>
<td>0.6512</td>
<td>-0.11508</td>
<td>79.2</td>
<td>0.792</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.19</td>
<td>0.6072</td>
<td>-0.14181</td>
<td>80.52</td>
<td>0.8052</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>3.09</td>
<td>0.5192</td>
<td>-0.20165</td>
<td>81.84</td>
<td>0.8184</td>
<td></td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>2.91</td>
<td>0.3608</td>
<td>-0.34075</td>
<td>82.896</td>
<td>0.82896</td>
<td></td>
</tr>
</tbody>
</table>

Figure (6): Relation between log $k_{rate}$ against 1/T at different temperatures in presence and absence of 200 ppm of D$_{n22}$ and D$_{n90}$ inhibitors.

3.4. Thermodynamic Functions of Activation:

The free energy of adsorption ($\Delta G^*$) at different temperature was calculated from the following equation:

$$\Delta G^* = RT (\log W - \log KT/h) \tag{6}$$

Where, $K$ is equilibrium constant, which given by equation

$$K = \frac{\Box}{Ci (1 - \Box)} \tag{7}$$

The values of $E_{active}$ and $\Delta G^*$ were listed in Table (3). The negative values of $\Delta G^*$ indicate that the spontaneous adsorption of inhibitors on the surface of carbon steel and strong interaction of the inhibitor molecules onto the steel surface [25].

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp., °K</th>
<th>$E^*$</th>
<th>$-\Delta G^*$, k.J.mol$^{-1}$</th>
<th>$H^*$, k.J.mol$^{-1}$</th>
<th>$S$, k.J.mol.k$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>303</td>
<td>82.72</td>
<td>31.8032</td>
<td>23.056</td>
<td>0.15664</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>32.7448</td>
<td>23.584</td>
<td>0.16368</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>33.1368</td>
<td>24.024</td>
<td>0.17244</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td></td>
<td>33.7368</td>
<td>24.724</td>
<td>0.18144</td>
</tr>
<tr>
<td>D$_{n22}$</td>
<td>303</td>
<td></td>
<td>57.9044</td>
<td>28.952</td>
<td>0.13112</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>59.9288</td>
<td>30.096</td>
<td>0.13464</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>61.4248</td>
<td>30.624</td>
<td>0.13992</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td></td>
<td>63.6248</td>
<td>31.328</td>
<td>0.14344</td>
</tr>
<tr>
<td>D$_{n90}$</td>
<td>303</td>
<td></td>
<td>143.44</td>
<td>28.952</td>
<td>0.13112</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>160.16</td>
<td>30.096</td>
<td>0.13464</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>161.84</td>
<td>30.624</td>
<td>0.13992</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td></td>
<td>163.58</td>
<td>31.328</td>
<td>0.14344</td>
</tr>
</tbody>
</table>
The thermodynamic functions, entropy of activation, $\Delta S^*$, enthalpy of activation, $\Delta H^*$ and free energy of activation, $\Delta G^*$ is calculated from the equation:

$$\Delta H^* = E_a^* + RT$$ (8)

Where, $R$ is the universal gas constant. Entropy of inhibitor adsorption ($\Delta S^*$) can be calculated using the following equation:

$$\Delta S^* = \frac{(\Delta H^* - \Delta G^*)}{T}$$ (9)

The data were listed in Table (3), show that $\Delta S^*$ values are positive and increased by increasing temperature which indicate that the inhibitors more oriented and more disordered on the surface of the metal and the data of $\Delta H^*$ has negative values, indicating that, the reaction is exothermic. On the other hand, the negative value of $\Delta H$ indicated that the adsorption of inhibitors is a chemical one and the surfactant forms stable layer at the surface of steel. This behavior protects surface of steel from the environmental conditions (HCOOH) and decreased the corrosion rate. On the other hand, the data in Table (3) show that the $E_a$ increases with increasing number of ethylene oxide in the prepared inhibitors from n22 to n90.

3.5. Potentiodynamic Polarization Measurements:

Anodic and cathodic polarization curves for Carbon steel in 1 M HCOOH with and without various concentrations of used inhibitors were represented in Figures (7 and 8). The curves were swept from -800 to 0.25 V (SCE) with scan rate of 5 mVs$^{-1}$. Figures (7 and 8) illustrate the effect of adding progressive addition (50 – 200 ppm) of selected inhibitors on the cathodic and anodic polarization curves of carbon steel alloy in 1 M HCOOH at 30°C. The addition of the used inhibitors decreases the corrosion current densities ($I_{corr}$) and shifts the corrosion potential ($E_{corr}$) towards more positive values. 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 [26]. 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 [26]. The cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is controlled [20]. The addition of inhibitors under study 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 indicate that $D_{n22}$ and $D_{n90}$ products inhibit HCOOH 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 [20].

The corrosion potential ($E_{corr}$), the corrosion current density ($I_{corr}$) were determined from extrapolation of cathodic and anodic Tafel lines. The values of $E_{corr}$, $I_{corr}$, $R_p$, Tafel slopes ($b_c$, $b_a$), degree of surface coverage ($\theta$) and inhibition efficiency (IE %) were calculated for each sample and listed in Table (4). It is clear that the values of corrosion potentials $E_{corr}$ remain almost unchanged and indicate that the prepared surfactants acts mainly as mixed type inhibitors [22]. Addition of all prepared inhibitors to HCOOH solution decreases the values of $I_{corr}$ and increases the values of $R_p$ for carbon steel alloy.
Figure (7): Potentiodynamic polarization curves of C-steel in 1 N HCOOH in absence and presence of different concentration of inhibitor D$_{n22}$ at 303 K

Figure (8): Potentiodynamic polarization curves of C-steel in 1 N HCOOH in absence and presence of different concentration of inhibitor D$_{n90}$ at 303 K

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

$$\text{IE} \% = 1 - \left( \frac{I_{\text{corr}}}{I_{\text{corr}}} \right) \times 100$$ (10)

Where, $I_{\text{corr}}$ and $I_{\text{corr}}$ are the corrosion current densities in the absence and presence of inhibitor respectively. Also, the surface coverage $\theta$ was obtained from the relation:

$$\theta = 1 - \left( \frac{I_{\text{corr}}}{I_{\text{corr}}} \right)$$ (11)

The inhibition efficiency calculated from the polarization measurements and listed in Table (4). It is obvious that the inhibition efficiency increases with increase of the concentration of inhibitors. These results are comparable with those obtained from weight loss measurements. However there is difference in the values obtained by the two methods. This difference was also mentioned by several investigators [21].

The relation between the measured efficiency and concentrations of the selected surfactants was represented in figure (9). S-shaped adsorption mode, indicated from figure (9), which proved that the mechanism of inhibition involves the formation of monolayer at the metal-solution interface. 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 all active sites on the surface are not partially 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 amine and ester groups reinforces the adsorption phenomenon by inducing the anodic action.

Table 4. Polarization data of the prepared inhibitors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc., ppm</th>
<th>$I_{\text{corr}}$, mA/cm$^2$</th>
<th>-$E_{\text{corr}}$, mV</th>
<th>$R_b$, ohm.cm$^2$</th>
<th>$b_a$, mV</th>
<th>$-b_c$, mV</th>
<th>IE %</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>1.9485</td>
<td>55.656</td>
<td>34.038</td>
<td>168.2</td>
<td>203.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n$_{22}$</td>
<td>50</td>
<td>0.3339</td>
<td>443.88</td>
<td>80.55</td>
<td>116.6</td>
<td>152.2</td>
<td>75.2</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.3258</td>
<td>441.27</td>
<td>92.88</td>
<td>106.2</td>
<td>156.8</td>
<td>76.8</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.3807</td>
<td>434.25</td>
<td>122.67</td>
<td>108.1</td>
<td>129.9</td>
<td>79.4</td>
<td>0.79</td>
</tr>
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3.6. Open Circuit Potential Measurements:
The potential of carbon steel electrode immersed in 1 M Formic acid solution was measured as a function of immersion time in the absence and presence of 200 ppm of both Dn22 and Dn90, as shown in figure (10) it is clear that the potential of steel electrode immersed in 1 M HCOOH solution (blank) tend towards more negative potential firstly, giving rise to short step. This behavior was reported by other investigators [27], which represents the breakdown of the pre-immersion air formed oxide film presents on the surface, followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established. Addition of inhibitors molecules to the corrosive medium produces a negative shift in the open circuit potential due to the retardation of the cathodic reaction. The results of final steady state potential (Es) without inhibitor is -580 mV (vs. SCE) while that using the best dose (200 ppm) of the used inhibitors are -453 and -442 mV (vs. SCE) in case of Dn22 and Dn90 respectively.

IV. Conclusions
Based on the previous results, the following conclusions are accomplished:

1- All studied oligomers derived from waste are excellent inhibitors and act as the mixed type
inhibitors for Carbon steel corrosion in 1 M formic acid solution.

2- Inhibition efficiencies increase by an increase in inhibitor concentration and an increase in temperature up to 333 K.

3- The activation parameters of the dissolution (Ea, DH and DS) were calculated and showed that the used inhibitors decrease the rate of corrosion.

4- The adsorption of these inhibitors on steel surface obeys Langmuir’s adsorption isotherm.

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

2- The data obtained from different techniques are in good agreement.

References