

Corrosion Inhibition performance of polyethylene glycol/ polytriethanolamine inhibitors on corrosion of carbon steel in acidic medium

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Abstract: The inhibition effect of three nonionic inhibitors on carbon steel corrosion in 1M H₂SO₄ was studied gravimetrically and electrochemically. Increasing the number of triethanolamine units in the inhibitor molecules increases their inhibition efficiencies. The inhibiting action of inhibitors was attributed to their adsorption on the carbon steel surface and the formation of dense protective layer which increased by increasing their concentration. Polarization measurements showed that inhibitors act as mixed-type inhibitor in 1 M H₂SO₄ with a domain of anodic one, and their inhibition on carbon steel proceeded by physical adsorption. Increasing the surface activity of inhibitors increased their inhibition efficiency

Keywords: A. Carbon steel, B. Polarization, B. Weight loss, C. Acid inhibition

I. Introduction

The study of iron and iron alloys corrosion phenomena has become important particularly in acidic media because of the increased industrial applications of acid solutions. As an example, the refining of crude oil results in a variety of corrosive conditions. Refinery corrosion is generally caused by a strong acid attacking the equipment surface [1]. The other important fields of applications are acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes [2]. Among the acid solutions, mineral acids including H₂SO₄ and HCl are the most widely used acids. Due to the exposure of steel to corrosive environments, they are susceptible to different types of corrosion mechanisms. The use of corrosion inhibitors to prevent metal dissolution is therefore essential. Large numbers of organic compounds were studied to investigate their corrosion inhibition potential. For example, the effect of organic nitrogen compounds on the corrosion behaviour of iron and steel in acidic solutions is employed for their corrosion inhibiting action [3–10]. Recently, the application of surfactants as effective corrosion inhibitors has attracted the attention of many researchers. The adsorption of the surfactant molecules through their hydrophilic head changes the corrosion resistance property of the metal. The inhibitor efficiency depends on the metal type, inhibitor concentration [11–20], chemical structure of surfactant [14], pH [21], temperature [22, 23], type of acid [23], immersion time [11, 24] and the presence of co-surfactant [25–28]. Surfactants as organic inhibitors are unique due to their special chemical and surface properties [29–31]. Ionic and non-ionic surfactants have been reported as corrosion inhibitors for various groups of metals, such as copper, aluminium, and mild-steel [32–35]. Non-ionic surfactants in particular where the polar head group is without charge are known to have many applications through industry, including cosmetics, detergents, and also as corrosion-inhibitors. In addition to these valuable properties, they can be mixed with other types of surfactants, e.g., anionic or cationic, to enhance their properties, and reduce surfactant precipitation [36–39]. This class of surfactants has substantially lower critical micelle concentrations CMC, than the corresponding ionic surfactants. That enriches their applicability as corrosion inhibitors. Surfactants exert the inhibition action by adsorption on the metal surfaces such that chemical structure of the ionic head (hydrophilic part) attacks the metal surface while its tail (hydrophobic part) extends to the solution face. The influence of the chemical structure of ionic head on inhibition efficiency was extensively studied [14, 26, 27, 30, 40]. In this study, the corrosion inhibition performances of three nonionic environmentally friendly surfactants (labelled as P₈, P₁₀ and P₁₂) for carbon steel corrosion in 1M H₂SO₄ solutions were investigated by weight loss and electrochemical techniques. The aim of this work is to assess the inhibition effectiveness of P₈, P₁₀ and P₁₂ inhibitors on the carbon steel corrosion in 1 M H₂SO₄ solutions and to explore interaction mechanism between the inhibitor molecules and the carbon steel surface.

II. Experimental

Synthesis of inhibitors

Polytriethanolamine was prepared by condensation polymerization of triethanolamine in presence of NaOH as a catalyst at 245 °C for different time interval of 3, 4, and 6 hours to produce three polytriethanol

amine polymers containing eight, ten and twelve triethanolamine units in the polymeric chain. [41]. **Figure 1** represents the synthetic steps of the different polytriethanolamine polymers.

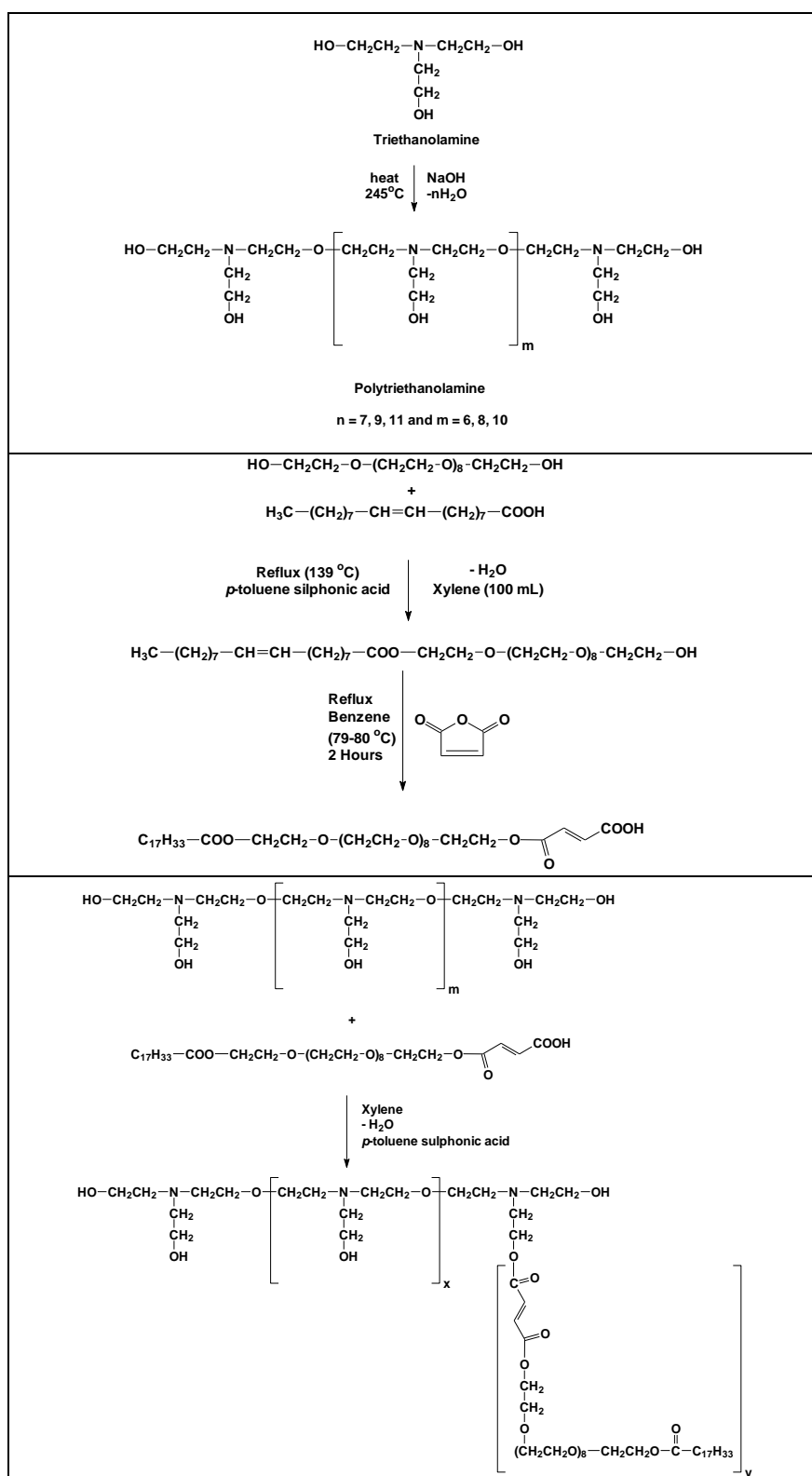


Figure 1: Synthesis of the inhibitors; P_8 : $x=6$, $y=2$; P_{10} : $x=8$, $y=3$; P_{12} : $x=10$, $y=4$.

0.21 mole of polyethylene glycol ($M_w = 400 \text{ g mol}^{-1}$) and 0.2 mole of oleic acid (28.2 g) were esterified individually under reflux conditions in the presence of 100 mL of xylene as a solvent and 0.1% by weight of p-toluene sulphonic acid as a dehydrating agent. The reaction was stopped when the theoretical amount of the water produced from the reaction (3.6 mL) was obtained. Then the solvent was removed under reduced pressure. The reaction product was dissolved in petroleum ether (250 mL) and then 100 mL of distilled water was added. The aqueous layer which contains the catalyst and the excess polyethylene glycol was separated by separating funnel and the ether layer was evaporated to obtain the polyethylene glycol/monooleate ester. Then, 0.2 mole of polyethylene glycol-monooleate was reacted by 0.2 mol of maleic anhydride in the presence of 150 mL of benzene as a solvent under continuous stirring. The reaction was followed by IR spectroscopy and was deemed complete at the point of disappearance of the anhydride linkage at 1850 cm^{-1} . The reaction product was dissolved in 200 mL (50:50 vol.) of ethyl acetate/diethyl ether mixture. The ethyl acetate layer contains the diester and the unreactants dissolved in diethyl ether layer. The lower layer was separated by separating funnel, and the solvent was evaporated under reduced pressure to obtain the desired ester.

Polymerized triethanolamine polymers were esterified individually by different molar amounts of polyethylene glycol-oleic-maleic anhydride ester in a sufficient amount of xylene and 0.1% by weight of p-toluene sulphonic acid under reflux condition until the theoretical amount of water was obtained. The product was washed with a hot supersaturated sodium chloride solution. Then the organic layer which contains the products was separated and the solvent was distilled off under vacuum [41]. The obtained inhibitors were designated as P₈, P₁₀, and P₁₂ as represented in **Figure 1**.

Weight loss method

Weight loss measurements were performed using carbon steel samples with a rectangular form with a total area of 37 cm^2 in 1 M H_2SO_4 solution in the presence and absence of P₈, P₁₀ and P₁₂ inhibitors at concentrations of 400, 200, 100, 50 and 25 ppm by weight. The inhibitors were completely soluble in the acidic medium with no precipitation or coagulation. Tests were performed on carbon steel of the following composition (wt.%): 0.11% C, 0.45% Mn, 0.04% P, 0.05% S, 0.25% Si and the remainder is Fe. Before the measurements, the carbon steel specimens were immersed in 1 M HCl solution for 10 s to remove the oxide layer on their surface (chemical method to remove rust products), then washes by distilled water and dried. Finally, they were abraded by 180, 400, 600, and 1200 grades of emery paper, degreased with acetone, and washed by distilled water two times and finally dried. After weighed accurately, each sample was suspended statically in the deaerated acid solution (500 mL) using glass hook and for different immersion time intervals of 1, 3, 6 and 24 h in thermostatically controlled temperature at $25 \text{ }^\circ\text{C}$. Then, the surface of each specimen was cleaned by double distilled water followed by rinsing in acetone, dried and weighed to calculate the loss in weight (w) of each specimen. For each experiment, a freshly prepared solution was used, and the solution temperature was thermostatically controlled. The aggressive solutions (1 M H_2SO_4) were prepared by diluting analytical grade of H_2SO_4 in double distilled water. The corrosion rate (C_r), surface coverage (θ) and inhibition efficiency (η %) were determined using equations 1-3 [42-45]:

$$C_r = \frac{w_o - w_i}{At} \quad (1)$$

$$\theta = \frac{w_o - w_i}{w_o} \quad (2)$$

$$\eta\% = \frac{w_o - w_i}{w_o} \times 100 \quad (3)$$

where, w_i and w_o are the weight loss values (mg) in presence and absence of inhibitor, respectively. A is the total area of the specimen in cm^2 and t is the immersion time in minutes.

Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were conducted using VoltaLab-PGZ-301 Potentiostat (France). A conventional cylindrical glass cell of 250 mL with three electrodes was used. A platinum sheet of 2 cm^2 area and saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The working electrode in form of disc cut from mild steel with an area of 0.8 cm^2 was embedded with epoxy except the working surface. Potentiodynamic polarization curves were obtained by changing the potential automatically from -400 to $+400$ mV versus open circuit potential (OCP) with a scan rate of 2 mV s^{-1} . The inhibition efficiency (η %) was calculated using equation 4 as follows [43]:

$$\eta\% = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \quad (4)$$

Where $i_{corr(uninh)}$ and $i_{corr(inh)}$ are the corrosion current density values without and with inhibitors.

III. Results and discussion

Open circuit potential (OCP)

Open circuit potential versus time profile of carbon steel in 1 M H₂SO₄ solution at 25 °C in the absence and in the presence of different concentrations of the tested inhibitors are shown (representatively for P₈) in **Figure 2**. More negative potential is an indication for higher corrosion rate in acidic medium in OCP studies [46]. It is clear that at the first stage of the measurements, the corrosion potential starts at high negative values depending on the inhibitor concentration. Then, the potential shifts to more positive values until reaches almost a constant value called the open circuit potential, OCP. The blank solution (solution with no inhibitors) has the most negative OCP value than the inhibited solutions. Furthermore, increasing the inhibitor concentrations shifts the OCP to more positive values. So, the presence of higher concentrations of the inhibitors increases the corrosion potentials of the carbon steel than the uninhibited medium.

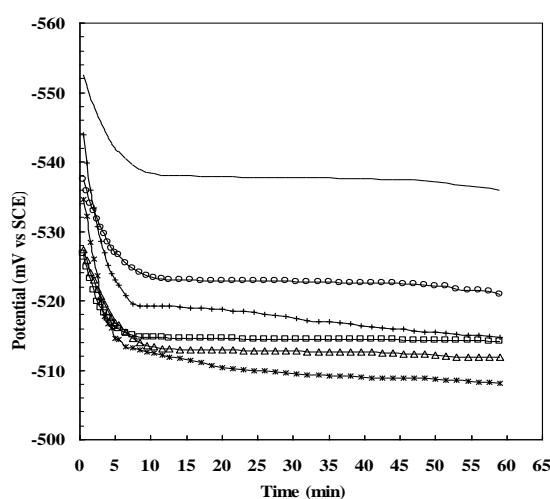


Figure 2: OCP vs. time of the carbon steel electrode immersed in 1 M H₂SO₄ solution in presence of different concentrations of P₈ inhibitor by weight (*: 400 ppm, Δ: 200 ppm, □: 100 ppm, +: 50 ppm, O: 25 ppm, —: blank) at 25 °C.

Potentiodynamic polarization

The effect of P₈, P₁₀ and P₁₂ inhibitors on the corrosion of carbon steel was studied electrochemically using potentiodynamic measurements. **Figure 3** shows typical polarization curves of carbon steel in 1 M H₂SO₄ solution in the absence and the presence of different concentrations of P₈ inhibitor as representative for the tested inhibitors (P₈, P₁₀ and P₁₂). It is apparent from the polarization profile that both anodic and cathodic corrosion reactions of carbon steel electrode were inhibited after the addition of the different inhibitors to the acidic solution. Furthermore, the inhibition becomes more noticeable by increasing the inhibitor concentration from 25 ppm to 400 ppm by weight. This behaviour indicates that the addition of the inhibitors lessens the anodic dissolution of iron and also retards the hydrogen ions reduction (hydrogen evolution) [47]. The cathodic current–potential curves (**Figure 3**) give rise to parallel lines indicating that the addition of P₈, P₁₀ and P₁₂ inhibitors to the 1 M H₂SO₄ solution do not modify the hydrogen evolution mechanism and the reduction of H⁺ ions at the carbon steel surface takes place mainly through a charge transfer mechanism [48-50]. The cathodic current densities decrease dramatically by increasing the inhibitors concentrations which reveals that the addition of P₈, P₁₀ and P₁₂ does not change the cathodic hydrogen evolution mechanism. In the initial stage of the anodic polarization, the corrosion current densities increased slowly and the anodic polarization was enhanced predominantly with the polarization potential shifting positively. That shows the adsorption rate is higher than the desorption rate of the inhibitor molecules on carbon steel surface, and the adsorption process controls the anodic reaction [51-52]. But, the increase in the anodic potential beyond a particular potential with regard to the reference solution is due to desorption of inhibitor molecules from the metal surface. The polarization behaviour shows similar appearance, which implies that, the inhibitor molecules are thoroughly adsorbed from the solution to the carbon steel surface and their inhibition effect is increased by increasing the concentration [53-54].

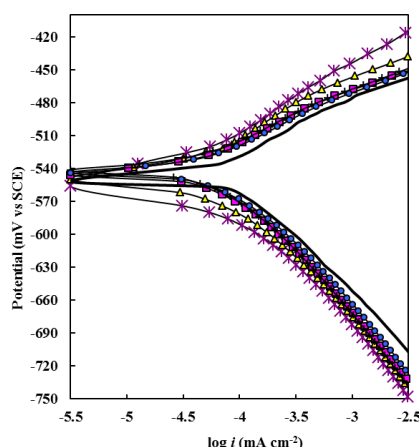


Figure 3: Polarization curve of carbon steel corrosion in 1 M H₂SO₄ in presence of different concentrations of P₈ inhibitor by weight (*: 400 ppm, Δ: 200 ppm, □: 100 ppm, +: 50 ppm, O: 25 ppm, —: blank) at 25 °C.

Table 1 collects the related corrosion electrochemical parameters, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c , β_a), and inhibition efficiency ($\eta\%$). It is evident that the increase of inhibitor concentration decreases the corrosion current densities and increases $\eta\%$, which suggests that the protective film adsorbed on the metal surface tends to be more complete at higher inhibitor concentrations. Furthermore, increasing the number of triethanolamine units in the inhibitors ($n=8, 10, 12$) decreased the corrosion current density (i_{corr}) considerably. The inhibition efficiencies increased by increasing the polymerization extent in the following trend: $P_{12} > P_{10} > P_8$. The inhibitor is classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank solution [53].

Table 1: Electrochemical parameters for the corrosion of carbon steel in 1 M H₂SO₄ solution containing different concentrations of P₈, P₁₀ and P₁₂ inhibitors at 25 °C

Inhibitor	Concentration, ppm by weight	E_{corr} (mV vs SCE)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	β_c (mV dec ⁻¹)	θ	$\eta\%$
Blank	0.0	-580.3	0.323	88.2	-142.6	---	---
P ₈	25	-565.6	0.075	63.1	-131.4	0.76	76.4
	50	-539.9	0.072	60.8	-135.1	0.78	77.8
	100	-542.9	0.067	60.3	-130.2	0.79	79.4
	200	-541.8	0.061	61.1	-132.7	0.81	81.1
	400	-553.3	0.056	58.2	-132.9	0.83	82.6
P ₁₀	25	-544.9	0.074	57.7	-130.3	0.77	77.0
	50	-536.5	0.068	53.3	-131.0	0.79	79.0
	100	-537.2	0.061	55.0	-139.9	0.81	81.3
	200	-533.4	0.052	57.8	-141.7	0.84	84.1
P ₁₂	400	-536.8	0.039	51.3	-129.7	0.88	87.8
	25	-544.5	0.055	61.5	-144.6	0.83	83.0
	50	-538.2	0.043	58.1	-141.4	0.86	86.3
	100	-534.3	0.039	50.4	-139.1	0.87	87.1
	200	-542.0	0.036	48.3	-136.0	0.89	89.4
	400	-550.8	0.034	50.6	-146.0	0.92	91.6

Data were average of three replicates with error ratio of 7%

The presence of P₁₂, P₁₀, and P₈ inhibitors resulted in slight shifts of corrosion potential compared to the potential obtained in the absence of inhibitor. However, the displacement of E_{corr} is less than 85 mV for all the studied inhibitors, but this displacement is not more than 43 mV. Therefore, these inhibitors can be classified as mixed-type inhibitors with a domain for anodic type inhibition [54–56]. Moreover, the values of the anodic and cathodic Tafel slopes (β_a , β_c) showed no obvious changes with the addition of the inhibitors, which suggests that the inhibiting action of the inhibitors occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing P₈, P₁₀, and P₁₂ inhibitor concentration [57–59]. The surface coverage values showed an increasing trend by increasing the inhibitor concentration from 25 ppm to 400 ppm by weight, **Table**

1. That shows a continuous increase of the adsorbed inhibitor molecules on the metal surface, which increases the inhibition efficiencies of the inhibitors. Increasing the inhibition efficiencies accompanied by increasing the inhibitors concentration can be attributed to the increase of the adsorbed layer thickness [60]. The inhibitors showed inhibition efficiencies in the following order: $P_{12} > P_{10} > P_8$, respectively.

Gravimetric measurements

The data obtained from the gravimetric measurements were: corrosion rate (C_r), surface coverage (θ) and inhibition efficiency ($\eta\%$). The measurements were obtained at different immersion periods of 1, 3, 6 and 24 hours and in the presence of 25, 50, 100, 200 and 400 ppm by weight of P_8 , P_{10} and P_{12} inhibitors at 25 °C.

Effect of inhibitors concentration

It is clear from data in **Figure 4a-d** that the increase of the inhibitors concentrations from 25 ppm to 400 ppm by weight decreased the corrosion rates of the carbon steel in 1 M H_2SO_4 solution. At a constant immersion time, the highest corrosion rates were obtained in the presence of 25 ppm by weight for all the used inhibitors at all immersion times.

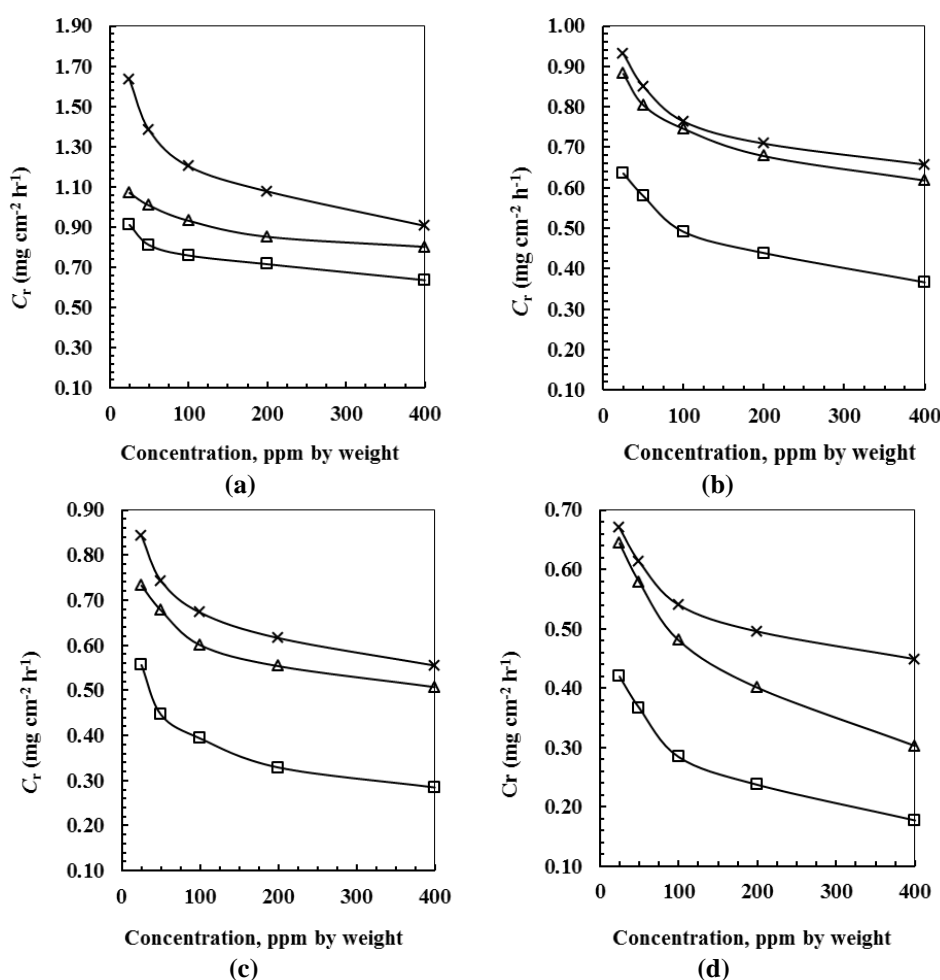


Figure 4: Effect of inhibitor concentration (ppm by weight) on the corrosion rate of the carbon steel in 1 M H_2SO_4 in the presence of: \times P_8 , Δ P_{10} , \square P_{12} inhibitors after: (a) 1 h, (b) 3 h, (c) 6 h, (d) 24 h, at 25 °C.

The gradual increase of the inhibitors concentration from 25 ppm to 400 ppm by weight decreased the corrosion rates from 1.64 to 0.91, 1.07 to 0.80 and 0.91 to 0.64 $mg.cm^{-2}.h^{-1}$ for P_8 , P_{10} and P_{12} after 1 hour immersion, respectively at 25 °C. The gradual decrease of the corrosion rates indicates the decrease of the carbon steel dissolution in the acidic medium. The decrease of corrosion rates by the increase of inhibitors concentration is an indication for the continuous accumulation of the inhibitor molecules on the metal surface. The adsorbed inhibitor molecules form a protective layer on the metal surface, which prevents the contact between the corrosive ions and the metal surface, and consequently decreases the corrosion extent. The increase of the inhibitor concentration increases the amount of adsorbed molecules at the metal surface, which can be

expressed in term of the surface coverage (θ). The calculated surface coverage (equation 2) revealed that the increase of the inhibitors concentration from 25 ppm to 400 ppm by weight increased the surface coverage considerably. The increase of the surface coverage reached its maximum values for P₈, P₁₀ and P₁₂ at 0.79, 0.82 and 0.86 after 1 hour immersion, and 0.87, 0.91 and 0.95 after 24 hour immersion in the presence of 400 ppm by weight. The increase of the inhibitor concentration increased the inhibition efficiencies of the different inhibitors to reach the maximum at 400 ppm by weight, **Table 2**.

Table 2: Surface coverage (θ) and inhibition efficiency ($\eta\%$) of the synthesized inhibitors (P₈, P₁₀ and P₁₂) at different concentrations and different immersion time at 25 °C

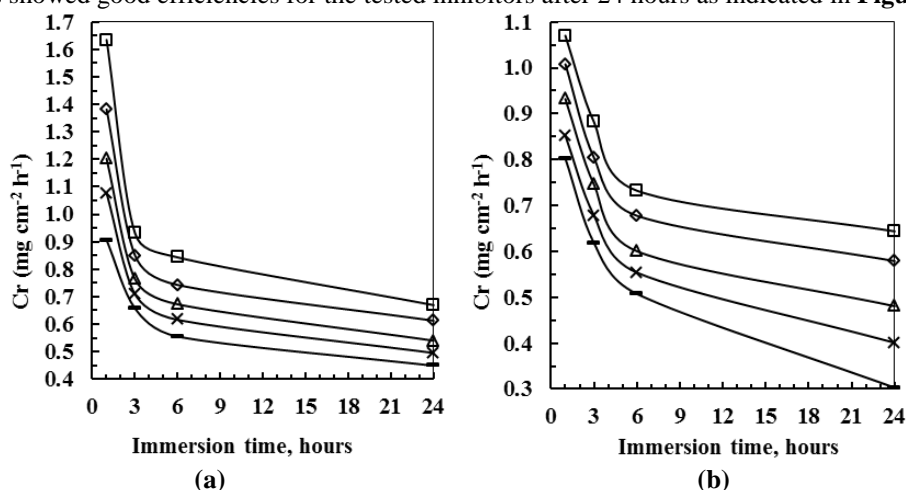
Inhibitors	Inhibitor concentration, ppm by weight	Immersion time, hours							
		1 h		3 h		6 h		24 h	
		θ	$\eta\%$	θ	$\eta\%$	θ	$\eta\%$	θ	$\eta\%$
P ₈	400	0.79	79.4	0.82	82.3	0.85	84.9	0.87	86.5
	200	0.76	75.5	0.81	80.9	0.83	83.3	0.85	85.1
	100	0.73	72.7	0.79	79.5	0.82	81.7	0.84	83.8
	50	0.69	68.6	0.77	77.1	0.80	79.8	0.82	81.6
	25	0.63	62.8	0.75	75.0	0.77	77.1	0.80	79.9
P ₁₀	400	0.82	81.8	0.83	83.4	0.86	86.2	0.91	90.9
	200	0.81	80.6	0.82	81.8	0.85	85.0	0.88	88.0
	100	0.79	78.8	0.80	80.0	0.84	83.7	0.86	85.6
	50	0.77	77.1	0.78	78.4	0.82	81.6	0.83	82.6
	25	0.76	75.7	0.76	76.3	0.80	80.1	0.81	80.7
P ₁₂	400	0.86	85.5	0.90	90.1	0.92	92.3	0.95	94.7
	200	0.84	83.7	0.88	88.2	0.91	91.1	0.93	92.9
	100	0.83	82.7	0.87	86.8	0.89	89.3	0.91	91.5
	50	0.82	81.6	0.84	84.4	0.88	87.9	0.89	89.0
	25	0.79	79.3	0.83	82.9	0.85	84.9	0.87	87.4

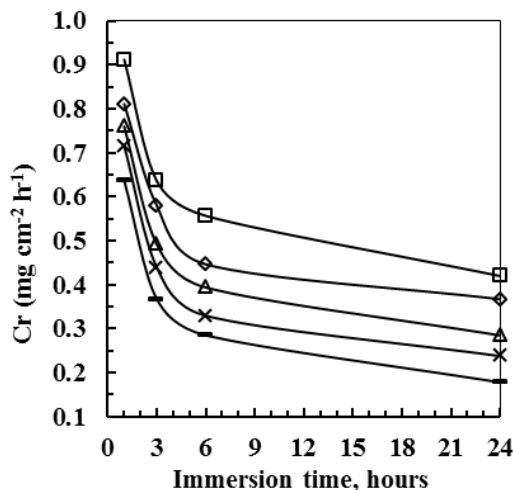
Data were average of three replicates with error ratio of 7%

The increase of the concentration increased the adsorbed inhibitor molecules on the metal surface, which is accompanied by a depression in the corrosion rates and an increase in the surface coverage. The adsorption of the inhibitor molecules on the metal surface is due to their surface activity. The surface activity of the inhibitor molecules is attributed to their amphipathic structure. The amphipathic structure is originated from the combination of hydrophilic groups (polar or charged groups) and hydrophobic groups in the inhibitor molecules. This combination increased the adsorption of the inhibitor molecules at the metal-solution interface by increasing their concentration [61].

Effect of immersion time

The influence of immersion time on the corrosion rate of carbon steel in the presence of the different inhibitors at different concentrations is represented in **Figure 5a-c**. The corrosion rates of the carbon steel in the absence of the inhibitors at 1, 3, 6 and 24 hours were: 4.40, 3.83, 3.76 and 3.33 mg cm⁻² h⁻¹ at 25 °C. At constant inhibitor concentration, the corrosion rate decreased by increasing the immersion time. That was attributed to the increase of the adsorbed amount of the inhibitor molecules on the metal surface. That increased the performance of the protective layer formed in the protection of the metal surface against the corrosion reaction [61, 62]. The results obtained from weight loss measurements for both the protected and unprotected carbon steel samples showed good efficiencies for the tested inhibitors after 24 hours as indicated in **Figure 5a-c**.





(c)

Figure 5: Effect of immersion time on the corrosion rate of carbon steel in 1 M H₂SO₄ in the presence of: □ 25 ppm, ◇ 50 ppm, △ 100 ppm, × 200 ppm, - 400 ppm (by weight) of (a) P₈, (b) P₁₀, (c) P₁₂ inhibitors at 25 °C.

Adsorption isotherm

The adsorption behaviour of the inhibitor molecules on metal surface is useful in explaining their inhibition mechanism [63,64]. The Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the inhibitor on carbon steel surface, which obeys Equation (5) [65,66].

$$\frac{C_i}{\theta} = \frac{1}{K_{ads}} + C_i \quad (5)$$

Where C_i is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant and θ is surface coverage.

The surface coverage (θ) for different concentrations of inhibitor in H₂SO₄ solution was obtained from weight loss results and listed in **Table 2**. The linear relationship of C_i/θ versus C_i displayed in **Figure 6** show that the adsorption of P₈, P₁₀ and P₁₂ on carbon steel surface is well fitted by the Langmuir adsorption isotherm (the slope is close to 1 and correlation coefficient (R^2) is close to 1). The intercept of C_i/θ versus C_i line is used to calculate the adsorption equilibrium constant.

Adsorption equilibrium constant (K_{ads}) is correlated to the standard free energy of adsorption (ΔG_{ads}°) of the inhibitor molecules on the metal surface according to equation (6) [67]:

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G_{ads}^\circ}{RT}} \quad (6)$$

Generally, ΔG_{ads}° values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, i.e., physisorption [68]. While, those of -40 kJ mol^{-1} or more negative regarded as chemisorption, which is formed by sharing or transferring of charges from the inhibitor molecules on the metal surface to form a covalent bonds [69]. ΔG_{ads}° values of the studied inhibitors ranged between $-36.42 \text{ kJ mol}^{-1}$ and $-38.74 \text{ kJ mol}^{-1}$, **Table 3**. These values are indicate that the inhibitors adsorbed on the metal surface via mixed mechanism; involved physical and chemical adsorption. Physical adsorption occurred between the active positive centres on the metal surface and the lone electron pair of the nitrogen atoms. Chemical adsorption occurred by forming coordination bonds between the inhibitor molecules and the d-orbital of Fe on the steel surface through lone pair of electron of O and N atoms [70-72]. Increasing the number of triethanol amine units and alkyl chains from oleic acid moieties in the inhibitors increased the negativity of ΔG_{ads}° values, which can be attributed to the role of the triethanol amine and oleic acid moieties in the adsorption on the carbon steel–H₂SO₄ solution interface [61, 67].

Table 3: Adsorption constant and free energy of adsorption of P₈, P₁₀ and P₁₂ inhibitors on the carbon steel surface in 1 M H₂SO₄ at 25 °C

Inhibitor	R ²	K _{ads} (M ⁻¹ ×10 ⁵)	ΔG ^o _{ads} , kJ mol ⁻¹
P ₈	1	4.3	-35.42±2.48
P ₁₀	0.9998	5.0	-37.46±2.62
P ₁₂	0.9999	11.1	-39.74±2.78

Data were average of three replicates with error ratio of 7%, SD=1

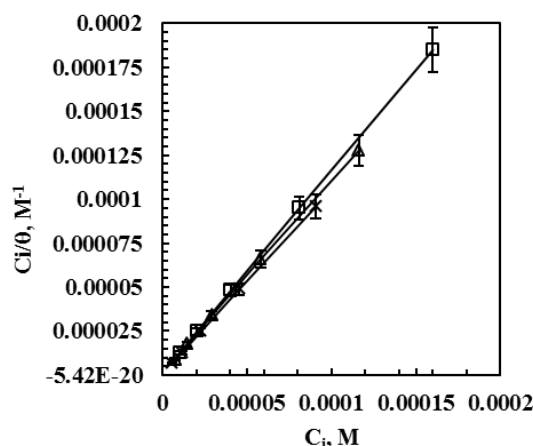


Figure 6: Langmuir adsorption isotherm of P₈, P₁₀ and P₁₂ inhibitors on carbon steel at 25 °C, error % = 7, SD=1.

Mechanism of corrosion inhibition

Electrochemical and weight loss methods were employed to study the behaviour of carbon steel corrosion in 1 M H₂SO₄, in the presence of P₈, P₁₀ and P₁₂ inhibitors. The inhibition efficiency is increased by the increasing of inhibitor concentrations, which indicated a gradual increase of the surface coverage of the different inhibitors on the metal surface. The first stage of the inhibition mechanism is the adsorption of inhibitors on the metal surface [61]. In most inhibition studies, the formation of donor–acceptor surface complexes between π -electrons of inhibitor and the vacant d-orbital of metal were assumed [73]. P₈₋₁₂ inhibitors contain several donating groups including: hydroxyl groups (OH), ether linkage (-O-) and double bonds (C=C) of oleic acid moiety. These groups acted as electron donating groups, which donate their lone pair of electrons to the vacant d-orbitals of Fe. In addition, the inhibitors transformed from the neutral to the cationic forms in the acidic medium [74]. That makes the inhibitor molecules adsorb on Fe surface by electrostatic interaction between the negatively charged centres on Fe surface and the positively charged nitrogen atoms (N⁺) [75–78]. Therefore, P₈, P₁₀ and P₁₂ inhibitors exhibit high efficiency in H₂SO₄. In addition, larger molecular area of P₈, P₁₀ and P₁₂ inhibitors [41] played an important role in retarding the corrosion by covering the wide area on the metal surface. The area of the inhibitors at the interface is increased by increasing the degree of polymerization of triethanolamine from 8 units to 12 units per molecule. That was accompanied by gradual increasing in their corrosion inhibition efficiency.

Surface activity-corrosion inhibition relationship

The surface activity of the synthesized inhibitors were measured based on the surface tension values and critical micelle concentrations (CMC). The relationship between the surface tension and $-\log C$ of the synthesized inhibitors is plotted in **Figure 7** as representative for the synthesized inhibitors at 25 °C. Two conclusions can be obtained from **Figure 7**. First, the gradual increase in the inhibitor concentration of decreases the surface tension values considerably. Second, within the homologue series of P₈, P₁₀, and P₁₂, increasing the number of the polyethylene glycol oleate chains attached to the polymer chain decreases the surface tension values. Increasing the number of polyethylene glycol oleate chains in the inhibitor molecule increases their hydrophobic characters which increases their tendency to adsorb at the air/water interface, which decreases their surface tension considerably.

The critical micelle concentration values (CMC) of these surfactants were determined by the intercept of the pre- and post-micellar regions in **Figure 7**. These values are listed in **Table 4**. Generally, CMC values depend on the number of polyethylene glycol oleate chains attached to the different molecules and the number of the triethanolamine molecules polymerized in the inhibitor molecules. The gradual increase of the polyethylene glycol oleate chain numbers from two to four in the inhibitor molecules decreases CMC values

considerably from 2.51 to 0.06 mM. Also, that behavior is predominant in P₁₀ and P₁₂ series due to the increase of the hydrophobic characteristics of the molecules. The same behavior was observed by increasing the triethanolamine units in the surfactant molecules and this was in good agreement with the previous study [79]. The increase of the polymerized units from eight to ten units decreases the values of CMC values by a factor of 0.1. Also the CMC value of P₁₂ is decreased by a factor of 0.1 more than P₁₀ derivatives, **Table 4**.

That is expected from the increase in hydrophobicity of the molecules as the number of methylene groups increases by increasing the degree of polymerization [80-81]. This decrease is linear as is seen in **Figure 7**. This usually happens in a homologous series of anionic [82], cationic [83-84] and nonionic [85] surfactants. The relation between the surface activity and $\eta\%$ was established in a previous work [86]. Increasing the number of hydrophobic chains in the inhibitor molecules increases their surface activity and the tendency towards adsorption at the interfaces [87] as represented from HLB values. Moreover, increasing the adsorption tendency increases the amounts of adsorbed molecules on the metal surface, which consequently increase the surface coverage values (θ), (**Table 2**). As a result, the metal surface is protected from the dissolution as the action of the acid solution.

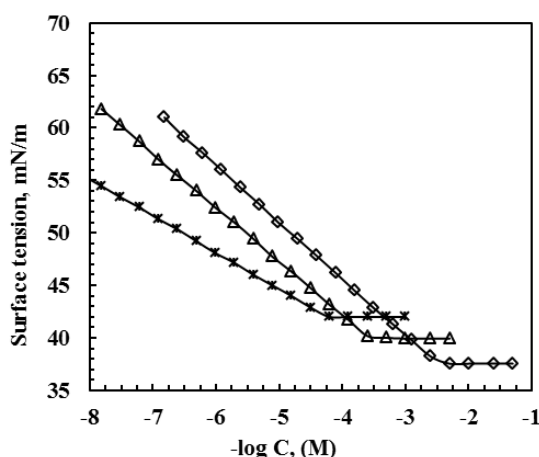


Figure 7: Surface tension vs. $-\log$ (concentration) profile of: \diamond : P₈; Δ : P₁₀; $*$: P₁₂ inhibitors at 25 °C.

Table 4: Surface parameters of the tested inhibitors at 25 °C

Surfactants	CMC, mM	HLB
P ₈	2.51	7.1
P ₁₀	0.20	7.7
P ₁₂	0.06	8.0

IV. Conclusions

- (1) The synthesized inhibitors P₈, P₁₀ and P₁₂ act as efficient inhibitor for the corrosion of carbon steel in 1 M H₂SO₄. Inhibition efficiency ($\eta\%$) increased by increasing the inhibitors concentration; and the maximum $\eta\%$ values at 400 ppm by weight are 86.5% - 94.7% at 25 °C.
- (2) The adsorption of the different inhibitors on carbon steel surface obeyed Langmuir adsorption isotherm.
- (3) The inhibitors act as mixed-type inhibitor with a domain of anodic type properties in 1 M H₂SO₄, and their inhibition on carbon steel proceeded by physical adsorption (physisorption).
- (4) Increasing the triethanol amine units and the critical micelle concentrations of the inhibitors increased the inhibition efficiency of the different inhibitors.

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