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Evaluation of nonionic surfactants from plastic waste as corrosion inhibitors of carbon steel in 1M HCl

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ABSTRACT

Recycled poly (ethylene terephthalate), PET, can be modified to produce nonionic surfactants. Recycling of PET waste was carried out in presence of triethanolamine (having 1:1 wt % of TEA : wt % of PET) and manganese acetate as catalyst. The produced oligomers were reacted with stearic acid and polyethylene glycol, PEG, which have different molecular weights 400, 1000 and 4000. The inhibition of corrosion of steel in 1 molar hydrochloric acid solution in the presence of the prepared surfactants is studied by weight loss and electrochemical polarization measurements. The polarization curves indicate that these compounds act as mixed-type inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration to reach their critical micelle concentrations. The temperature effect on the corrosion behavior of steel in 1M HCl with and without surfactants is studied in the temperature range from 308 to 343 K. The adsorption of inhibitors on the steel surface is found to increase with increasing the temperature. From the adsorption isotherm, some thermodynamic data for the adsorption process are calculated and discussed. The obtained results from weight loss and potentiodynamic polarization techniques are in a good agreement.

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KEYWORDS

PET glycolysis;
Corrosion;
Inhibition;
Steel;
Hydrochloric acid solution;
Recycling;
Surfactants.

INTRODUCTION

Poly (ethylene terephthalate), 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 has caused serious environmental problem^[2]. Researchers have begun to focus on recycling and management of plastic wastes^[3]. Today, PET bottles have become one of the most valuable and successfully recyclable materials. There are various meth-

ods focus with recycled PET bottles. These methods involve hydrolysis with acids or bases in aqueous solution^[4], noncatalytic hydrolysis or alcoholysis in supercritical media^[5] and alcoholysis or glycolysis by catalytic reactions^[6-8]. The recycled products include oligomers or low molecular weight compounds were used in chemical industry mainly for plastics^[9] as well used as in paint and lacquers production^[10]. Products of glycolysis of PET are used, among others, for the production of unsaturated polyester resins^[11], polyurethanes^[7,12],

Full Paper

epoxy resins^[13] and water-soluble surfactants^[14].

One of most important considerations in industry is the reduction of overall costs by protection and maintenance of materials used. Because steel is the backbone of industrial constructions, the inhibition of iron corrosion in acidic solutions has been studied in considerable detail^[15]. The effect of organic compounds containing heteroatoms on the corrosion behavior of iron and steel in acidic solutions has been well documented^[16-18]. Products of glycolysis of PET are used, among others, for the production of water-soluble surfactants^[19,20]. The overall policy of the present work is to alleviate environmental pollution caused from both plastic waste and corrosion and also to reduce the cost for production of corrosion inhibitors. In this respect, PET waste is converted into glycolyzed products via glycolysis reaction using triethanolamine (TEA). The glycolyzed products are used to synthesis the surface-active agents. On the other hand, PET waste was intended to be recycled into nonionic surfactants which can be used as corrosion inhibitors. The influence of the synthesized surfactants on inhibition of the corrosion of steel in 1M HCl was evaluated by weight loss and electrochemical polarization methods.

EXPERIMENTAL

Materials

PET waste was collected from beverage bottles., triethanolamine (TEA), were purchased from Aldrich Chemical Co. Ltd. (UK). β, β' -Dichloro diethylether (DCDE) is supplied from Fluka Chemika (Germany). Stearic acid and polyethylene glycol 400 (PEG₄₀₀), polyethylene glycol 1000 (PEG₁₀₀₀) and polyethylene glycol 4000 (PEG₄₀₀₀) were purchased from Aldrich Chemical Co. Ltd. (UK). Manganese acetate and sodium hydroxide, obtained from Aldrich Chemical Co. Ltd. (UK), were used as catalyst for depolymerization of PET and for reaction of PET oligomer with PEG, respectively. The solvents, methylene chloride, acetone, ethanol and benzene used in this work have analytical grads.

Techniques

Converting PET waste to glycolyzed products (GPs)

The reaction of PET with TEA was discussed in

previous articles^[19-21]. The reaction procedure was as following: PET bottle waste was depolymerized at weight ratio of PET to DEA or TEA ranging from 1 : 1 (Wt% of PET: Wt % of DEA or TEA) using 0.5% of manganese acetate as catalyst (by weight based on weight of PET). The reaction mixtures were mixed into four-neck reaction flask fitted with, mechanical stirrer, thermometer, condenser and nitrogen inlet. The reaction mixtures were heated under vigorous stirring in nitrogen atmosphere at temperature about 170-190 °C for 4h and at 200-210 °C for 3h. The temperature of the reaction was then lowered to 100 °C for 1h. The mixture was allowed to cool to room temperature. The glycolyzed product of PET with TEA is designated here as GT.

Ethoxylation of GT using β, β' -dichloro diethyl ether and PEG

Three different molecular weights of PEG, namely, PEG400, 1000 and 4000 g/mol were reacted with the glycolyzed products and β, β' -dichloro diethyl ether in presence of NaOH as a catalyst to produce the dispersants with the following procedure: In a 250 ml three neck round bottom flask, fitted with condenser, mechanical stirrer and thermometer were added 0.1 mole GP, 0.2 mole β, β' -dichloro diethyl ether, 0.2 mole PEG and 0.4 mole NaOH. The reactants were agitated and slowly heated to a temperature of 170°C. The reaction mixture was maintained at this temperature for 5 hr. The progress of the reaction was evaluated by determining the NaCl content that increases gradually to reach a constant value at the end of the reaction. The product was then treated with an equal volume of saturated NaCl solution, neutralized with dilute HCl. The temperature of the mixture was raised to 90°C and maintained for one hour. The upper waxy layer was separated and dried in vacuum oven at 50°C to a constant weight. The produced surfactants from GT are designated here as GT- EO9, GT- EO22, and GT- EO90. Where the numbers 9, 22 and 90 are related to the number of ethylene oxide in PEG 400, PEG 1000 and PEG 4000, respectively.

Measurements

The nitrogen content of recycled PET with TEA has measured using a Tecator Kjeltach Auto Analyzer.

A Tecator 1007 digester was used for the initial digestion of the samples. The hydroxyl values were determined by the conventional acetic anhydride/pyridine method. In order to determine the amount of free TEA, a weighed quantity (10% of the total weight of the reactants) of the glycolized product was dissolved in acetone and precipitated by diethyl ether. The oligomers were filtered and the solvents were removed under reduced pressure. The purified compounds were analyzed using ATI Mattson Genesis Series FTIR spectrophotometer. The prepared surfactants were dissolved in CDCl_3 and analyzed using Jeol NMR spectrometer model JNM-EX (270 MHz) as another spectroscopic technique for determining the chemical structures.

The number average molecular weights, M_n , of the modified PET products were measured by GPC Water model 600 E. The measurements were recorded at 303 K, under UV-visible spectrophotometer water, mobile phase toluene HPLC grade, Styragel column and injection volume chart.

Surfactants were subjected to surface tension measurements. Different concentrations of each sample were prepared and the surface tension at 298, 308, 318 and 328K was measured using a platinum plate tensiometer, model Dognon Abribat Prolabo. A specially designed double jacket glass cell connected with a thermostated oil bath was used for maintaining the adjusted temperature. Double distilled water ($\gamma = 72$ dyne/cm) was used for preparing the concentrated stock solutions of the grafts. Several concentrations were prepared by diluting the stock solution with double distilled water to the appropriate concentration to determine the critical micelle concentration (CMC). The diluted solutions were allowed to stand for 24 hr before the surface tension measurements were performed.

Different solutions of graft copolymers having 2 wt % of the polymer in both double distilled water and saline solutions (1-5 wt % NaCl) were prepared. Each solution was heated with stirring until it becomes turbid. Upon cooling, the turbidity starts to disappear. The temperature at which the solution becomes completely clear was recorded as the cloud point of this particular solution.

Gravimetric and polarization measurements

The aggressive solution (1M HCl) was prepared

by dilution of analytical grade 37% HCl with bidistilled water. Prior to all measurements, the steel samples were polished with different emery papers up to 1200 grade and washed thoroughly with bidistilled water and dried with acetone. The composition of the carbon steel (X42) used in this investigation is listed in TABLE 1.

TABLE 1 : The composition of the carbon steel (X42)

Element	C	Mn	P	S	Cr	Mo	Si	Fe
Weight (%)	0.29	1.25	0.03	0.03	0.04	0.04	0.27	Rest

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2 cm×2 cm×0.05 cm). Steel specimens were suspended from glass hooks in containers, each containing 100ml solution for 7days at different temperatures ranged from 293 to 343±1K.

Electrochemical measurements were carried out in conventional three electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) had the form of a disc cut from the steel sheet. The area exposed to the corrosive solution was 1 cm². A saturated calomel electrode (SCE) and a disc platinum electrode were used respectively as reference and auxiliary electrode. The temperature was thermostatically controlled at 298±1K. Electrochemical experiments were recorded using an EG&G potentiostat (263 A), coupled to a computer equipped with a software 352 Soft Corr III. Before recording the polarisation curves, the test solution was de-aerated and magnetically stirred for 30 min in the cell with pure nitrogen.

Gas pebbling was maintained throughout the experiments. The WE was then inserted and prepolarised at -800mV for 10 min in order to remove oxide film from the electrode and E_{corr} was monitored until stationary (30 min) state. The scan rate was 1mVs⁻¹.

RESULTS AND DISCUSSIONS

Three glycolized product, coded as GT, was obtained by depolymerization of PET with TEA having 1:1 % (weight percentage of PET to TEA). All depolymerization reactions of PET were carried out in nitrogen atmosphere and in presence 0.5% of manganese acetate as trans-esterification catalyst. The glycolysis

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consists of the trans-esterification of PET and the depolymerization of its polymer chain to low molecular weight oligomers. The oligoesters have two hydroxy end groups, i.e. oligoester diols are formed. The temperature of glycolysis reaction of PET with TEA must be fixed at 210°C throughout the reaction to prevent the formation of alicyclic derivatives between hydroxyl groups of the produced poly-hydroxy glycolyzed PET^[19]. The molecular weights of the glycolyzed PET with TEA were determined by GPC technique as de-

scribed in the previous works^[19,20]. The structure of the PET oligomers with TEA was verified from their IR and ¹HNMR spectra^[19,20].

Synthesis of nonionic surfactants from GT

The present work deals with synthesis of polymeric surfactants by reacting a dihydroxyl- or tetrahydroxyl oligomers of GT with PEG and stearic acid. The chemical structures of the prepared surfactants were represented in figure 1. The strategy of

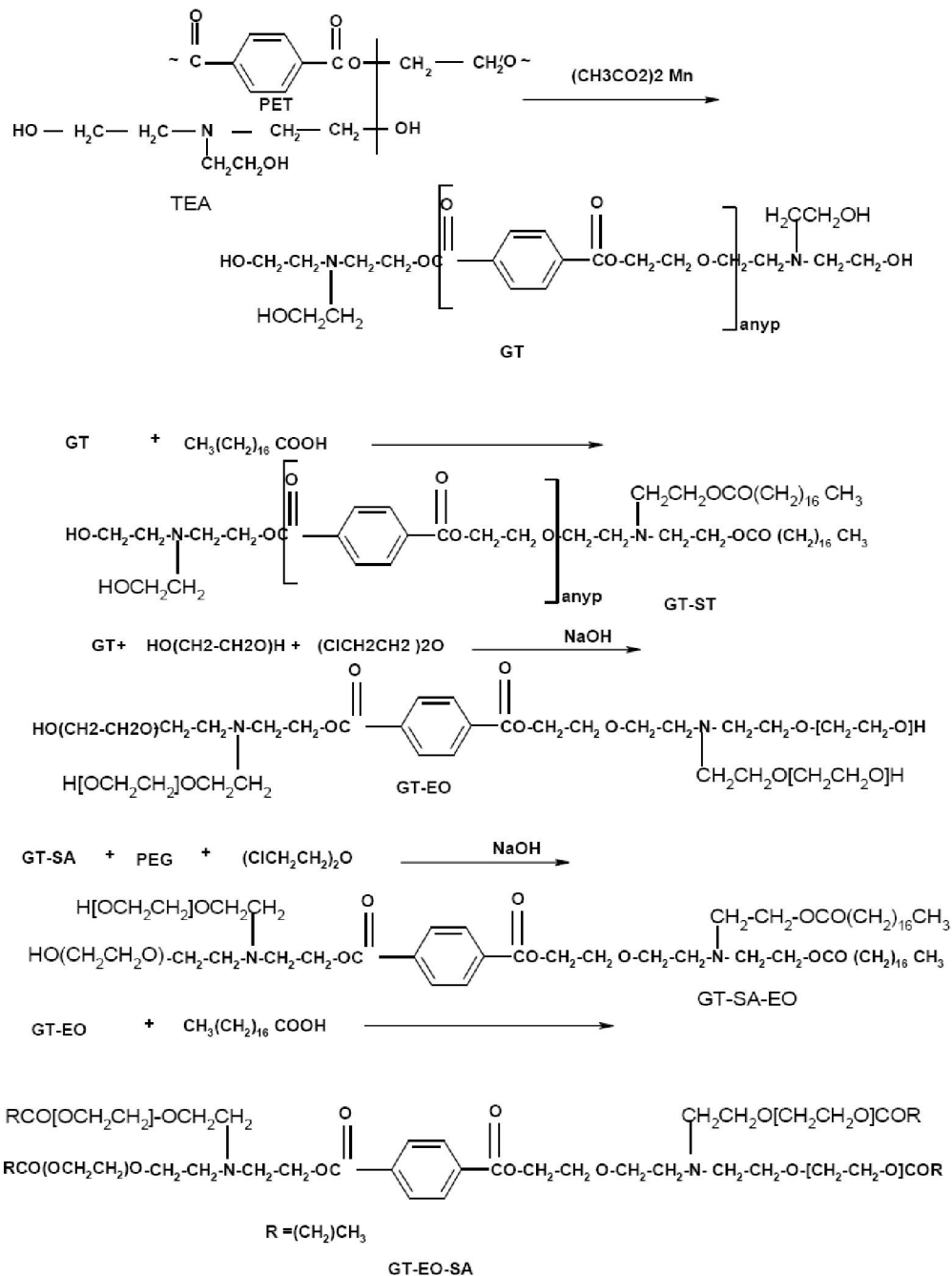


Figure 1 : Scheme of synthesis of surfactants based on GT.

synthesis is based on preparation of polymeric surfactants having different hydrophile-lipophile balance to study effect of surfactant structure on its properties. Accordingly, the scheme of synthesis is classified to prepare four different groups of nonionic polymeric surfactants. The structures of the produced surfactants were confirmed by using IR spectroscopy^[19,20]. On the other hand ¹HNMR spectrum of GT-EO90-SA were represented in Figure 2 to confirm the structure of nonionic surfactants based on SA as hydrophobic group. The protons of oxyethylene

units at $\delta = 3.6$ ppm, -OH proton of PEG at $\delta = 2.5$ ppm, 8 ppm which represent p- substituted phenyl group, OOCCH₂CH₂COO at 4.8 ppm and OCH₂CH₂N of glycolized PET at 4.3 ppm are observed in the spectra of all surfactants except the disappearance of singlet OH band at 2.5 ppm in all spectrum of GT-EO-SA surfactants. New signals of methylene (CH₂)₁₆, CH₃ and COOCH₂ protons of SA appear as an intense broad band at $\delta = 1.35$, 0.87 and 3.85 ppm were used to assign the incorporation of SA with GT-SA and GT-EO-SA surfactants.

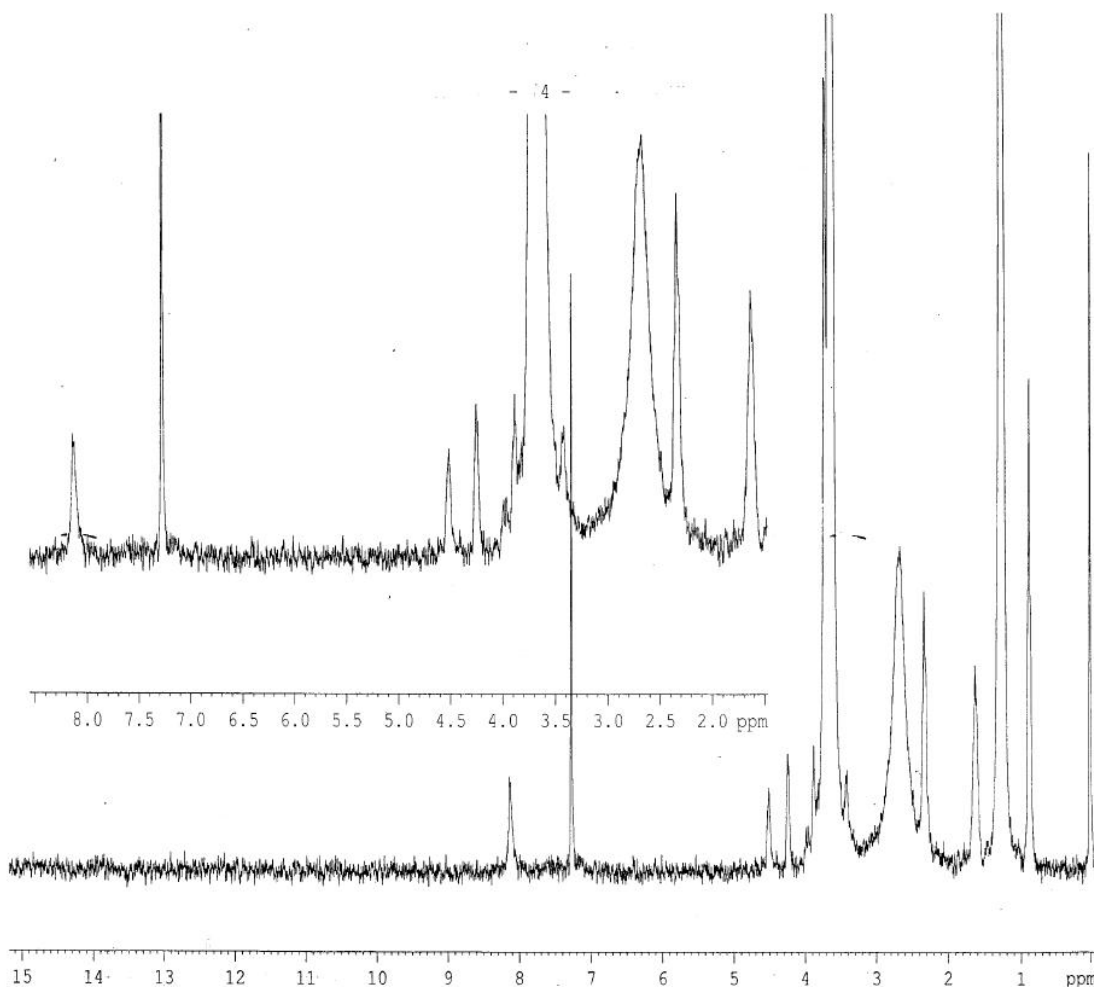


Figure 2 : ¹HNMR spectrum of GD-EO90-SA.

Solubility and surface activity of the prepared surfactants

The solubility of the prepared surfactants depends on the method of purification. However, the different segments in the modified PET and PEG copolymers have dissimilar solubility properties. This difference in solubility is due to the difference in hydrophil-lipophil

balance (HLB) of the surfactants. The HLB values were calculated by using the general formula for nonionic surfactants^[22]. The molecular weight of the prepared surfactants were determined by GPC and listed in TABLE 2. The good agreement between two values of calculated and measured molecular weights of the prepared surfactants indicate the purity of surfactants. HLB val-

Full Paper

ues of nonionic surfactants based on GT were calculated and listed in TABLE 2.

TABLE 2 : GPC characteristics and HLB values of ethoxylated PET oligomers.

Glycolyzed products	Designation	M.Wt. (Cal.) (g mol ⁻¹)	M.wt. (Det.) (g mol ⁻¹)	Polydispersity	HLB
GT	GT	1128	1131.4	1.003	-
	GT-EO9	2068	2064	1.003	13.74
GT-EO	GT-EO22	3268	3260	1.002	15.23
	GT-EO90	9268	9264	1.002	17.26
GT-ST	GT-SA	1660	1740	1.009	12.59
	GT-SA-EO9	1776	1865	1.005	15.2
GT-SA-EO	GT-SA-EO22	2376	2435	1.115	15.91
	GT-SA-EO90	5376	5486	1.116	16.81
	GT-EO9-SA	2569	2617	1.231	14.67
GT-EO-SA	GT-EO22-ST	3792	3813	1.004	15.1
	GT-EO90-ST	9769	9812	1.009	16.9

The critical micelle concentrations (CMC) was determined by the surface balance method. The CMC values of the prepared polymeric surfactants were determined at 298, 308, 318 and 328K from the change in the slope of the plotted data of surface tension (γ) versus the natural logarithm of the solute concentration. The obtained values of CMC for nonionic surfactants at different temperatures are listed in TABLE 3 and discussed in previous works^[19,20]. It was found that the CMC values show an increase with decreasing in the number of oxyethylene groups in the molecule. This can be attributed to the hydrophobic interaction between phthalic groups which increases coiling of terminated polyethylene oxide. So the solubility of surfactants in water is controlled by structure of hydrophobic groups. It can be observed that the incorporation of SA in GT-EO and GD-EO surfactants increases the CMC values due to increasing the interaction between EO and water^[20]. It was also observed that the surfactants have SA at two ends of surfactant possess lower CMC value that that ended with OH group of PEG. This can be attributed to the formation of hydrogen bonds between hydroxyl two ends with water will increase the solubility of surfactants which increase its CMC value.

The same results can be obtained from measuring of the cloud temperatures of the prepared surfactants in water. It was established that aqueous solutions of polyoxyethylenated nonionic having oxyethylene con-

tent below about 80%, become turbid on being heated at a temperature known as the cloud point, above which there is a separation of the solution into two phases. This phase separation occurs at a narrow temperature range (fairly constant) for surfactant concentrations below a few percent^[20].

TABLE 3 : CMC data of surfactants based on TEA at different temperatures.

Designation	Cloud point (°C)	n	Surface Property	Temperature (K)			
				298	308	318	328
GT-SA	62	-	*CMC x 10 ⁴	250	26.3	4.65	0.846
			** γ_{CMC}	37	36.4	35.8	34.7
GT-EO9-SA	58	9	*CMC x 10 ⁴	11	2.4	0.5	0.068
			** γ_{CMC}	28.8	28.1	27.6	26.9
GT-SA-EO9	64	9	*CMC x 10 ⁴	55	11.7	7.1	0.275
			** γ_{CMC}	34.3	33.2	32.5	31.8
GT-EO22-SA	69	22	*CMC x 10 ⁴	100	15.5	2.58	0.553
			** γ_{CMC}	33.1	32.5	31.3	30.4
GT-SA-EO22	66	22	*CMC x 10 ⁴	145	37.2	7.74	2.13
			** γ_{CMC}	33.2	32.8	31.4	29.7
GT-EO90-SA	69	90	*CMC x 10 ⁴	30	6.17	0.517	0.167
			** γ_{CMC}	38.7	37.5	36.1	35.7
GT-SA-EO90	74	90	*CMC x 10 ⁴	100	26.3	3.04	0.55
			** γ_{CMC}	35.7	34.4	33.6	31.5

* CMC x10⁴ in (mol dm⁻³); ** γ_{CMC} in (mNm⁻¹)

The phase appears to consist of an almost micelle-free dilute solution of the nonionic surfactant at a concentration equal to its CMC at this temperature and a surfactant-rich micellar phase, which appears only when the solution is above its cloud point, the two phases merge to form once again a clear solution by cooling. The temperature at which clouding occurs depends on the structure of the polyoxyethylenated nonionic surfactant. The cloud temperatures were measured and listed in TABLE 3. As seen from the presented data, the cloud points were progressively higher with increasing lengths of the hydrophilic side chains and molecular weight of PEG. This is in agreement with the data observed for polyoxyethylenated nonionic^[20].

As a result, a plot of surface (or interfacial) tension as a function of equilibrium, concentration of surfactant in one of the liquid phases, rather than an adsorption isotherm, is generally used to describe adsorption of this interface can readily be calculated as surface excess concentration Γ_{max} . The concentration of surfac-

tant at the interface may therefore be calculated from surface or interfacial tension data^[20].

From the surface excess concentration, the area per molecule at interface A_{\min} is calculated (20). The effectiveness of surface tension reduction, $\pi_{\text{CMC}} = \gamma_o - \gamma_{\text{CMC}}$, where γ_o is the surface tension of water and γ_{CMC} is the surface tension of solution at CMC^[20], was determined at different temperatures. The Γ_{\max} , A_{\min} and π_{CMC} values are calculated and listed in TABLE 4. The data, listed in TABLE 4, show that the minimum areas per molecule at the aqueous solution / air interface increase with the increase of the number of oxyethylene units in the molecule. The A_{\min} of nonionic surfactants that contain PEG in their molecular structure increases with the number of oxyethylene units^[20]. This can be attributed to the behavior surfactants with hydrophilic groups at opposite ends of the molecule, which show large area per molecule at the interface and are probably lying flat at the interface with both hydrophilic groups in contact with the aqueous phase. The data of A_{\min} and Γ_{\max} indicates the dependence of the effectiveness of adsorption at the aqueous solution / air interfaces on the structure of surfactants. It was found that incorporation of TEA appears to have an unusual small increase in A_{\min} at the interface. This can be attributed to that TEA has a branched hydroxyethyl group, which makes coiling of hydrophobic chain with a consequent increase in A_{\min} ^[20]. In the present system it was found that the minimum area per molecule also increases with increase in temperature, as would be expected from the increased thermal agitation of the molecules in the surface film^[20].

The effectiveness of surface tension reduction, π_{CMC} , in these compounds shows a steady decrease with increase in the number of oxyethylene units. In polyoxyethylenated nonionic, an increase in the number of oxyethylene units in the hydrophilic group above six units, in contrast to its large effect in decreasing the effectiveness of adsorption, seems to cause only small decreases in the efficiency of adsorption. This appears to indicate a very small change in the free energy of transfer of the molecule from bulk phase interior to the interface with change in the number of EO above six in the hydrophilic head. The effectiveness of adsorption, however, may increase, decrease or show no change with increase in the length of the hydrophobic group depending on the orientation of the surfactant at inter-

face. If surfactant is perpendicular to the surface in a close-packed arrangement, an increase in the length of the straight-chain hydrophobic group appears to cause no significant change in the number of moles of surfactant adsorbed per unit area of surface at surface saturation^[19,20]. This is because, the cross-sectional area occupied by the chain-oriented perpendicular to the interface dose not change with increase in the number of units in the chain.

TABLE 4 : Surface properties of the surfactants based on TEA at different temperatures.

Designation	Surface property	Temperature (K)			
		298	308	318	328
GT-SA	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.99	0.94	0.90	0.83
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.167	0.176	0.184	0.199
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	35.27	35.12	34.23	34.56
GT-EO9-SA	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.74	0.64	0.59	0.52
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.223	0.258	0.281	0.317
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	43.47	43.42	42.43	42.36
GT-SA-EO9	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.51	0.43	0.41	0.36
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.324	0.385	0.403	0.459
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	37.97	38.32	37.53	37.46
GT-EO22-SA	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.66	0.59	0.54	0.49
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.251	0.281	0.306	0.337
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	39.17	39.02	38.73	38.86
GT-SA-EO22	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.485	0.451	0.410	0.330
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.341	0.367	0.403	0.501
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	39.07	38.72	38.63	39.56
GT-EO90-SA	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.78	0.71	0.61	0.52
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.212	0.233	0.271	0.318
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	33.57	34.02	33.93	33.56
GT-SA-EO90	$\Gamma_{\max} \times 10^{10} (\text{mol cm}^{-2})$	0.42	0.38	0.35	0.32
	$A_{\min} (\text{nm}^2/\text{molecule})$	0.394	0.435	0.472	0.517
	$\Pi_{\text{CMC}} (\text{mNm}^{-1})$	36.57	37.12	36.43	37.76

Evaluation of the prepared surfactants as corrosion inhibitors

The inhibition of corrosion of steel in 1 molar hydrochloric acid solution by two oligomers derived from glycolysed products of PET with diethanol and triethanol amines is studied by weight loss and electrochemical polarization measurements^[23]. The two methods The temperature effect on the corrosion behavior of steel in 1M HCl with and without oligomers is studied in the temperature range from 308 to 343 K. The adsorption

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of inhibitors on the steel surface is found to increase with increasing the temperature. From the adsorption isotherm, some thermodynamic data for the adsorption process are calculated and discussed. The present investigation extended work to use GT nonionic surfactants as corrosion inhibitors for steel in 1M HCl. In this respect, the present corrosion inhibitors were designed to prepare from recycled PET waste and introducing TEA, PEG and stearic acid in their chemical structure to increase their abilities to soluble in water and to use as corrosion inhibitors for carbon steel. By analyzing the presented surface properties listed in TABLES 3&4, it is found that the greatest reduction of surface tension (effectiveness, $DCMC$) was achieved by GT -EO90-SA compared with that obtained by the other surfactants. This is in harmony with the maximum inhibition efficiency result achieved by GT -EO90-SA as obvious from TABLES 3&4. Accordingly GT -EO90-SA surfactant will be investigated in the present work. The corrosion inhibition of mild steel in 1 N HCl by using water soluble surfactants based on recycled PET has been studied at 293-343 K using electrochemical and weight loss measurements.

Weight loss measurements

Weight loss (in mg/cm^2) of the surface area were determined in an open system at various time intervals in absence and presence of different concentrations of the additives. Experimental results of weight loss of the GT -EO90-SA sample vs. time of immersion at different concentration of additives is selected as representative sample and plotted in Figure 3. It is evident from this figure that in all cases, the dissolution of carbon steel in hydrochloric acid solution is characterized by an initial slow rate. This may be due to the oxide film originally present on the metal surface. As reflected from the graphs, the weight loss of the carbon steel samples increases with increasing the time of immersion. The curves obtained in the presence of additives fall significantly below that of free acid in all cases. The increase in the additive concentration was accompanied by a decrease in weight loss and an increase in the percentage of inhibition^[23]. The inhibition efficiency ($\eta\%$) was calculated^[23] and summarized in TABLE 5, which show that rate of corrosion (k) decrease with increase of inhibitor concentration and increase with time. The inhi-

bition efficiency increases with increasing inhibitor concentration. This fact suggests that the inhibitor molecules may first be chemically adsorbed on the steel surface and cover some sites of the electrode surface. Then probably form monomolecular layers (by forming a complex with iron ions) on the steel surface. These layers protect steel surface from attack by chloride ions. From these results it can be concluded that there is no interaction between the molecules adsorbed at the metal surface^[23]. In the structure of the inhibitors, the atoms of the benzene ring and the C=O group can form a big π bond. Then, not only can the π electron of the benzene carbonyl enter unoccupied orbital of iron, but the π^* orbital can also accept the electrons of d orbital of iron to form feed back bonds, then produce more than one center of chemical adsorption action^[24]. The presence of the electron donating groups on the TEA structure (CH_2-CH_2), increases the electron density on the nitrogen resulting high inhibition efficiency. Adsorption can also be occurred via electrostatic interaction between a negatively charged surface, which is provided

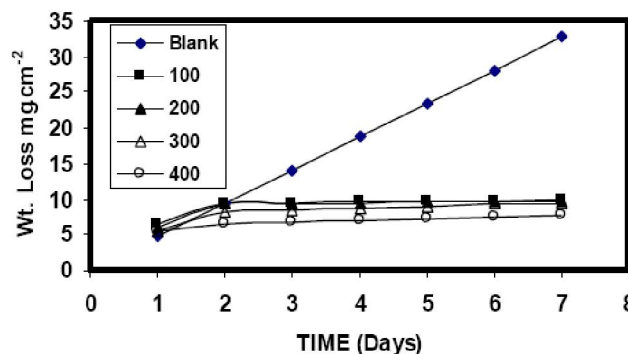


Figure 3 : Effect of concentration on inhibition efficiency of inhibitor of GT-EO90-SA for carbon steel alloy from weight measurement in 1M HCl at 298 K.

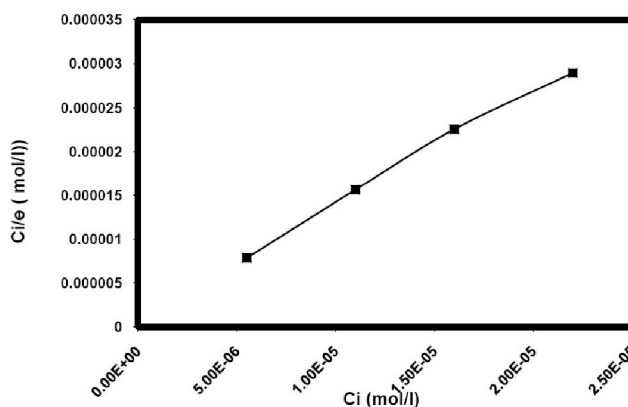


Figure 4 : Langmuir adsorption isotherm for the GT-EO90-SA surfactant at temperature 298 K.

TABLE 5 : Degree of surface coverage (θ) and percentage inhibition efficiency (η %) of the inhibitor GT-EO90-SA in 1M HCl at 293 °K, obtained from weight loss measurements after 7 days.

Conc. Ppm	Conc. Mole/Liter $\times 10^4$	Wt. loss mg.cm^{-2}	Corrosion rate (k) $\text{mg.cm}^{-2} \text{day}^{-1}$	θ	η %
0		32.8	4.68		
100	5.50E-06	9.80	1.4	0.701	70.1
200	1.10E-05	9.70	1.38	0.704	70.4
300	1.60E-05	9.50	1.35	0.710	71.0
400	2.20E-05	7.77	1.11	0.760	76.0

with a specifically adsorbed anion on iron and the positive charge of the inhibitor. Consequently, the nitrogen groups of GT cannot easily interact with steel and decreases their corrosion inhibition efficiencies^[25].

The inhibition efficiency data show that, at low inhibitor concentration, the corrosion of steel is 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^[25]. This increase is due to the formation of hemimicelles or admicelles^[25]. At higher inhibitor concentration, the corrosion inhibition reaches a steady state for all prepared surfactants. This behavior is attributed to the saturation of the surface with surfactant molecules and the formation of multilayer^[26].

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

$$C_i / \theta = (1 / K_{\text{ads}}) + C_i \quad (1)$$

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 have been evaluated from weight loss measurements by using the following equation^[27]:

$$\theta = 1 - (\Delta W_i / \Delta W) \quad (2)$$

Careful inspection of these results showed also that, the inhibition efficiency increase with increasing concentration and surface coverage (θ). 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^[16-18,23]. The results of dissolution of carbon steel in 1M hydrochloric acid solution in presence of GT -EO90-SA might to interpret

on the basis of interface inhibition mode. The inhibitors are acting effectively at the metal solution interface, so, a small concentration of inhibitor exhibits an effective corrosion inhibition. This is due to the formation of adsorbed monolayer at the metal solution interface. The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm. The relations between C_i / θ against C_i , not represented here for brevity, of all inhibitors under examination yield a straight line, clearly proving that the adsorption of the used inhibitors from 1 M HCl solutions on the carbon steel surface obeys the Langmuir adsorption isotherm.

Effect of temperature

The influence of solution temperature on the corrosion behavior of carbon steel in 1N HCl has been studied by the weight loss method over temperature range (293 – 343°K). the data of both blank and GT-EO90-SA were represented in Figures 5 & 6. The data display that the rate of corrosion rate increases with an increase in temperature from 293 to 343°K as represented in TABLE 6. Also, the Figure 5 indicate that the weight loss of carbon steel in 1N HCl increase with increase temperature and also increase with increase time of immersion. It is evident from these figures that the dissolution of carbon steel in hydrochloric acid solution is characterized by an initial slow rate; this may be due to the oxide film originally present on the metal surface. The results of carbon steel inhibition efficiency of the blank and different concentrations of the

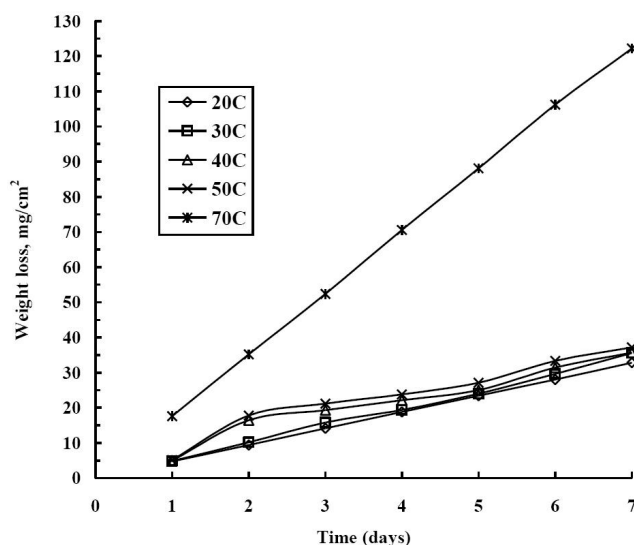


Figure 5 : Effect of temperature on weigh loss measurement of blank carbon steel alloy.

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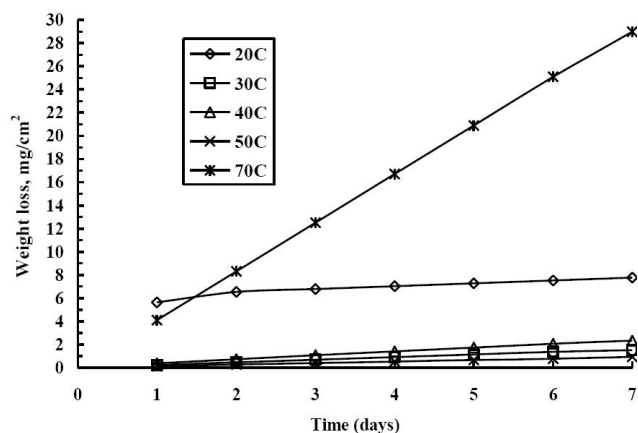


Figure 6 : Effect of temperature on weight loss measurement in presence of GT-EO90-SA.

prepared surfactants at different temperatures produced from weight loss measurements, listed in TABLE 6, show that the weight loss decrease (corrosion rate) with increase temperature from 293 – 323°K which indicate chemical adsorption^[28]. On the other hand, when the temperature was increased up to 343°K, the corrosion rate (weight loss) was increased for all the prepared surfactants. It may be explained with desorption of adsorbed inhibitor on the steel surface.

TABLE 6 : Degree of surface coverage (θ) and percentage inhibition efficiency (η %) of the inhibitor. GT-EO90-SA in 1M HCl solution at different temperatures.

T _i (K)	1/T (K ⁻¹)	Krate Mg. cm ⁻² .day ⁻¹	Log (Krate)	η (%)	θ	Eactiv kJ.mol ⁻¹
293	0.003413	1.11	0.04532298	79.2	0.792	
303	0.0033	0.21	-0.67778071	95.1	0.951	
313	0.003195	0.33	-0.48148606	96.1	0.961	52.42061
323	0.003096	0.133	-0.87614836	97.0	0.97	
343	0.002915	4.14	0.61700034	76.4	0.764	

Activation energy of corrosion

Corrosion is an electrochemical phenomenon and follows the laws in chemical kinetics. The corrosion rate will increase with temperature as a result of decreasing the apparent activation energy, E_a^* of the charge transfer reactions. Increasing of the temperature will also enhance the rate of H⁺ ion diffusion to the metal surface beside the ionic mobility, thus increasing the conductivity of the electrolyte. The study of the effect of temperature on the inhibition efficiency of corrosion inhibitors is important in the elucidation of mechanism and the kinetics of their action and ultimately the proper

selection of these inhibitors for specific practical situation. Accordingly, the effect of temperature of the corrosion medium on the reaction proceeding in pure acids was reported by many investigators^[16-18,23]. Moreover, at lower temperature, absorbed hydrogen atoms (exothermic process) blocked the cathodic area. With increasing the solution temperature, desorption of hydrogen takes place leading thus to increase of cathodic area.

The values of K obtained permit the calculations of activation energy (E_a) according to Arrhenius equation^[27]:

$$\log K = \log A - E_a/2.303RT \quad (3)$$

A is pre-exponential factor related to concentration, steric effect and metal surface characteristics, etc, plotting of log k against 1/T for the free acid solution (blank) and 400ppm of the GT-EO90-SA inhibitor as representative sample, Figure 7. From the slopes of the plots, the respective activation energies were calculated and recorded in TABLE 6. 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 controls by surface reaction, since the energy of activation for corrosion process is over 20KJ^[29].

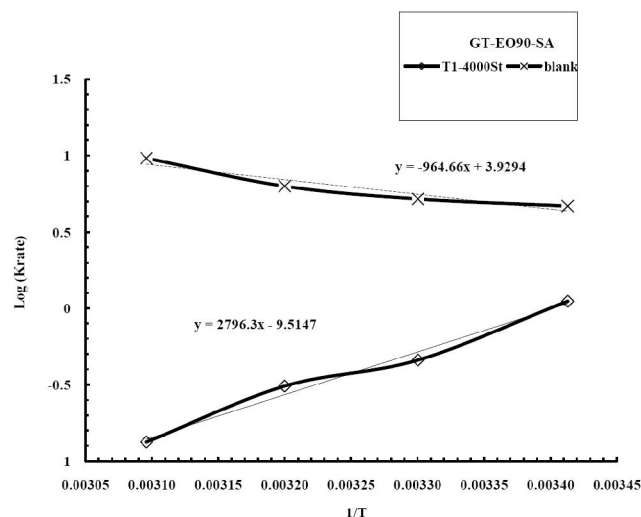


Figure 7 : Relation between log Krate of corrosion from weight loss measurement at different temperatures in presence of GT-EO90-SA.

Thermodynamic functions of activation

The values of activation energy for steel corrosion reaction (E_a) were obtained from Arrhenius equation^[27].

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

$$\Delta G^* = RT (\log K_{rate} - \log KT/h) \quad (4)$$

K, equilibrium constant, values is given by

$$K = \frac{\theta}{C_i (1 - \theta)} \quad (5)$$

The values of E_a and ΔG^* are given in TABLE 7. The low and 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^[26]. It is found that E_a values for inhibited systems are higher than E_a for uninhibited systems, which propose the conclusion that physical adsorption occurs in the first stage explains the nature of organic molecules–metal interactions^[16-18,23].

TABLE 7 : Thermodynamic functions of activation of the prepared surfactants.

Compound	Temp., °K	* $E_{activ.}$ kJ mol ⁻¹	ΔG^* kJ mol ⁻¹	ΔH^* kJ mol ⁻¹	ΔS^* kJ mol ⁻¹ K ⁻¹
Blank	293	75.2333	-22.0434	-12.2088	0.079839
	303		-22.7957	-12.5579	0.079839
	313		-23.548	-12.907	0.079839
	323		-24.3004	-13.2561	0.079839
	293		-64.4938	-12.209	0.366704
GT-EO90-SA	303	220.1152	-66.6949	-12.5581	0.366704
	313		-68.8961	-12.9072	0.366704
	323		-71.0972	-13.2563	0.366704

The thermodynamic functions, entropy of activation, ΔS^* , enthalpy of activation, ΔH^* and free energy of activation, ΔG^* are calculated from the equation:

$$\Delta H_{ads} = E_a + RT \quad (6)$$

where, R is the universal gas constant. In this case the values of Q_{ads} equal to enthalpy of adsorption (ΔH_{ads}) with good approximation, because pressure is constant. The negative values of Q_{ads} indicated that the adsorption of used inhibitors on the mild steel surface is exothermic. Entropy of inhibitor adsorption (ΔS^*) can be calculated using the following equation:

$$\Delta S^* = (\Delta H^* - \Delta G^*)/T \quad (7)$$

The calculated ΔS^* data are given in TABLE 7. All obtained data show that ΔS values are positive and increase by increasing the temperature which indicate that the inhibitors more oriented and more or-

dered on the surface of the metal. It can be seen that as the temperature increase, there is a decrease in corrosion rate values, accompanied by decrease in the free energy ΔG^* and increase in enthalpy of activation, ΔH^* .

If $\Delta G = -$ value therefore potential is + value which indicated that the cell act as galvanic cell and the reaction is spontaneously by increasing the temperature the reaction shift to more negative free energy more spontaneously. TABLE 7 show that ΔH value is negative this indicated that the reaction is exothermic and the negative value of ΔH is more than 10 indicated that the adsorption is chemical adsorption and the surfactant forms stable layer at the surface of iron which good protect iron form the environment (HCl) and decrease the corrosion rate this illustrated also from the values of inhibition efficiency.

Potentiostatic polarization measurements

Anodic and cathodic polarization curves for mild steel in 1 M HCl with and without various concentrations of used inhibitors are shown in Figure 8. Corrosion inhibition effects of GP and their products (ethoxylated and esterified products) were also studied for the carbon steel alloys in 1M HCl at 25°C by Potentiostatic cathodic and anodic polarization (electrochemical method. The curves were swept from -800 to 0 V (SCE) with scan rate of 20mVs⁻¹. Figure 8. illustrate the effect of adding progressive addition

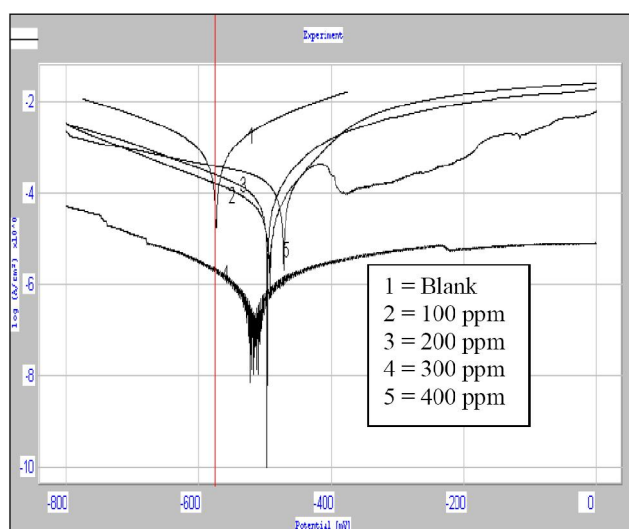


Figure 8 : Potentiostatic polarization curves for carbon steel in 1 M HCl in absence and presence of different concentration of inhibitor (GT- EO 90 -SA), at 298 °K.

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(100–400ppm) of selected inhibitors on the cathodic and anodic polarization curves of carbon steel alloy (X46) in 1M HCl at 25°C. The addition of the used inhibitors decrease 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^[30]. The variable values of the cathodic Tafel slopes suggest that the inhibiting action of such compounds occurs by simple blocking of the electrode surface area, thus decreasing the surface area available for hydrogen evolution without affecting the reaction mechanism^[28,11].

The cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the studied surfactants does not modify the mechanism of this process^[31].

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, those compounds

could be classified as mixed type (anodic/cathodic) inhibitors. These results indicate that GP and their ethoxylated products inhibit HCl corrosion of carbon steel via their adsorption on both anodic and cathodic active sites without modifying the mechanism of corrosion reaction his means that the adsorbed inhibitor molecules block the surface active sites and decrease the area available for hydrogen evolution and metal dissolution reactions^[31]. The measured free corrosion potential was found to be -517.8mV vs. SCE in satisfactory agreement with the published data^[31].

The corrosion potential (E_{corr}), the corrosion current density (I_{corr}) were determined from extra-potential of cathodic and anodic Tafel lines. The polarization resistance (R_p), the slope plotting of potential vs. current density were also determined.

The values of E_{corr} , I_{corr} , R_p , Tafel slopes (b_c , b_a), degree of surface coverage (θ) and inhibition efficiency ($\eta\%$) were calculated for each sample and recorded in TABLE 8. It is clear that the values of corrosion potentials E_{corr} remain almost unchanged indicating that the prepared surfactants acts mainly as mixed type inhibitors^[26].

TABLE 8 : Polarization data of the prepared surfactants.

Sample	Conc. Ppm	I_{corr} mA/cm ²	$-E_{corr}$ mV	R_b Ohm.cm ²	b_a mV	$-b_c$ mV	H	θ	C_i 10 ⁴ Mol/L
Blank	0.0	1.285	57.48	27.39	175.9	206.3	0.0	0.0	0.0
	100	0.0997	497.2	195.93	98.6	185.7	92.2	0.922	0.055
GT-EO90-SA	200	0.0589	493.7	374.9	65.1	181.2	95.4	0.954	0.11
	300	0.0210	473.0	353.3	122.7	368.6	98.3	0.983	0.16
	400	0.01466	517.8	354.7	60.38	176.0	98.8	0.988	0.22

Addition of all prepared inhibitors to HCl solution decreases the values of I_{corr} and increases the values of R_p for carbon steel alloy in such a manner that the higher the concentration of inhibitors added, the lower are the values of I_{corr} and the higher are the values of R_p within inhibitor concentration range used. Since, corrosion rate is directly related to corrosion current density, the inhibition efficiency $\eta\%$ of inhibitors was calculated from polarization measurements by using the following equation:

$$\eta\% = 1 - (I_{corr}/I_{corr}^0) \times 100 \quad (8)$$

where I_{corr}^0 and I_{corr} are the corrosion current densities in the absence and presence of inhibitor respectively. Also, the surface coverage θ was obtained from the relation:

$$\theta = 1 - (I_{corr}/I_{corr}^0) \quad (9)$$

The inhibition efficiency calculated from the polarization measurements are listed in TABLE 8. According to the data of TABLE 8 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^[16-18,23].

The increase in the inhibition efficiency of GT-EO90-SA is due to its large head group size (90 EO units and 90 ethereal bonds) which lies flat on the surface^[32]. An increase in the inhibition efficiency is observed slightly above the CMC^[33] then the efficiency

plateau becomes nearly constant. This may be attributed to a change in the orientation of the adsorbed molecules at the interface resulting from hydrophobic interaction between chains. In this situation, it is likely that the surfactant molecules bind perpendicularly to the surface^[32], which lead to more adsorbed molecules and thus saturation of the surface with surfactant. The film formed corresponds to the saturation of the surface explains the inhibitory effects observed^[33].

GT compounds are characterized by the existence of multipolar functions having amide, C=O and phenyl groups. These polar functions or reaction centers can block the active sites accessible for corrosion^[32]. The other end of the organic molecules can form a barrier between the steel and the medium^[32]. It was also noted that the inhibition efficiency of GT-SA-EO90 is lesser than GT-EO90-SA. This behavior can be attributed to the presence of two adsorbable nitrogen atoms beside free hydroxyl groups and also due to elongation in the molecule by branching which decreases the adsorbability of the surfactant on the surface of the metal.

In spite of greater surface excess, \tilde{A}_{max} , and area per molecule, A_{min} , for other surfactants compared with GT-EO90-SA, the corrosion inhibitive efficiency for the latter is greater than that for the formers. The highest inhibition efficiency of GT-EO90-SA may be attributed to its high molecular weight, high charge density and greatest number of adsorption centers (90 ethereal bonds). This lead to strong adsorption of the surfactant on mild steel surface producing a barrier thus isolates the surface from the medium. The protective film appeared to be very smooth and covered approximately the whole surface. This explains the higher inhibition efficiency of GT-EO90-SA surfactant as corrosion inhibitor compared with the other surfactants.

CONCLUSIONS

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

➤ Nonionic surfactants are produced from reaction of the produced oligomers with PEG, having M.Wt. 400, 1000 and 4000, in presence of β - β' dichloro diethyl ether as a linking agent and NaOH as a catalyst.

- Inhibition efficiencies increase by an increase in inhibitor concentration and an increase in temperature up to 50 °C.
- The uniform increasing inhibition efficiency as the function of concentration are dealing with adsorption phenomenon and the adsorption of all additives obeys the Langmuir adsorption isotherm. The negative values of enthalpies identifies that the adsorption is a physical-sorption type.
- All entropy parameters for adsorption of inhibitors molecules on steel are positive and increase by increasing the temperature which indicate that the inhibitors more oriented and more ordered on the surface of the metal.
- Activation energy increases with addition of inhibitors. It is shown that physical adsorption occurs in the first stage.
- GT-EO90-SA shows an inhibiting effect on the corrosion of mild steel in 1M HCl which increases with inhibitor concentration.
- The activation parameters of the dissolution (E° , ΔH° and ΔS°) were calculated and showed that the used inhibitors decrease the rate of corrosion.

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