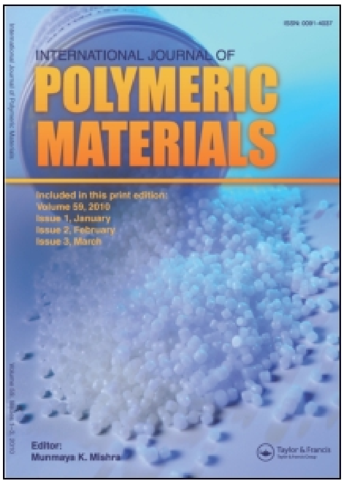

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Synthesis of Some Nonionic Polymeric Surfactants Based on Aminolized PET as Corrosion Inhibitors

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The present work deals with the preparation of nonionic polymeric surfactants based on aminolytic degradation of PET by using diethanolamine (DEA) in the presence of Na-acetate as a catalyst to produce bis(4-hydroxyethylene)terephthalamide (B4HETA) monomer. The monomer produced was reacted with stearic acid and poly (ethylene glycol) with different number average molecular weights, namely 600, 2000 and 4000 gmol^{-1}*, to produce nonionic polymeric surfactants having different hydrophile–hydrophobe balances. The molecular weights and polydispersity of the prepared surfactants were determined by the GPC technique. Surface tension as a function of concentration for different solutions of the prepared surfactants was measured at 298, 308, and 318 K to calculate surface and thermodynamic properties of the investigated compounds. Furthermore, corrosion inhibition efficiency of the investigated nonionic polymeric surfactants was thoroughly studied.*

Keywords: aminolysis, corrosion inhibitors, nonionic surfactant, PET, thermodynamic parameters

INTRODUCTION

The development of new processes for polymer recycling is currently a relevant area of academic and technological research with two main goals: (i) to reduce the increasing volumes of polymer waste coming from different sources and (ii) to convert low-cost sources such as plastic wastes into value-added materials with technological applications [1].

Poly(ethylene terephthalate) (PET) is considered one of the most important engineering polymers in the past two decades due to rapid

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growth in its use. For this reason, recycling PET waste is increasingly demanded for both ecological and economical motivations [2].

There are three distinct approaches to the recycling of post-consumer PET: (i) direct reuse, (ii) physical reprocessing, e.g., grinding, melting, and reforming, and (iii) chemical recycling whereby its components are isolated and reprocessed for use in manufacturing.

Because of the economic appeal, the chemical recycling of PET has been attracting much more attention due to a large variety of processes resulting in a great number of different products. For example, PET can be recycled by catalytic hydrolysis [3], aminolysis [4], alcoholysis [5], glycolysis [6] and even the production of copolymers by reaction with other polymers [7].

The recycled products are used in the chemical industry mainly for plastics [8] as well as in paint, composite applications, and lacquer production. [9]. Products of recycled PET are used for production of unsaturated polyester resins [10], polyurethanes [11], [12], epoxy resins [13] and water-soluble surfactants [14].

Products of the glycolysis of PET were used to produce unsaturated polyester resins and vinyl ester resins in our previous works. [15,16].

Many organic compounds containing oxygen, nitrogen and sulfur atoms have been used as corrosion inhibitors for carbon steel in various aggressive environments [17–25]. The usage of high molecular weight organic compounds such as polymeric surfactants to combat corrosion of carbon steel has found wide application in many fields.

It has been reported that the inhibition process by surfactants is attributed primarily to the adsorption of the surfactant molecules via their functional group onto the metal surface [26]. There are many studies exploring the relationship between adsorption and corrosion with the aid of many recent analytical methodologies [27–32]. In fact, introduction of ethylene oxides into surfactant molecules (ethoxylation) increases the inhibitive effect of surfactant [33–35]. The presence of these groups increases the solubility of the surfactant and, hence, the extent of its adsorption on the metal surface increases and consequently its inhibitive action improves.

The present communication investigates the effectiveness of newly synthesized, environment-friendly, nonionic polymeric surfactants on the corrosion rate of carbon steel. In this respect, diethanolamine (DEA) is used for the aminolytic degradation of PET waste to produce a polymeric surfactant. The surface and thermodynamic properties of the prepared surfactants were measured and correlated to their chemical structures.

EXPERIMENTAL

Materials

PET waste was collected from beverage bottles. DEA was purchased from Aldrich Chemical Co. Ltd (UK). β,β'-dichlorodiethyl ether (DCDE) was supplied by Fluka Chemika (Germany). Stearic acid (SA), *p*-toluenesulfonic acid (PTSA) and poly(ethylene glycol) (PEG) of molecular weights 600 (PEG600), 2000 (PEG2000) and 4000 $\mathrm{g\,mol^{-1}}$ (PEG4000) were purchased from Aldrich Chemical Co. Ltd (UK). Sodium acetate (Na-acetate) was used as a transesterification catalyst for the aminolysis of PET and sodium hydroxide for the reaction of PET monomer with PEG, and were obtained from Aldrich Chemical Co. Ltd (UK). The solvents methylene chloride, acetone, ethanol and benzene used in this work were of analytical grade and used without further purification.

The substrate specimens were cut from unused petroleum pipelines as regular-edged cuboids with dimensions $2 \times 2 \times 0.2$ cm. The percentage chemical composition of the carbon steel alloy used is listed in Table 1.

TECHNIQUES

Aminolysis of PET

Diethanolamine was used for the aminolysis of PET waste materials in the molar ratio 1:6 (PET: ethanolamine) under reflux, in the presence of 0.1% (by weight) of sodium acetate based on the weight of the PET, for time periods varying up to 8 h. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the aminolytic product, bis(4-hydroxyethylene) terephthalamide (B4HETA). The filtrate contained mainly

TABLE 1 Chemical Composition of the Carbon Steel

Element	Analysis (wt %)
C	0.18
Mn	0.25
P	0.12
S	0.05
Al	0.01
Si	0.17
Fe	Rest

unreacted ethanolamine and little quantities of a few water-soluble PET degradation products. The precipitate obtained was filtered and dissolved in distilled water by boiling for about 30 min. Then, the filtrate was concentrated by boiling and then chilled to obtain a white crystalline powder of B4HETA. It was further purified by recrystallization in water. It was then dried in an oven at 80°C and weighed to estimate the yield [36].

Esterification of B4HETA

The esterification reaction was carried out in a reactor fitted with a Dean–Stark separator, mechanical stirrer, a thermometer and nitrogen inlet. B4HETA (0.1 mol) was mixed with 0.1 mol and/or 0.2 mol of SA in a reactor in the presence of *o*-xylene and 0.1 wt% PTSA (based on total weight of reactants). The esterification reaction was carried out under nitrogen atmosphere. The reaction temperature was raised to 413 K until the calculated amount of water was collected from the reaction mixture, which was then cooled to room temperature. The products were precipitated with methanol as non-solvent to remove unreacted materials.

Esterification of B4HETA Using DCDE and PEG

PEG600, PEG2000, and PEG4000 were reacted with B4HETA-SA and DCDE in the presence of NaOH as a catalyst to produce nonionic surfactants using the following procedure: Amounts of 0.1 mol B4HETA-SA, 0.2 mol DCDE, 0.2 mol PEG and 0.4 mol NaOH in 250 mL water were added into a reaction flask fitted with a condenser, mechanical stirrer, and thermometer. The reactants were agitated and slowly heated to a temperature of 443 K. The reaction temperature was maintained for 5 h. The product was treated with an equal volume of an aqueous saturated NaCl solution and neutralized with dilute HCl. The temperature of the mixture was raised to 363 K and maintained for 1 h. The upper waxy layer was separated and dried in a vacuum oven at 323 K to constant weight.

Measurements

Elemental analysis of B4HETA was carried out by using the Heraus combustion apparatus. The purified monomer B4HETA was characterized by FTIR-spectroscopy using a Mattson-Infinity Series Bench to P 961 FTIR-spectrophotometer. The number average molecular weights, *M*n, of the modified PET product and prepared surfactants were measured using gel permeation chromatography (GPC; Waters model 600E).

Surfactants were subjected to surface tension measurements. Here, different concentrations of each sample were prepared and the surface tension at 298, 308, and 318 K was measured using a platinum ring model K9 tensiometer, Krüss (Germany). A specially designed double-jacket glass cell connected to a thermostatted oil bath was used for maintaining the adjusted temperature. Double-distilled water ($\gamma = 72\ \mathrm{dyn\,cm^{-1}}$) was used to prepare the concentrated stock solutions of the prepared surfactants.

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 h before the surface tension measurements were performed. Different solutions of the prepared surfactants having 2 wt% in both double-distilled water and saline solutions (1–5 wt% NaCl) were prepared. Each solution was heated with stirring until it became turbid. Upon cooling, the turbidity started to disappear. The temperature at which the solution became completely clear was recorded as the cloud point of that particular solution.

Weight loss measurements were carried out using a Sartorius analytical balance with precision of 0.1 mg. The solutions were prepared by dissolving the desired weight of the selected surfactants in HCl solution to prepare five different concentrations, 100, 200, 300, 400, and 500. The substrate specimens were polished with 600-grit SiC paper until previous coarseness was removed, degreased with hot acetone [34], then washed with bi-distilled water, and finally dried. Triplicate specimens were used in each experiment and the mean weight losses were reported. The corrosion product is a colloidal precipitate of Fe $(OH)_3$, thus it was washed several times with bi-distilled water and then an ultrasonic bath was used to clean the surface of the samples.

The surface examination of carbon steel was carried out using scanning electron microscope (SEM) (Jeol 5400, Japan).

RESULTS AND DISCUSSION

Aminolysis of PET

Zahn and Pfeifer [37] carried out aminolysis of PET with solutions of hydrazine, benzyl amine, ethylene diamine, hexamethylene diamine, piperidine and aniline. They obtained different reaction products as the diamides of terephthalic acid, which do not possess any potential for further chemical reactions.

According to Popoola [38], the basicity of an amine relative to water, as well as its steric hindrance due to size, control the rate of degradation of PET. During aminolysis of PET with methylamine, the methyl terephthalamide is obtained, which is not reactive enough for recycling into any useful product through further reactions.

The present work applied aminolysis as a route to depolymerization of PET using diethanolamine in the presence of catalyst to yield bis(4-hydroxyethylene) terephthalamide (B4HETA) since the amine group of diethanolamine attacks on the ester linkage of PET. The catalyst used in this reaction form complex with the carbonyl group [39,40] and increases its polarity. The reaction scheme is presented in Figure 1. The optimization of reaction time and concentration of the catalyst during depolymerization of PET waste to obtain maximum yield of B4HETA was achieved at 8 h and 1% (w/w) concentration. Upon exceeding this selected time and concentration, (8 h and 1% (w/w)) the yield decreased, probably due to further degradation of the amide formed [36].

The elemental analysis and molecular weight of the purified product, which confirm that the product of PET depolymerization is B4HETA, are provided in Table 2. From IR spectroscopy, it is clear that the peaks at 1053 and 3452 cm^{-1} indicate the presence of primary alcohol. Disappearance of the peaks for –NH group indicates the formation of tertiary amino group.

Synthesis of Nonionic Surfactants from B4HETA

The present work deals with the synthesis of polymeric surfactants by reacting a hydroxyl end of monomer (B4HETA) with PEG and SA. The plan of synthesis is based on the preparation of polymeric surfactants having different hydrophile-lipophile balances in order to study the effect of the surfactant structure as corrosion inhibitors. To achieve this goal, the work involved the preparation of two different groups of nonionic polymeric surfactants. First, esterification of B4HETA with (1 mol and/or 2 mol) of SA in order to increase the hydrophobicity of the monomer prepared. In this case, SA was reacted at one and two end(s) of B4HETA and the products designated as B4HETA-SA1 and B4HETA-SA2, respectively. Second, etherification of B4HETA-SA1 or B4HETA-SA2 with PEG in the presence of DCDE to produce two groups of the surfactant. Here, three different PEGs used, were namely PEG600, PEG2000, and PEG4000. The first group is designated as B4HETA-SA1-EO13, B4HETA-SA1-EO45, and B4HETA-SA1-EO90, respectively. The same designation was also given to the

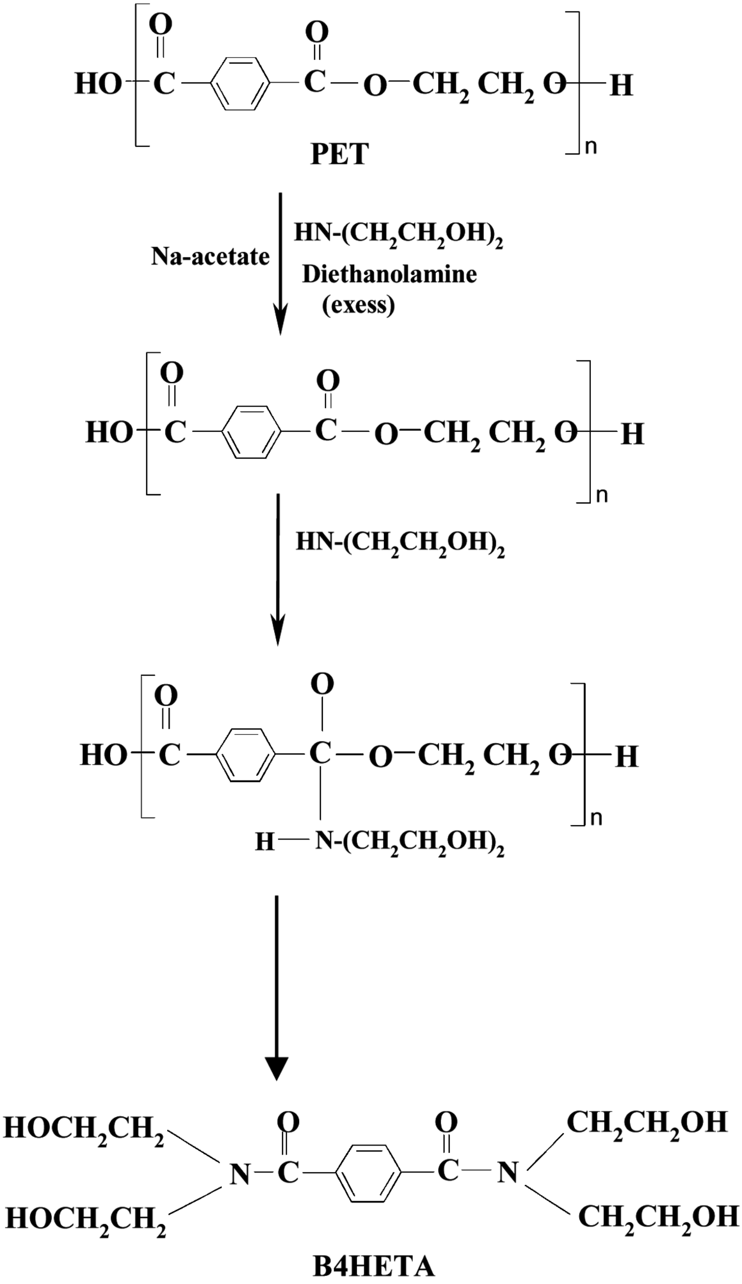


FIGURE 1 Mechanism of aminolysis of PET.

TABLE 2 Characterization of B4HETA ($C_{16}H_{24}N_2O_6$)

			M · Wt	
Elemental analysis (%)	calculated	observed	calculated	observed
C	56.47	54.85	340	350
H	7.05	6.85		
N	8.23	8.0		

other group of surfactant (B4HETA-SA2-EOn). The numbers (n) 13, 45, and 90 refer to the number of ethylene oxide units in the PEG.

Surface Activity

It is well known that modification of a polymer backbone yields different hydrophobicity, chain flexibility and solubility due to the difference of inter- and intramolecular interactions. Accordingly, the selection of the proper solvent depends largely on the type and quantity of the branches attached to the backbone. In our case, the prepared surfactants based on B4HETA are soluble in cold or hot water. The solubility and state of polymer solutions should depend on the backbone composition and hydrogen bonds between the polar groups of the modified PET. The solubility of the prepared surfactants also depends on the method of purification.

However, different segments in the modified PET and PEG copolymers have dissimilar solubility properties, which leads to the difference in the hydrophilic-lipophilic balance (HLB) of the surfactants. The HLB values are calculated using the following formula [41,42] for nonionic surfactants:

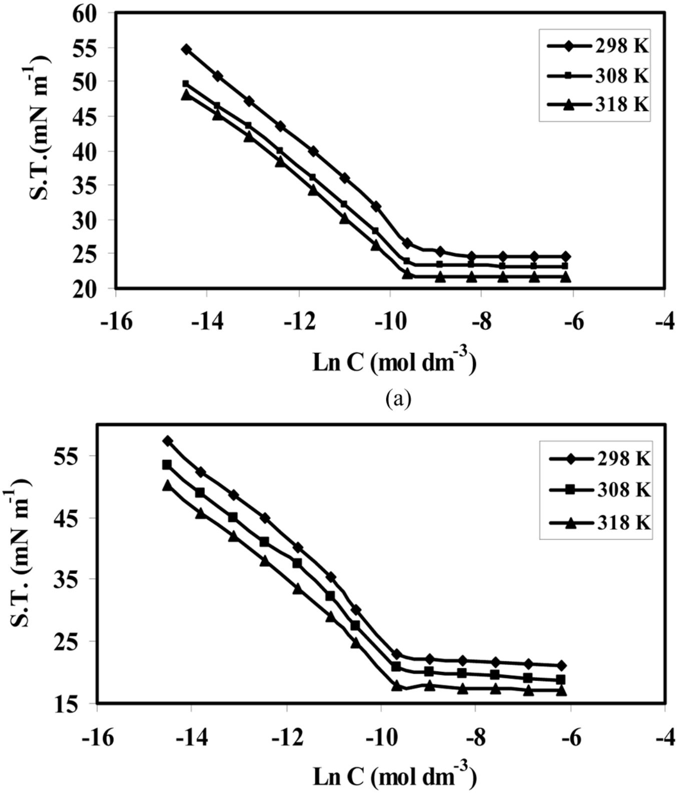
$$\mathrm{HLB} = [M\mathrm{H}/(M\mathrm{H} + M\mathrm{L})] \times 20,$$

where MH is the formula weight of the hydrophilic portion of the surfactant molecule and ML is the formula weight of the hydrophobic portion. HLB values of nonionic surfactants based on B4HETA were calculated and are listed in Table 3. The data indicate that the HLB values of the surfactants prepared varied from 10 to 17, which reflect their good solubility in water. Inside the solution, the soluble molecules tend to form micelles. The micellization process leads to a reduction of the free energy of the system. The micellization and adsorption of surfactants are based on their CMC, which was determined by the surface balance method. The CMC values of the prepared polymeric surfactants were determined at 298, 308, and 318 K from

TABLE 3 GPC Characteristics and HLB Values of Ethoxylated PET Monomer

Aminolytic product	Designation	$Mn(\text{gmol}^{-1})$ det.	Polydispersity	HLB
B4HETA	B4HETA	350	1.12	—
B4HETA-SA1	B4HETA-SA1	630	1.02	—
B4HETA-SA1-EO	B4HETA-SA1-EO13	1240	1.10	13.5
	B4HETA-SA1-EO45	2420	1.12	17.5
	B4HETA-SA1-EO90	4500	1.13	18.6
B4HETA-SA2	B4HETA-SA2	960	1.03	—
B4HETA-SA2-EO	B4HETA-SA2-EO13	1600	1.12	11.5
	B4HETA-SA2-EO45	2880	1.14	15.6
	B4HETA-SA2-EO90	4975	1.15	17.5

the change in the slope of the plotted data of surface tension (γ) vs. natural logarithm of the solute concentration (log C). Some selected plots of the relation between surface tension (ST) and log C are supplied in Figure 2. This kind of plot is used for estimating the surface activity and confirming the purity of the studied surfactants. It is of interest to mention that all isotherms showed one phase, which is considered as an indication of the purity of the prepared surfactants. The CMC values for nonionic surfactants at different temperatures are given in Table 4, together with values for the surface tension at CMC. Generally, increasing the number of ethylene oxide units increases CMC values [43] due to increasing hydrophilicity and solubility of the surfactants in water. Such improved solubility lowers the tendency for the surfactant to form micelles. Some investigators [44,45] found that increasing the number of EO units decreases CMC. However, as these surfactants have very long hydrophobic tails (at least 16 carbons) and relatively few EO (6–19) units, it may be possible in these cases that the low water solubility of these surfactants is due to the long alkyl chain, not to the EO chain. This behavior is obvious only over some EO ranges, as would be expected from the increase in the hydrophilic character of the molecule resulting from this change. This behavior is based on coiling of the poly (ethylene oxide) chains [46]. In the present system, it was found that the CMC values show an increase with decreasing number of EO groups in the molecule. This can be attributed to the fact that as the number of EO units increases the total molecular weight of the surfactants increases and, consequently, the area occupied by each molecule at the aqueous/air interface increases. Hence, the number of molecules required to cause interface saturation is decreased and the process



(a)

(b)

FIGURE 2 Surface tension concentration isotherm of (a) B4HETA-SA1-EO90 and (b) B4HETA-SA2 EO90.

of micellization commences earlier compared to the surfactants having lower oxyethylene content. This speculation is in accordance with a previous explanation [47].

It was also observed that surfactants bearing SA at both ends possess lower CMC values than those ended at one end. This can be attributed to the formation of hydrogen bonds between both hydroxyl ends with water that increases the solubility of surfactants, which in turn increases the CMC value. It is of interest to mention that the CMC for the same surfactant decreases with increasing temperature. This may be attributed to the increase in the radius of gyration of the molecule as a result of increasing the temperature [48]. The same results were obtained from measuring the cloud temperatures of the prepared surfactants in water. It was established [48] that aqueous

TABLE 4 CMC of Surfactants Based on B4HETA at Different Temperatures

		CMC*			γ_{CMC}*		
Designation	Cloud point (°C)	298 K	308 K	318 K	298 K	308 K	318 K
B4HETA-SA1-EO13	55–57	2.07×10^{-4}	1.03×10^{-4}	5.16×10^{-5}	39.3	35.6	33.1
B4HETA-SA1-EO45	65–67	1.12×10^{-4}	5.36×10^{-5}	2.68×10^{5}	32.1	30.2	29.6
B4HETA-SA1-EO90	70–72	2.65×10^{-5}	2.65×10^{-5}	1.59×10^{-5}	27.9	28.2	26.2
B4HETA-SA2-EO13	60–62	9.9×10^{-5}	5.77×10^{-5}	2.98×10^{-5}	34	34.7	31.9
B4HETA-SA2-EO45	69–71	8.27×10^{-5}	5.17×10^{-5}	3.04×10^{-5}	31	29.7	26.9
B4HETA-SA2-EO90	73–75	3.34×10^{-5}	1.67×10^{-5}	8.36×10^{-6}	30.1	27.5	24.7

*CMC in mol L^{-1}; γ_{CMC} in mNm^{-1}.

solutions of nonionic surfactants having oxyethylene content below about 80 wt% 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. The temperature at which clouding occurs depends on the structure of the polyoxyethylenated nonionic surfactant. The cloud temperatures were measured and listed in Table 4. As seen from the presented data, the cloud points were progressively higher with increasing length of the hydrophilic side chains and molecular weight of PEG.

The direct determination of the amount of surfactant adsorbed per unit area of liquid-gas or liquid–liquid interface is possible, but not generally undertaken because of the difficulty of isolating the interfacial region from the bulk phase for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from the surface or interfacial tension measurements. Some other parameters can also be measured, they include the following,

- The concentration of surfactants at the water–air interface is known as surface excess concentration $\Gamma_{\max}$, and calculated from the following equation:

$$\Gamma_{\max} = \frac{1}{RT}\left(\frac{-\delta\gamma}{\delta \ln c}\right)_{\tau} \tag{1}$$

where

$$\left(\frac{-\delta\gamma}{\delta \ln c}\right)_{\tau}$$

is the slope of the plot of γ *versus* ln c at constant temperature (T) and (R)) is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$). The surface excess concentration at surface saturation is a useful measure of the effectiveness of adsorption of surfactant at the liquid-gas or liquid–liquid interface, since it is the maximum value that adsorption can attain.

- The Γ_{max} values were used for calculating the minimum area A_{min} at the aqueous-air interface (Eq. (2)). The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecules, when compared with the dimensions of the molecule as obtained from models.

$$A_{min} = 10^{16}/N\Gamma_{max} \tag{2}$$

where N is Avogadro's number.

The effectiveness of surface tension reduction, $\Pi_{CMC} = \gamma o - \gamma_{CMC}$ where γo is the surface tension of water and γ_{CMC} is the surface tension of solution at (CMC) [49], was determined at different temperatures. The Γ_{max}, A_{min} and Π_{CMC} values were calculated and are listed in Table 5. From the mathematical equations used for calculating Γ_{max} and A_{min}, it is obvious that A_{min} of nonionic surfactants is inversely proportional to Γ_{max}. The data showed that the A_{min} at aqueous/air interface increase with the increase in the number of EO units in the molecule. This finding is in harmony with the data observed for nonionic polyoxyethylenated surfactants [50–53]. In addition, A_{min} increases with increasing temperatures as a result of breakdown of the intramolecular bondings by the effect of heat [54].

TABLE 5 Surface Properties of Surfactants Based on B4HETA at Different Temperatures

	Γ_{max} X 10^{10*}			$A_{min}{}^*$			$\Pi_{CMC}{}^*$		
Designation	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
B4HETA-SA1-EO13	3.31	3.04	2.44	0.050	0.054	0.068	32.7	36.4	38.9
B4HETA-SA1-EO45	2.17	2.02	2.01	0.076	0.082	0.082	39.9	41.8	42.4
B4HETA-SA1-EO90	1.48	1.35	1.31	0.111	0.122	0.126	44.1	43.8	45.8
B4HETA-SA2-EO13	2.68	2.66	2.40	0.061	0.062	0.069	36.6	37.3	40.1
B4HETA-SA2-EO45	2.64	2.55	2.35	0.062	0.065	0.070	41	42.3	45.1
B4HETA-SA2-EO90	2.44	2.38	2.30	0.067	0.069	0.071	41.9	44.5	47.3

$^*\Gamma_{max}$ in mol $\mathrm{cm^{-2}}$; A_{min} in $\mathrm{nm^2}$ $\mathrm{(molecule)^{-1}}$; Π_{CMC} in $\mathrm{mNm^{-1}}$.

Thermodynamic Parameters of Micellization

The values of free energy, ΔG_{mic}, enthalpy, ΔH_{mic}, and entropy, ΔS_{mic} for nonionic surfactants were calculated from the following equations and are listed in Table 6.

$$\Delta G_{\mathrm{mic}} = RT \ln(\mathrm{CMC}) \tag{3}$$

$$-\Delta S_{\mathrm{mic}} = \delta \Delta G_{\mathrm{mic}} / \delta T \tag{4}$$

$$\Delta H_{\mathrm{mic}} = \delta G_{\mathrm{mic}} + T \Delta S_{\mathrm{mic}} \tag{5}$$

Analyzing the thermodynamic parameters of micellization leads to the fact that micellization is spontaneous ($\Delta G_{\mathrm{mic}} < 0$). The data showed that ΔG_{mic} values are more negative with increasing number of EO units and sulfate content. This indicates that the increase of hydrophilic groups favors the micellization process, thus covering the most important requirement for surfactant detergency. On the other hand, the data reveal that ΔG_{mic} increases with increasing temperature from 298 to 318 K. The data listed in Table6 show that ΔS_{mic} values are all positive, indicating increased randomness in the system upon transformation of the nonionic surfactant molecules into micelles, or increasing freedom of the hydrophobic chain in the nonpolar interior of the micelles compared to the aqueous environment. The increase of positive ΔS_{mic} value with increasing number of oxyethylene units in the surfactant molecule has been observed by other investigators [15,55]. This can be attributed to the fact that increasing molecular weights of PEG leads to increasing hydrogen bonds between water and PEG, which introduces some restriction on the motion of surfactants. The dissolution of the oxyethylene units has been stated [55]

TABLE 6 Thermodynamic Parameters of Micellization for Surfactants

	298 K		308 K		318 K		
Designation	$-\Delta G_{\mathrm{mic}}$	ΔH_{mic}	$-\Delta G_{\mathrm{mic}}$	ΔH_{mic}	$-\Delta G_{\mathrm{mic}}$	ΔH_{mic}	ΔS_{mic} (KJ mol^{-1} K^{-1})
B4HETA-SA1-EO13	21.28	6.5112	23.07	6.7297	24.85	6.9482	0.100
B4HETA-SA1-EO45	21.84	13.512	23.61	13.96	25.80	14.900	0.122
B4HETA-SA1-EO90	25.53	14.696	26.39	15.189	27.24	16.000	0.135
B4HETA-SA2-EO13	22.02	26.31	23.50	26.45	25.26	27.31	0.1622
B4HETA-SA2-EO45	22.03	29.65	24.30	29.95	27.06	30.35	0.1711
B4HETA-SA2-EO90	26.11	35.751	26.98	36.90	29.51	38.15	0.2076

$-\Delta G_{\mathrm{mic}}$ and ΔH_{mic} in KJ mol^{-1}.

to be the major contributing factor to the positive entropy of micellization in polyoxyethylenated nonionics.

The listed values of ΔH_{mic} are all positive, in contrast to those of Crook *et al.* [56] who reported negative ΔH_{mic} values at 298 K for *p*-*tert*-octylphenoxypoly(ethylenoxy ethanol)s containing less than four oxyethylene units. By increasing the number of oxyethylene units in the molecule, the values of ΔH_{mic} increase. This is in accord with the observations of other investigators [55] indicating that a greater number of hydrogen bonds between polyoxyethylene chain oxygen and water molecules is broken in the micellization process as the number of oxyethylene units in the molecule increases.

Thermodynamic Parameters of Adsorption

The values of ΔG_{ad}, ΔH_{ad} and ΔS_{ad} for nonionic surfactants were calculated from the following equations and are listed in Table 7.

$$\Delta G_{\mathrm{ad}} = RT\ \ln(\mathrm{CMC}) - 0.6023\,\Pi_{\mathrm{CMC}}A_{\min} \tag{6}$$

$$-\Delta S_{\mathrm{ad}} = \delta\,\Delta G_{\mathrm{ad}}/\delta T \tag{7}$$

$$\Delta H_{\mathrm{ad}} = \Delta\,G_{\mathrm{ad}} + T\Delta S_{\mathrm{ad}} \tag{8}$$

All ΔG_{ad} values are more negative than ΔG_{mic}, indicating that adsorption at the interface is associated with a decrease in the free energy of the system. This may be attributed to the effect of steric factor on inhibition of micellization more than its effect on adsorption. The values of ΔS_{ad} are all positive and are greater than ΔS_{mic} for nonionic surfactants based on B4HETA. This may reflect the greater freedom of motion of the hydrophobic chains at the planar air-aqueous solution

TABLE 7 Thermodynamic Parameters of Adsorption for Surfactants

	298 K		308 K		318 K		
Designation	$-\Delta G_{\mathrm{ad}}$	ΔH_{ad}	$-\Delta G_{\mathrm{ad}}$	ΔH_{ad}	$-\Delta G_{\mathrm{ad}}$	ΔH_{ad}	ΔS_{ad} (KJ mol^{-1} K^{-1})
B4HETA-SA1-EO13	23.27	7.908	24.26	8.15	26.22	8.18	0.1085
B4HETA-SA1-EO45	24.88	15.48	25.68	15.99	28.00	16.00	0.1388
B4HETA-SA1-EO90	27.56	16.47	28.56	16.959	29.51	17.48	0.1478
B4HETA-SA2-EO13	24.27	28.05	25.26	28.07	26.44	28.76	0.1722
B4HETA-SA2-EO45	25.88	33.04	26.68	33.19	28.65	34.048	0.1886
B4HETA-SA2-EO90	27.69	40.66	28.80	41.660	29.97	42.886	0.2288

$-\Delta G_{\mathrm{mic}}$ and ΔH_{mic} in KJ mol^{-1}.

interface compared to that in the relatively cramped interior beneath the convex surface of the micelle. This indicates that the steric factor inhibits micellization more than adsorption does for nonionic surfactants based on B4HETA. On the other hand, the positive values of ΔH_{ad} are much greater in all nonionic surfactants than the corresponding values of ΔH_{mic}, indicating that more bonds between polyoxyethylene chain oxygen and water molecules are broken in the process of adsorption at the air-aqueous solution interface than in micellization [57]. In general, it is observed that an increase in the size of the hydrophilic group in the synthesized nonionic surfactants based on B4HETA inhibits micellization more than adsorption at the air-aqueous solution interface. This may indicate that these surfactants are more readily adsorbed at air-aqueous solution interface and thus could show marked corrosion inhibition efficiency.

Due to their best thermodynamic properties, B4HETA-SA1-EO90 designated as (I) and B4HETA-SA2-EO90 designated as (II) were selected to be used as corrosion inhibitors. This means that the inhibition efficiency increases with the increase of the number of ethylene oxide units. This may be attributed to an increase of the electron density distribution exerted by the incorporation of ethylene oxide units in the chemical structure [58].

Weight Loss Measurement

The weight loss was calculated using the following equation:

$$\Delta W = W_1 - W_2 \tag{9}$$

where W_1 and W_2 are the weight of the specimen before and after reaction, respectively. The inhibition efficiency $\eta\%$ was computed by the equation:

$$\eta\% = \left(\omega_0 - \frac{\omega}{\omega_0}\right) \times 100 \tag{10}$$

where w_0 and w are the values of weight losses in the absence and presence of the inhibitor, respectively. And

$$k = \frac{\text{weight loss}\,(\text{mg}\,\text{cm}^{-2})}{\text{time}\,(\text{h})} \tag{11}$$

where k is the corrosion rate of carbon steel.

For brevity, Figure 3 shows the weight loss-time curves for the inhibitor II as a representative sample. It is evident from the figure that the weight loss of carbon steel decreases with increasing the

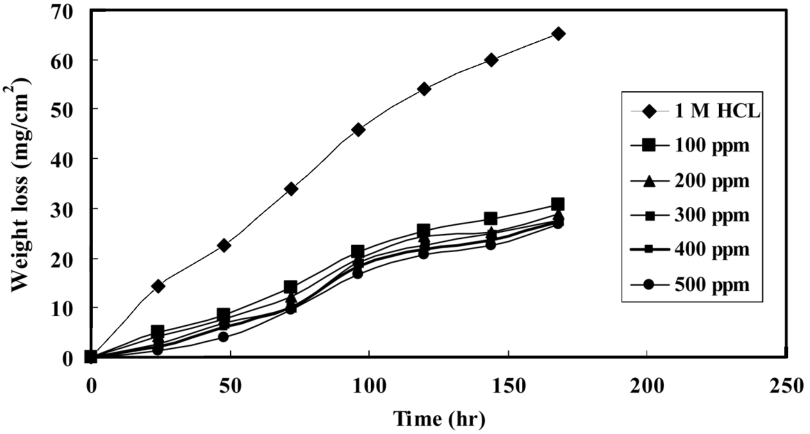


FIGURE 3 Weight loss-time curves for carbon steel dissolution in 1 N HCL in absence and presence of different concentrations of B4HETA-SA2-EO90 at 298 K.

inhibitor concentration and increases with increasing the immersion time. Furthermore, the effect of these inhibitors increases with increasing the length of the hydrocarbon chain (R).

The percentage inhibition efficiency (η%) at different concentrations was calculated and summerized in Table 8. The results indicated that the inhibition efficiency of the inhibitors decreases in the following order I < II. This is due to the inhibitor II having a longer hydrocarbon chain than inhibitor I [59]. Figure 4 shows the effect of various concentrations of the inhibitors I and II on the corrosion rate of carbon steel in 1 M hydrochloric acid solution after 6 days immersion time.

TABLE 8 Variation of the Degree of Surface Coverage (θ), Percentage Inhibition Efficiency (η%) and the Corrosion Rate of Carbon Steel as Determined by Weight Loss Measurements at 25 ± 1°C

	I			II		
Conc. ppm	Corrosion rate (k)	θ	η%	Corrosion rate	θ	η%
100	0.1984	0.5695	56.951	0.1125	0.6224	60.247
200	0.1804	0.6077	60.771	0.0910	0.6959	69.463
300	0.0910	0.6959	69.463	0.0694	0.7659	76.591
400	0.0694	0.7659	76.591	0.0622	0.7889	78.890
500	0.0622	0.7889	78.890	0.0437	0.8484	84.846

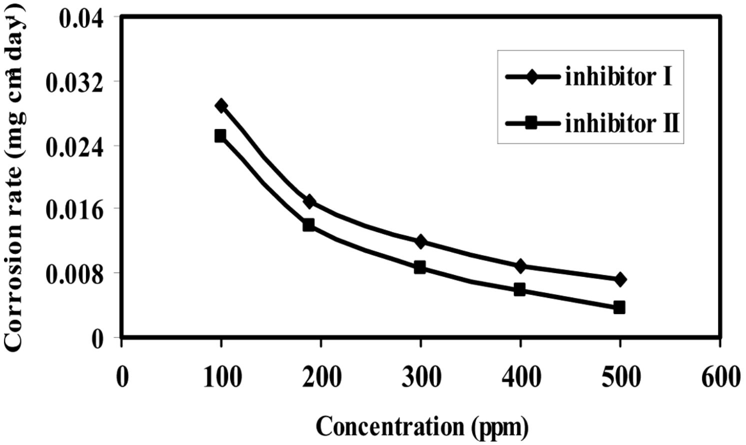


FIGURE 4 Effect of concentration of the inhibitors I and II on the corrosion rate of carbon steel in 1 M HCl after 6 days.

From these curves, one can gather that the corrosion rate decreases with the increasing concentration. Various adsorption isotherm equations, namely, Temikin, Langmuir and Freundlich, were applied to the inhibition data for the surfactants I and II. A plot of log $(\theta/1-\theta)$ vs. log C is given in Figure 5, where θ is the fractional coverage of the surface with the inhibitors. All the investigated inhibitors, therefore, seem to obey best the Langmuir adsorption isotherm, indicating that the inhibitor molecules are adsorbed on the metal surface and form

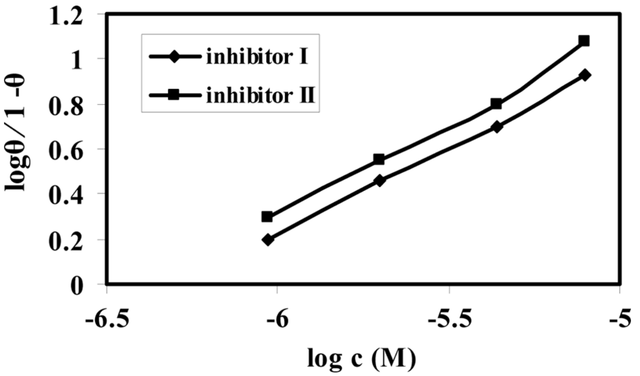


FIGURE 5 Dependence of $\log(\theta/1-\theta)$ on logarithm of concentration of the inhibitors I and II.

a barrier, which isolated the metal surface from the electrolyte. The deviation may be explained on the basis of the interaction between the adsorbed species and the metal surface [60].

The SEM image of polished carbon steel samples are not shown here for brevity. They shows that the surface of the carbon steel was strongly damaged in the absence of the inhibitors after immersion in 1 M hydrochloric acid solution for 6 days. Also, there is a good protective film present on other carbon steel surfaces after immersion for the same time interval in 1 M hydrochloric acid solution containing 500 ppm of the inhibitor II. This confirms the highest inhibition efficiency of the inhibitor II at 500 ppm concentration.

CONCLUSIONS

- New polymeric surfactants based on recycled PET through aminolysis were prepared.
- The synthesis of B4HETA through aminolysis of PET results in high yield and shorter reaction time.
- B4HETA has the potential of recycling it into useful products through various chemical reactions.
- The prepared surfactants favor adsorption at interface more than micellization in bulk aqueous solution.
- The critical micelle concentration is considered a key factor in determining the effectiveness of surfactants as corrosion inhibitors.
- The inhibition effectiveness of the selected nonionic surfactants (I and II) increases with the total number of carbon atoms in the aliphatic hydrocarbon chain.
- Surfactant II shows superior performance over surfactant I.
- The inhibition mechanism is attributed to the strong adsorption ability of the selected surfactants on carbon steel surface, forming a good protective layer, which isolates the surface from the aggressive environment.
- The results of SEM indicate that the inhibitor II forms a good protective film on the carbon steel surface.

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