

Surfactants from Recycled Poly (ethylene terephthalate) Waste as Water Based Oil Spill Dispersants

Ayman M. Atta*, Manar E. Abdel-Rauf, Nermine E. Maysour, A. M. Abdul-Rahiem and Abdel-Azim A. Abdel-Azim

Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt
(*Author for correspondence; E-mail: khaled_00atta@yahoo.com)

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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 different weight ratios of diethanolamine and triethanolamine and manganese acetate as catalyst. The molecular weights of the prepared oligomers were calculated from hydroxyl number and determined from GPC measurements. The produced oligomers were reacted with polyethylene glycol, PEG, which have different molecular weights 400, 1000 and 4000. Interfacial tension and the effectiveness in oil dispersion of the synthesized surfactants were reported. It was found that, the maximum efficiency of oil spill dispersants was reached to maximum when the surfactant molecules ended with two PEG 1000 moities.

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

Surfactants find applications in different operations of petroleum production. They have become important in drilling, cement, slurries, fracturing, acidization, demulsification, corrosion inhibitors, transportation, cleaning, water flooding, chemical, foam and steam flooding and environment protection as oil spill dispersants [15]. They are essential used to improve the production economics and total recovery of petroleum [16].

This manuscript explores the surfactants from recycled PET and the use for oil spill dispersants. The overall policy of the present work is to alleviate environmental pollution caused from both plastic waste and oil spill and also to reduce the cost for production of dispersants. In this respect, PET waste is converted into glycolyzed products via glycolysis reaction using different ratios of diethanolamine (DEA) and 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 oil spill dispersants. In addition it is important for academic and scientific research to determine surface active properties of the prepared surfactants. Accordingly, the surface properties, dispersion efficiency and the washing power of the prepared compounds will be investigated.

Experimental

Materials and methods

PET waste was collected from beverage bottles. The intrinsic viscosity of PET in *m*-chlorophenol at 298.15 K was found to be 0.015 dm³ kg⁻¹. The weight average molecular weight, determined by gel permeation chromatography (GPC), was close to 63,200 g mol⁻¹. Diethanolamine DEA, triethanolamine (TEA), were purchased from Aldrich Chemical Co. Ltd. (UK). β β' dichloro diethylether

(DCDE) is supplied from Fluka Chemika (Germany). 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, dimethyl formamide, methylene chloride, acetone, ethanol and benzene used in this work have analytical grads.

Techniques

Converting PET waste to Glycolized Products (GPs)

PET bottle waste was depolymerized at different weight ratios of PET to DEA or TEA ranging from 1:1 to 1:3 (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 4 h and at 200–210 °C for 3 h. The temperature of the reaction was then lowered to 100 °C for 1 h. The mixture was allowed to cool to room temperature. The glycolized products of PET with DEA are designated here as GD1, GD2 and GD3. The glycolized products of PET with TEA are coded as GT1, GT2 and GT3. Where, the number 1, 2 and 3 are related to the weight ratios between DEA or TEA and PET.

Ethoxylation of GPs 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 glycolized 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 mol GP, 0.2 mol β , β' -dichloro diethyl ether, 0.2 mol PEG and 0.4 mol NaOH. The reactants were agitated and slowly heated to a temperature of 170 °C. The reaction mixture was maintained at this temperature for 5 h. 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 1 h. The upper waxy layer was separated and dried in vacuum oven at 50 °C to a constant weight. The produced surfactants from GD are designated here as GD1-EO9, GD2-EO22, and GD3-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. Similarly the designations as GT1-EO9, GT2-EO22, and GT3-EO90 are assigned for the surfactants of GTA with PEG.

Measurements

The nitrogen content of recycled PET with both DEA and 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 [17]. In order to determine the amount of free DEA, a weighed quantity (10% of the total weight of the reactants) of the glycolized product was dissolved in ethyl alcohol and precipitated by diethyl ether. 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 difference between the initial and final weights represents the amount of free DEA and TEA.

The purified compounds were analyzed using ATI Mattson Genesis Series FTIR spectrophotometer. The prepared surfactants were dissolved in CDCl₃ 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 328 K 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 ($\gamma = 72$ dyn/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 h before the surface tension measurements were performed.

Spinning drop interfacial tensiometer, Model Kruss Site-04, was used for measuring the interfacial tension between surfactants aqueous solutions and benzene as an oil phase for which the elongation of the injected drop in the capillary was measured at an adjusted temperature (298 K) and speed of rotation. The interfacial tension (γ) was calculated from the equation, $\gamma = 3.427 \times 10^{-7} (0.17 \delta)^3 \times n^2 \times \Delta\rho$, where δ , n and $\Delta\rho$ are the diameter of the drop, the speed of rotation and the density difference between the oil phase and the surfactant aqueous solution, respectively.

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

Table 1. Specifications of land Belayim crude oil.

Test	Method	Value
API gravity at 60 F	Calculated	21.7
Viscosity at 60 F (CST)	IP71	762.8
Specific gravity at 60 F	IP 160/87	0.843
Asphaltenes contents (wt.%)	IP 143/84	8.8

at which the solution becomes completely clear was recorded as the cloud point of this particular solution.

Evaluation of prepared surfactants as oil spill dispersants

The dispersions test [18] was used to evaluate the efficiency of the prepared surfactants as oil spill dispersants. The Egyptian land Belayim crude oil was used throughout this study for testing the efficiency of the prepared surfactants. The specification of land Belayim crude oil was listed in Table 1. The Environmental Protection Agency [EPA] test method [18] has been applied for testing the prepared surfactants as oil spill dispersants. The test is based on plotting the absorbance of crude oil solutions vs. their concentrations. Different concentrations were prepared by successive dilution of a stock solution having a concentration of 3.5 mg/l. A Shimadzu spectrophotometer, model UV-120-02 was used for measuring the absorption spectra. The characteristic peak was determined at 260 nm. The absorbance for each concentration was determined at this wavelength and the absorbance values were plotted versus surfactant concentrations for constructing the calibration curve. However, the oil sample (100 ml) was poured on the surface of Suez gulf water contained in a cylindrical glass container. The dispersant was applied to the oil in a fine stream. After one minute energy is imparted to the oil/dispersant mixture by hosing and agitating the mixture with pressurized water stream. Samples were then withdrawn from the tank after 10 min. The oil was then extracted with methylene chloride and its amount was determined calorimetrically by calibration of the standard curve.

Results and discussions

Three glycolized products, coded as GD1–GD3, were obtained by depolymerization of PET with DEA having

1:3% (weight percentage of PET to DEA). The same glycolized products, coded as GT1–GT3, were obtained when TEA was replaced by DEA at overall reaction time 8 h. 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 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 either DEA or 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 glycolized PET [19]. The glycolized products were analyzed for hydroxyl values (in mg KOH/g) after removal of free DEA and TEA (expressed as wt.%). The characteristic data of the produced oligomers are listed in Table 2. It was found that, the data of hydroxyl number of the oligomers increase with increasing DEA or TEA percentage. Accordingly, the increase of the DEA and TEA contents in the reaction medium affords better chance for dissolving the initially destructed materials and hence enhances the reactivity between the solvent (DEA or TEA) and the dissolved glycolized product. This certainly leads to more and more destruction due to the increased probability of collisions between the reactants. It is well known that the use of a large excess of glycol in destructing PET leads to formation of secondary OH groups in the formed oligoesters [20]. The data listed in Table 2 also, reveal that the amount of glycol consumed in producing GD1 is only 10.77%. This percentage increases to 12.6% and 14.42% for GD2 and GD3, respectively. This supports the previous speculation that relates the extent of degradation reaction with the amount of glycol. The theoretical molar mass of the glycolized PET products could be easily calculated from the data of nitrogen content and the percentage of reacted DEA or TEA. In fact, if one macromolecule of PET ($M_w = 63.200$) reacts with n molecules of DEA or TEA, its molecular weight becomes $63.200/(1 + n)$. Thus, for the GD1 sample reacted for 8 h, 100 g of PET (= 1.58 mmol) have reacted with 10.77 g of DEA (= 102 mmol) and the molecular weight should have been lowered to be equal to $(63.200/(1 + 102/1.58)) = 957$. The results of calculations are shown in Table 2. The molecular weights of the

Table 2. Characterization of the glycolized PET products.

Designations	Wt. ratio of DEA or TEA: PET	Percentage of DEA or TEA		N%	OH values	Mn	
		Percentage (%) ¹	Percentage (%) ²			Theo.	Cal.
GD1	1:1	10.77	10.68	1.424	182.5	957	965
GD2	2:1	12.60	12.49	1.665	242	826	827
GD3	3:1	14.42	14.31	1.908	289	722	724
GT1	1:1	13.02	12.95	1.217	318	1131.4	1128
GT2	2:1	14.93	14.85	1.395	415	988.7	986
GT3	3:1	17.61	17.52	1.646	516	839	838

¹Calculated from N₂ content.

²% unreacted glycol = $\frac{\text{wt of free glycol}}{\text{wt of glycol used in glycolysis process}} \times 100$.

Table 3. GPC characteristics and HLB values of ethoxylated PET oligomers.

Glycolyzed product	Designation	M.wt. (Cal.) (g mol ⁻¹)	M.wt. (Det.) (g mol ⁻¹)	Polydispersity	HLB
GT1	GT1-EO9	2068	2064	1.003	7.74
	GT1-EO22	3268	3260	1.002	12.23
	GT1-EO90	9268	9264	1.002	17.26
GT2	GT2-EO9	1926	1920	1.004	8.31
	GT2-EO22	3126	3118	1.006	12.8
	GT2-EO90	9126	9121	1.006	17.53
GT3	GT3-EO9	1778	1770	1.004	8.99
	GT3-EO22	2978	2971	1.007	13.43
	GT3-EO90	8978	8973	1.007	17.82
GD1	GD1-EO9	1905	1901	1.008	8.86
	GD1-EO22	3105	3100	1.009	12.88
	GD1-EO90	9105	9103	1.007	17.57
GD2	GD2-EO9	1767	1760	1.009	9.03
	GD2-EO22	2967	2961	1.006	13.48
	GD2-EO90	8967	8962	1.006	17.84
GD3	GD3-EO9	1664	1660	1.007	9.61
	GD3-EO22	2864	2862	1.009	13.97
	GD3-EO90	8864	8859	1.008	18.13

glycolyzed PET with DEA or TEA were determined by GPC technique as described in the experimental section. The data of the molecular weights of the glycolyzed PET with DEA or TEA were tabulated in Table 3. The appearance of sharp peak in the chromatograms obtained from the GPC analysis, not represented for brevity, indicates the purity of the glycolyzed PET oligomers with either DEA or TEA. The calculated number average molecular weight (Mn) of glycolyzed PET and nitrogen contents for PET oligomers after removing the free DEA or TEA indicate

that the extent of PET depolymerization increases with increasing the amount of DEA or TEA.

The structure of the PET oligomers with DEA or TEA was verified from their IR spectra. The spectra of GD and GT were not represented for brevity. The presence of strong peak at 3450 cm⁻¹, in all spectra, indicates the termination of the glycolyzed products with hydroxyl groups. The band observed at 810 cm⁻¹ for all depolymerized PET is assigned to -CH out-of-plane bending of *p*-substituted phenyl indicates that the oligomers contain terephthalate moiety. This confirms the presence of phenyl rings in depolymerized products. The presence of strong peaks at 1745 cm⁻¹ and 1150 cm⁻¹, which were assigned for C=O stretching and C-O stretching of ester groups, indicates the incorporation of ester groups in all depolymerized PET products.

A further confirmation for glycolysis of PET with DEA and TEA was detected by ¹HNMR. In this respect the spectra of GD1 and GT1 were selected and represented in Figure 1a and b, respectively. The signals at chemical shifts 7.4, 4.8 and 4.3 ppm, which represent *p*-substituted phenyl group, OOCCH₂CH₂COO and OCH₂CH₂N of glycolyzed PET respectively, were observed in all spectra. The signal observed at 2.6 ppm in the spectra of GD1 and GT1, which represent OH group of glycolyzed DEA and TEA, indicates the presence of terminal OH in all glycolyzed PET.

Synthesis of polymeric surfactants from GD and GT oligomers

Breen and Towner [21] prepared surfactants by reacting a polyol with an aromatic hydrocarbon containing a single

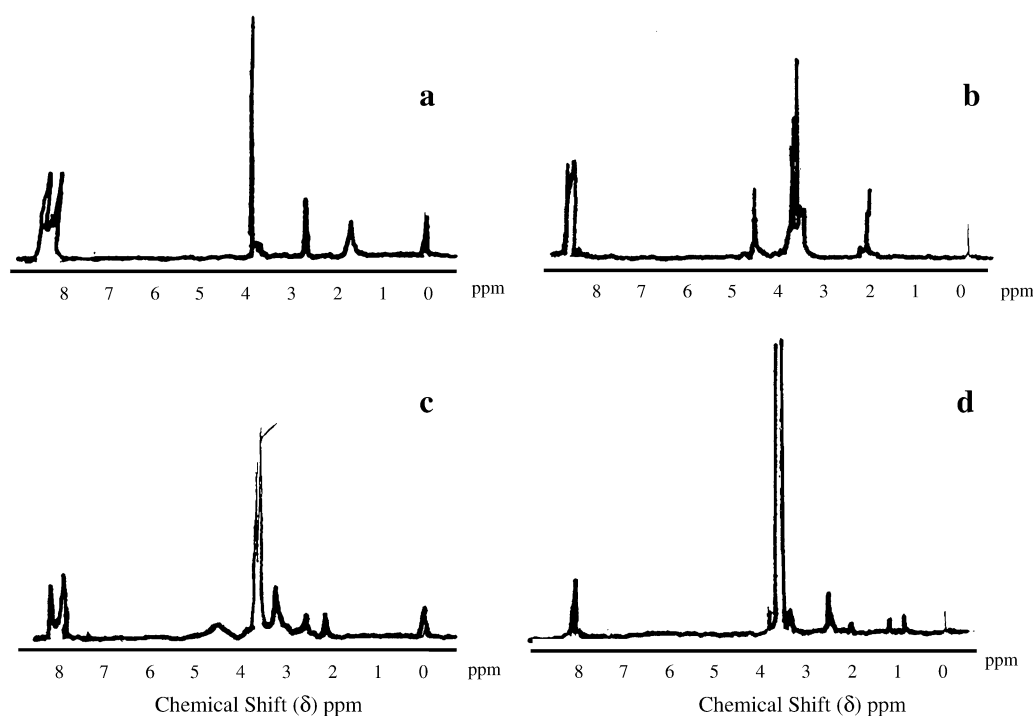


Figure 1. ¹H NMR spectra of (a) GD1, (b) GD2, (c) GD2-EO9 and (d) GT3-EO90.

reactive functionality to be used as oil spill dispersants. The present work deals with polymer compositions made by reaction of diol with an aromatic hydrocarbon containing two reactive functionalities. In this respect, three different molecular weights of polyethylene glycol (PEG), namely, PEG400, 1000 and 4000 g/mol, were reacted with GD oligomers to produce the surfactants GD-EO9, GD-EO22 and GD-EO90, respectively. The numbers 9, 22 and 90 are referred to number of ethylene oxide groups in PEG. While the surfactants produced from reaction of GT with PEG are designed as GT-EO9, GT-EO22 and GT-EO90. Scheme of synthesis was illustrated in Figure 2 to show the proposed chemical structure of the prepared surfactants.

The structures of the produced surfactants were confirmed by using IR spectroscopy. It was observed that the spectra of all GD-EO derivatives are nearly identical. Also the spectra of GT-EO are identical. The IR spectrum of GD2-EO9 is quite similar to that of GT3-EO90 as they possess the same backbone. The stretching bands at 1745 cm^{-1} for carbonyl (C=O) of ester and the peak at 3450 cm^{-1} for

OH are observed in both spectra of GD2-EO9 and GT3-EO90. The band at 810 cm^{-1} in the IR spectra of both GD2-EO9 and GT3-EO90 is assigned to C-H out-of-plane bending for *p*-substituted aromatic. The appearance of this band confirms the incorporation of PET backbone in all cases.

Further confirmation for the structure of GD-EO and GT-EO surfactants was determined by ^1H NMR spectroscopy. The ^1H NMR spectra of GD2-EO9 and GT3-EO90 were selected as representative samples to illustrate the structure of the modified oligomers as represented in (Figure 1c and d). The protons of oxyethylene units at $\delta = 3.6\text{ ppm}$, -OH proton of PEG at $\delta = 2.5\text{ ppm}$, 7.9 ppm which represent *p*-substituted phenyl group, $\text{OOCCH}_2\text{CH}_2\text{COO}$ at 4.8 ppm and $\text{OCH}_2\text{CH}_2\text{N}$ of glycolized PET at 4.3 ppm are observed in the spectra of all surfactants.

The ^1H NMR spectroscopic analysis was used previously for determining the propylene oxide/ethylene oxide ratio for the PO-EO block copolymers [22]. In the present investigation the ^1H NMR spectroscopic analysis is used to determine the ratio between the oxyethylene units in the

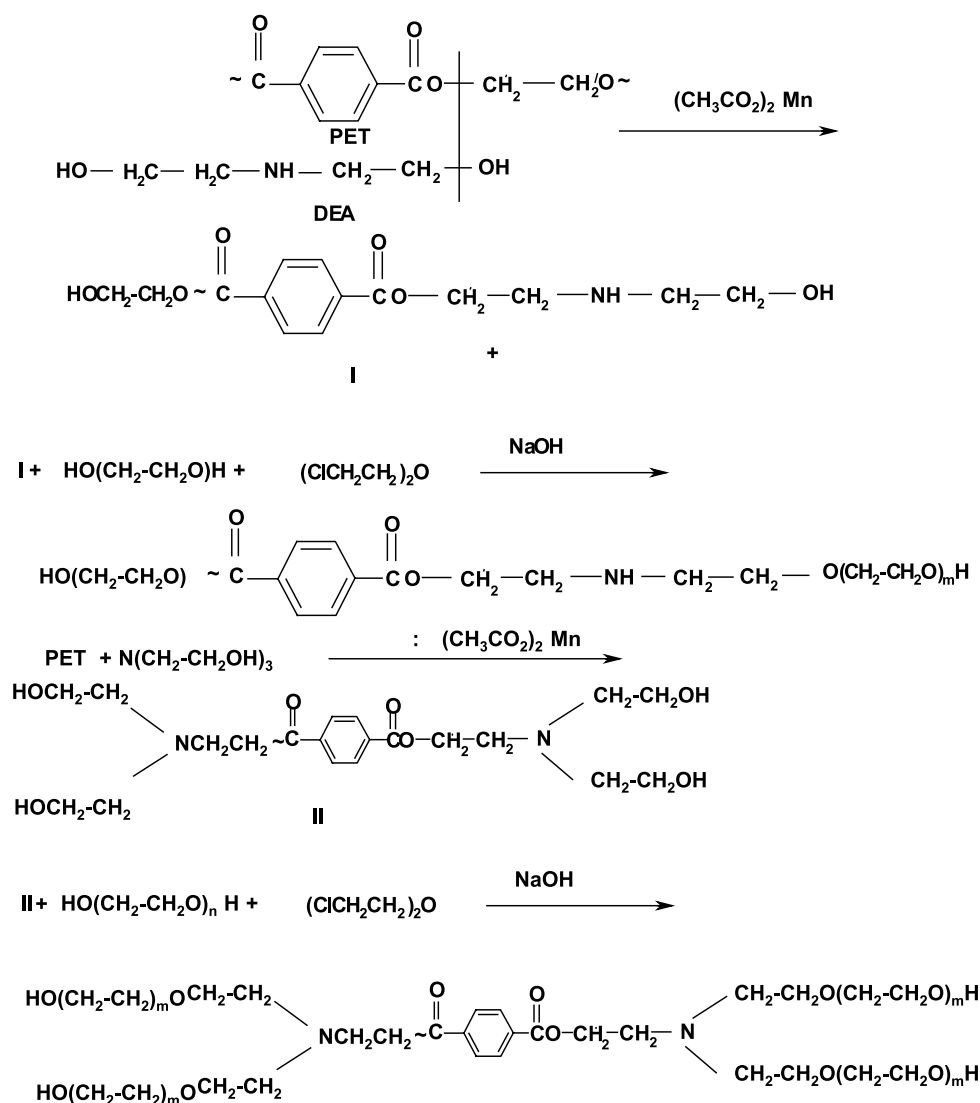


Figure 2. Scheme of synthesis of nonionic surfactants based on PET oligomers.

hydrophilic moiety and the phenyl rings in the hydrophobic moiety, (EO/phenyl) ratio). In this respect, two signals are considered. The first is 3.6 ppm signal (assigned for CH₂ group protons of oxyethylene units), whereas the second is at 7.9 ppm signal (assigned for para substituted aromatic ring). The introduction of polar groups into the GD and GT chains increases their solubility in water at room temperature. The chemical structures of both GD and GT, as proved from IR and ¹HNMR analyses, indicate that these oligomers have terminals hydroxyl groups and secondary amine groups for GD or tertiary amine groups for GT oligomers.

Solubility and surface activity of the prepared surfactants

It is well known that the modification of 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 to a large extent on the type and quantity of the branches attached to the backbone. In this respect, the prepared surfactants based on PET oligomers are soluble in cold or hot water. The solubility and state of polymer solutions should depend on the backbone composition and hydrogen bonds between polar groups of modified PET. Consequently, because of different types of interactions, the solution behaviors of PET oligomers are difficult to predict.

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 [23], $HLB = [M_H / (M_H + M_L)] \times 20$, where M_H is the formula weight of the hydrophilic portion of the surfactant molecule and M_L is the formula weight of the hydrophobic portion. The molecular weight of the prepared surfactants were determined by GPC and listed in Table 3. The expected molecular weights of the prepared surfactants, as described in Figure 2, were calculated and listed in Table 3. The good agreement between two values of calculated and measured molecular weights of the prepared surfactants indicate the purity of surfactants. HLB values of nonionic surfactants based on GT and GD were calculated and listed in Table 3. It is obvious that the HLB values of surfactants based on GT have lower values than that based on the corresponding GD. This can be attributed to the structure of GD surfactants is more hydrophilic than GT surfactants.

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 328 K from the change in the slope of the plotted data of surface tension (γ) versus the natural log-

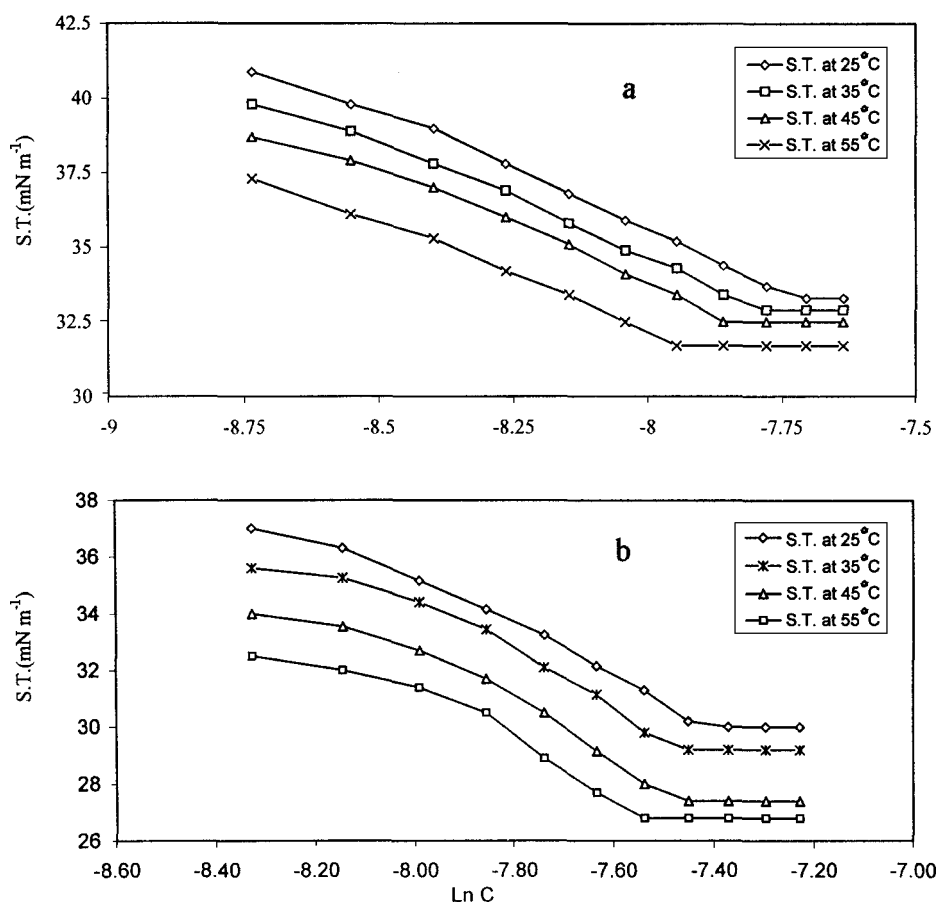


Figure 3. Adsorption isotherms of (a) GD1-EO9 and (b) GD1-EO90.

arithmetic of the solute concentration. Some representative plots [Figures 3a, b] were illustrated here for brevity. The presented plots and all other plots are used for estimating surface activity and confirming the purity of the studied surfactants. It is of interest to mention that all obtained isotherms showed one phase, which is considered as an indication on the purity of the prepared surfactants. The obtained values of CMC for nonionic surfactants at different temperatures are tabulated in Tables 4 and 5, together with values for the surface tension at CMC. Generally, the increasing number of ethylene oxide units increases CMC values [24] due to increasing the hydrophilicity and the solubility of the surfactants in water. Such improved solubility lowers the tendency for the surfactant to form micelles. Some investigators [25] found that increasing of EO units decreases CMC. However, these surfactants have very long hydrophobic tails (at least 16 carbons) and relatively low EO (about 6–19). It may be possible in these cases that the low water solubility of these surfactants is due to the long alkyl chain, not 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. Other investigators [26, 27] explain this behavior on the basis of coiling of the polyethylene oxide chains. In the present system, 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. Careful inspection of CMC values listed in Tables 4 and 5, indicates lowering of CMC with incorporation of TEA which in surfactant structure than DEA. This can be attributed to that the presence

of third hydroxyethyl groups of TEA that will increase the polymer–polymer interaction and decrease their interaction with water [28]. It can be observed that the increasing of DEA and TEA contents in GT and GD surfactants increases the CMC values due to the hydrophilicity of DEA and TEA. 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 content 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 [29].

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 Tables 4 and 5. 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 [29].

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 surfactant at the interface may there-

Table 4. CMC data of surfactants based on DEA at different temperatures.

Designation	Cloud point (°C)	<i>n</i>	Surface property	Temperature (K)			
				298	308	318	328
GD1-EO9	76	9	*CMC × 10 ⁴	6.56	6.04	5.51	4.99
			** γ_{CMC}	33.5	33.15	32.9	32.1
GD1-EO22	81	22	*CMC × 10 ⁴	4.35	4.025	3.7	3.38
			** γ_{CMC}	36.6	36.45	36.2	35.4
GD1-EO90	92	90	*CMC × 10 ⁴	1.375	1.2	1.16	1.044
			** γ_{CMC}	38.4	37.75	35.8	35.05
GD2-EO9	83	9	*CMC × 10 ⁴	7.64	7.075	6.51	5.945
			** γ_{CMC}	36.25	35.45	34.95	34.55
GD2-EO22	89	22	*CMC × 10 ⁴	4.21	3.875	3.54	3.2
			** γ_{CMC}	36.9	36.35	35.9	35
GD2-EO90	97	90	*CMC × 10 ⁴	1.395	1.375	1.175	1.06
			** γ_{CMC}	37.6	36.7	35.9	34.9
GD3-EO9	>100	9	*CMC × 10 ⁴	8.11	7.51	6.91	6.31
			** γ_{CMC}	38.6	37.35	36.6	35.8
GD3-EO22	>100	22	*CMC × 10 ⁴	4.365	4.015	3.665	3.315
			** γ_{CMC}	39.15	38.3	37.45	36.8
GD3-EO90	>100	90	*CMC × 10 ⁴	1.525	1.41	1.295	1.185
			** γ_{CMC}	39.25	39.05	38.25	37.7

*CMC × 10⁴ in (mol dm⁻³).

** γ_{CMC} in (mN m⁻¹).

Table 5. CMC data of surfactants based on TEA at different temperatures.

Designation	Cloud point (°C)	n	Surface property	Temperature (K)			
				298	308	318	328
GT1-EO9	19	9	*CMC $\times 10^4$	6.45	5.56	4.9	4.9
			** γ_{CMC}	30.1	29.5	27.7	27.45
GT1-EO22	58	22	*CMC $\times 10^4$	3.52	3.17	2.91	2.6
			** γ_{CMC}	31.9	31.58	31.1	30.45
GT1-EO90	88	90	*CMC $\times 10^4$	1.14	1.04	1.03	0.92
			** γ_{CMC}	32.55	32.05	31.35	30.85
GT2-EO9	31	9	*CMC $\times 10^4$	6.49	5.97	5.45	4.93
			** γ_{CMC}	34.25	33.60	33.20	32.85
GT2-EO22	48	22	*CMC $\times 10^4$	4.31	3.99	3.67	3.35
			** γ_{CMC}	36.65	36.4	35.6	34.95
GT2-EO90	>100	90	*CMC $\times 10^4$	1.37	1.26	1.16	1.04
			** γ_{CMC}	39.15	38.1	37.7	37.05
GT3-EO9	37	9	*CMC $\times 10^4$	7.59	7.03	6.47	5.91
			** γ_{CMC}	36.5	35.7	35.2	34.65
GT3-EO22	54	22	*CMC $\times 10^4$	4.2	3.86	3.3	3.19
			** γ_{CMC}	36.6	36.35	35.65	35.35
GT3-EO90	>100	90	*CMC $\times 10^4$	1.5	1.3	1.3	1.17
			** γ_{CMC}	37.81	37.5	36.2	34.45

*CMC $\times 10^4$ in (mol dm⁻³).

** γ_{CMC} in (mN m⁻¹).

fore be calculated from surface or interfacial tension data by using of the following equation:

$$\Gamma_{\max} = \frac{1}{RT} \left(\frac{-\partial\gamma}{\partial \ln c} \right)_T \quad (1)$$

Where $\left(\frac{-\partial\gamma}{\partial \ln c} \right)_T$ is the slope of the plot of γ versus $\ln c$ at a constant temperature (T), and R is the gas constant in 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 values to which adsorption can attain.

From the surface excess concentration, the area per molecule at interface is calculated using Equation (2).

$$A_{\min} = \frac{10^{16}}{N\Gamma_{\max}} \quad (2)$$

Where N is Avogadro's number.

The effectiveness of surface tension reduction, $\Pi_{CMC} = \gamma_0 - \gamma_{CMC}$, where γ_0 is the surface tension of water and γ_{CMC} is the surface tension of solution at CMC [30], was determined at different temperatures. The Γ'_{\max} , A_{\min} and Π_{CMC} values are calculated and listed in Tables 6 and 7. The data, listed in Tables 6 and 7, 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. This is in agreement with the data observed for polyoxyethylenated nonionic [36]. The A_{\min} of nonionic surfactants that contain PEG in their molecular structure increases with the number of oxyethylene units [31]. 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 instead of DEA in surfactant structure 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} [32]. 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 [33, 34].

The effectiveness of surface tension reduction, n_{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 interface. 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 [35].

Table 6. Surface properties of the surfactants based on DEA at different temperatures.

Designation	Surface property	Temperature (K)			
		298	308	318	328
GD1-EO9	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.751	0.758	0.792	0.890
	A_{\min} (nm ² /molecule)	0.222	0.219	0.210	0.187
	Π_{CMC} (mN m ⁻¹)	38.77	38.17	37.13	37.16
GD1-EO22	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.957	1.081	1.133	1.331
	A_{\min} (nm ² /molecule)	0.174	0.154	0.147	0.125
	Π_{CMC} (mN m ⁻¹)	35.67	34.87	33.83	33.86
GD1-EO90	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.447	1.514	1.476	1.546
	A_{\min} (nm ² /molecule)	0.115	0.109	0.113	0.108
	Π_{CMC} (mN m ⁻¹)	33.87	31.51	34.23	34.21
GD2-EO9	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.864	0.977	0.9881	0.9884
	A_{\min} (nm ² /molecule)	0.192	0.17	0.168	0.167
	Π_{CMC} (mN m ⁻¹)	36.02	35.87	35.08	34.71
GD2-EO22	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.074	1.08	1.07	1.11
	A_{\min} (nm ² /molecule)	0.155	0.153	0.152	0.149
	Π_{CMC} (mN m ⁻¹)	35.37	34.97	34.13	34.26
GD2-EO90	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.194	1.16	1.13	1.12
	A_{\min} (nm ² /molecule)	0.139	0.43	0.147	0.148
	Π_{CMC} (mN m ⁻¹)	34.67	34.62	34.13	34.36
GD3-EO9	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.77	0.866	0.942	1.1
	A_{\min} (nm ² /molecule)	0.216	0.192	0.176	0.151
	Π_{CMC} (mN m ⁻¹)	33.67	33.97	33.43	33.46
GD3-EO22	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.799	0.912	1.08	1.09
	A_{\min} (nm ² /molecule)	0.208	0.182	0.154	0.152
	Π_{CMC} (mN m ⁻¹)	33.12	33.02	32.58	32.46
GD3-EO90	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.862	0.899	0.976	1.042
	A_{\min} (nm ² /molecule)	0.193	0.185	0.17	0.16
	Π_{CMC} (mN m ⁻¹)	33.02	32.27	31.78	31.56

Table 7. Surface properties of the surfactants based on TEA at different temperatures.

Designation	Surface property	Temperature (K)			
		298	308	318	328
GT1-EO9	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.06	0.801	0.73	0.57
	A_{\min} (nm ² /molecule)	0.157	0.207	0.228	0.292
	Π_{CMC} (mN m ⁻¹)	42.17	41.82	42.33	42.01
GT1-EO22	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.812	0.782	0.673	0.571
	A_{\min} (nm ² /molecule)	0.205	0.212	0.247	0.291
	Π_{CMC} (mN m ⁻¹)	40.37	39.74	38.93	38.81
GT1-EO90	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.694	0.669	0.721	0.794
	A_{\min} (nm ² /molecule)	0.240	0.249	0.231	0.210
	Π_{CMC} (mN m ⁻¹)	39.72	39.27	38.68	38.46
GT2-EO9	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.450	0.429	0.384	0.354
	A_{\min} (nm ² /molecule)	0.37	0.388	0.434	0.470
	Π_{CMC} (mN m ⁻¹)	38.02	37.72	36.83	36.46
GT2-EO22	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.733	0.661	0.624	0.493
	A_{\min} (nm ² /molecule)	0.227	0.252	0.267	0.337
	Π_{CMC} (mN m ⁻¹)	35.62	34.92	34.38	34.31
GT2-EO90	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.012	0.962	0.917	0.881
	A_{\min} (nm ² /molecule)	0.133	0.173	0.181	0.189
	Π_{CMC} (mN m ⁻¹)	33.12	33.22	32.33	32.21
GT3-EO9	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.05	0.998	0.885	0.858
	A_{\min} (nm ² /molecule)	0.158	0.167	0.188	0.194
	Π_{CMC} (mN m ⁻¹)	35.77	35.62	34.83	34.61
GT3-EO22	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	1.08	0.964	0.864	0.545
	A_{\min} (nm ² /molecule)	0.154	0.173	0.193	0.305
	Π_{CMC} (mN m ⁻¹)	35.67	34.97	34.38	33.91
GT3-EO90	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	0.713	0.702	0.789	0.865
	A_{\min} (nm ² /molecule)	0.233	0.237	0.211	0.192
	Π_{CMC} (mN m ⁻¹)	34.47	33.82	33.81	33.80

This is because, the cross-sectional area occupied by the chain-oriented perpendicular to the interface does not change with increase in the number of units in the chain.

When the area of hydrophilic group is greater than that of the hydrophobic chain; the larger the hydrophilic group, the smaller the amount adsorbed at surface saturation. If the arrangement is predominantly perpendicular but not close-packed, there may be some increase in the effectiveness of adsorption with increase length of hydrophobic group, resulting from greater Van der Waals attraction and consequent closer packing of longer chains [36]. However if the orientation of surfactant is parallel to the interface, when the surfactant has two ionic groups or when the hydrophobic chain interacts strongly with the surface e.g., electron rich aromatic nuclei, the effectiveness of adsorption may decrease with increase in the chain length, due to increase the cross-sectional area of the molecule on the surface. Thus saturation of the surface will be accomplished by a smaller number of molecules [37]. Nonionic surfactants with short PEG chains show decrease in both efficiency and effectiveness with increase in the length of PEG [38].

Evaluation of the prepared surfactants as oil spill dispersants

Dispersants are oil spill treating agents formulated to disperse oil into water in the form of fine droplets. In this respect, the dispersion capability of individual non-ionic surfactants (ethoxylated GD and GT) was tested on asphaltic crude oil. The surfactants to oil ratio (SOR) were ranged from 1:10 to 1:100. The relation between SOR and dispersion efficiency for all prepared surfactants was represented in Figures 4a–c. The data showed that nonionic surfactants based on GT have high dispersion capabilities than those based on GD. The data reveal that GT1-EO22 has the maximum efficiency (95%) at SOR from 1:1 to 1:20. The dispersion efficiencies for GD and GT surfactants based on PEG 400 (EO9) show maximum values at SOR 1:20. While, the dispersion efficiencies of surfactants based on PEG 1000 and 4000 have higher values at SOR from 1:1 to 1:20. These results can be correlated with the thermodynamic data of micellization and adsorption that indicate the dependence of adsorption process on the chemical structure of surfactants. It was found in previous section that the prepared surfactants favor adsorption than micellization that is sensitive to the molecular weight of PEG and percentage of DEA or TEA in the prepared surfactants.

The data of dispersion capabilities of the prepared surfactants can be also correlated with HLB values of these surfactants. Typically the HLB of common commercial dispersants ranges from 9 to 11. The parameter used to characterize surfactants is the hydrophil–lipophil balance [39]. HLB is determined using theoretical equations that relate the length of the water-soluble portion of the surfactant to the oil-soluble portion of the surfactant. A surfactant having HLB between 1 and 8 promotes the for-

mation of water-in-oil emulsions and one with an HLB between 12 and 20 promotes the formation of oil-in-water emulsions. A surfactant having HLB between 8 and 12 may promote either type of dispersants. In the present study, it was observed that the surfactants have HLB (9–12.2) show good dispersion efficiencies. While, surfactants having HLB below 8.5 and above 17.8 show low dispersion efficiencies. Careful inspection of dispersion efficiency data reveals that surfactant having HLB below 10 show maximum dispersion efficiency at SOR 1:20. While the surfactants having HLB above 10 show maximum dispersion efficiency at SOR from 1:1 to 1:5. This behavior reflects the dependence of the dispersion power on the presence of surfactant molecules in the soluble form rather than micelles [40]. This was proved from Figures 4a, b, which decline that the dispersion power of surfactants based on PEG 400 and PEG 1000 increases with increasing the surfactant concentration, SOR, to a limit above their CMC, but it decreases at concentration far above CMC. This can be attributed to the solubilization of crude oil into the hydrophobic interior core of micelle [41]. The decrease in dispersion power at surfactant concentration far above CMC may be referred to the saturation of bulk phase by micelles that lead to a reduction in the availability of crude oil to solubilize into surfactant micelles. The high dispersion power of surfactants based on PEG 4000 at low SOR reflect the hydration of long hydrophilic groups into bulk phase which prevents the crude oil to penetrate the exterior region of micelle to arrive to their interior core and solubilize there [40]. In the same time, the long hydrophilic chain reduces the hydrophobicity of the surfactant molecule; hence, the solubilization efficiency is reduced [42]. This behavior can be correlated with the ability of surfactants to reduce surface tension at CMC (γ_{CMC}), Tables 4 and 5, which indicate that the ability of surfactants based on PEG 400 and 1000 to reduce γ_{CMC} is more than that for those based on PEG 4000. This facilitates the dispersion of oil into fine droplets [40]. From the previous results, it can be concluded that surfactants based on PEG 400 and 1000 have better dispersion efficiency than that based on PEG 4000. This is in agreement with the result given by Broch et al. [43]. They deduce that better dispersions are referred to the solubility and structure of hydrophilic groups.

Dispersion capability of blends of PET surfactants

Some dispersants contain ionic surfactants in small proportions, yielding a total HLB more toward 15 than 10. Studies on the specific effect of this (HLB) on effectiveness or mode of action have not been done. A typical dispersant formulation consists of a pair of non-ionic surfactants in proportions to yield an average HLB of 10. Studies have been done on this mixture, one of which is used statistical procedures in an attempt to determine the best mixture of the three ingredients [44]. In order to estimate the validity of this observation with asphaltic crude oil dispersions, blends of the prepared nonionic surfactants were prepared.

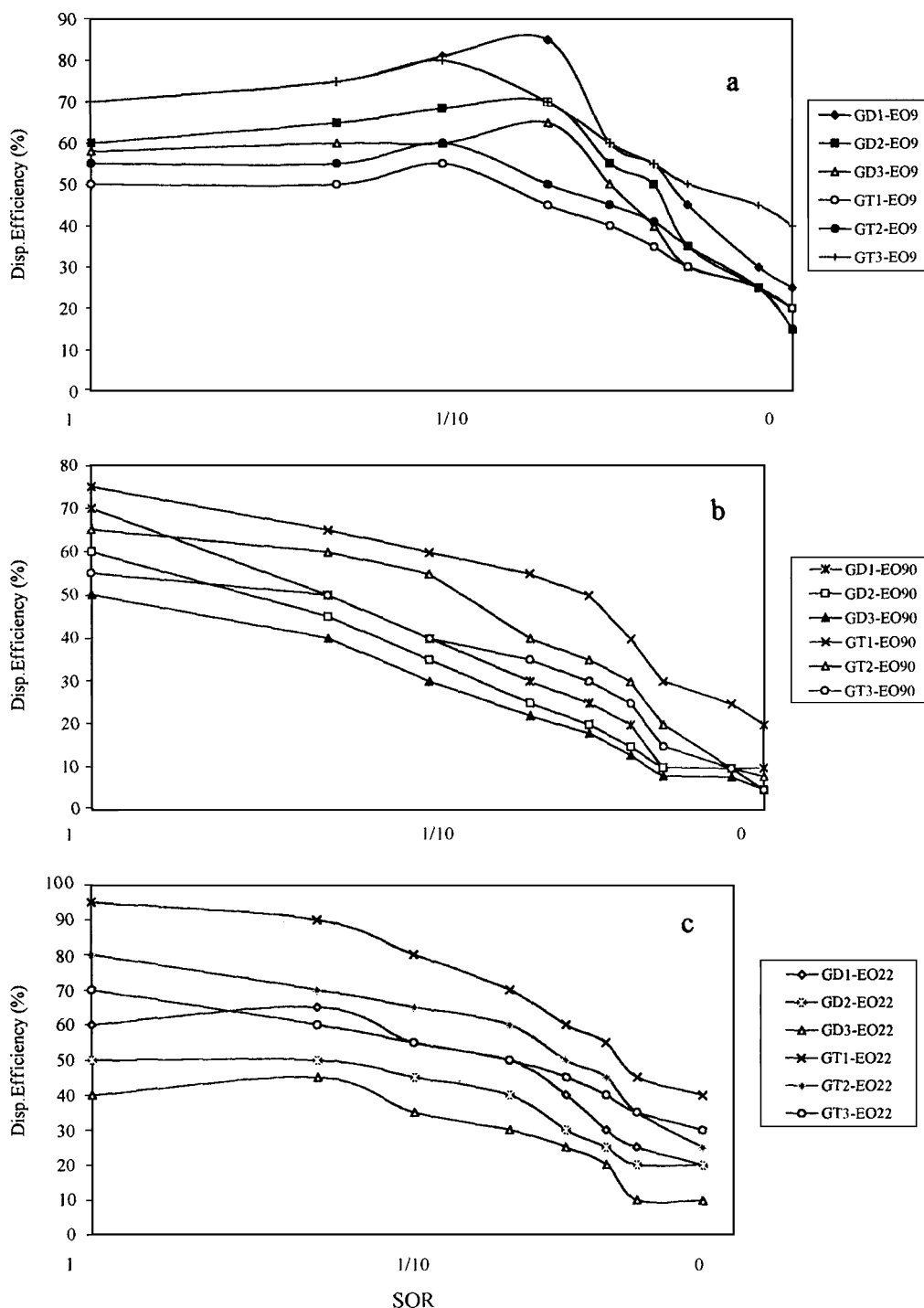


Figure 4. Relation between dispersion efficiency of the surfactants and SOR for (a) GD-EO9 and GT-EO9, (b) GD-EO22 and GT-EO22, and (c) GD-EO90 and GT-EO90.

It is readily apparent that both HLB and chemical constitution of the dispersants exert a large influence on the percentage of dispersion. Synergism of GT1-EO22 (non-ionic) with a second surfactant were studied as binary mixtures. On the other hand, a third surfactant was added, in some cases, to form ternary surfactant systems. In all cases the surfactant were blended in different weight percentages. HLB values of the surfactant blends were calculated as, $HLB_{blends} = HLB_a X_a + HLB_b X_b + HLB_c X_c$, where X is mole fraction of surfactant a, b and c . In this

respect, dispersant 1 (GT1-EO22, GD1 EO9 and GT3-EO9), dispersant 2 (GT1-EO22, GD1 – EO22, GT1-EO9 and GD1-EO9) and dispersant 3 (GT1-EO90, GD1 EO90, GT1-EO9 and GD1-EO9) were selected to study the effect of SOR on dispersion efficiency and interfacial tension reduction (IFT) between oil and water. The composition of the blends, their designation and HLB values were recorded in Table 8 for the preped surfactant blends. It can be seen that, from Table 8, that increasing the number of EO units in the molecule leads to an appreciable

Table 8. HLB values of dispersant 2 and dispersant 3.

HLB	Dispersant 2				Dispersant 3			
	X*GD1-EO22	X*GT1-EO22	X*GD1-EO9	X*GT1-EO9	X*GD1-EO90	X*GT1-EO90	X*GD1-EO9	X*GT1-EO9
8	0.01	0.01	0.18	0.8	0.01	0.01	0.08	0.9
9	0.1	0.1	0.3	0.5	0.025	0.025	0.75	0.2
10	0.2	0.2	0.3	0.3	0.05	0.1	0.8	0.05
11	0.05	0.6	0.3	0.05	0.2	0.1	0.3	0.4
12	0.75	0.05	0.15	0.05	0.2	0.2	0.35	0.25
13	—	—	—	—	0.26	0.26	0.24	0.24
14	—	—	—	—	0.5	0.1	0.35	0.05
15	—	—	—	—	0.05	0.7	0.05	0.2
16	—	—	—	—	0.55	0.3	0.05	0.1
17	—	—	—	—	0.9	0.045	0.025	0.03

*X = Mole fraction of the individual surfactant in the blend.

increase in the HLB values of blends. The relations between HLB of blends and their IFT values at 1000 ppm were represented in Figure 5. As mentioned before, the oil-water interfacial tension (IFT) falls as the surfactant concentration increases and then attains a constant value at and above the concentration where surfactant aggregation occurs (CMC). The aggregation may occur either in the oil phase or in the aqueous phase, depending on conditions. This work will concern the dependence of IFT on the chain length of the hydrophobic moiety of the surfactant molecule and upon the number of EO units in the hydrophilic moiety. The lowering of IFT and the improved stability of O/W emulsions combining surfactants with high and low HLB have been explained through some specific molecular association of surfactants at the interfaces [30]. The minimum interfacial tensions of asphaltenic crude oil in presence of blends, Figure 4, were obtained at HLB range from 9 to 11. It was also observed that the lower IFT values were determined for dispersant 1 (which has HLB = 12) at SOR 1:5. This may give indirect evidence that the HLB and interfacial tension are linked in the same way by the dispersion capability. In this respect,

the interfacial tension of the mixed surfactants is less than of individual surfactant. On the other hand, increasing the dispersion capability could be attributed to the intermolecular interaction between the two polymeric molecules [45].

The relation between dispersion efficiency of the selected blends, which have lower IFT values, and their SOR were presented in Figure 6. It was observed that the maximum dispersion was reached from 90% to 100 % for dispersant blends as shown in Figure 6. A real improvement in the percentage of dispersed oil was observed for the blends when compared to the individual *GT1-EO22* performance. The interactions between components of dispersant 1 are favorable to the interface stabilization and give a quite good dispersion test, as in Figure 5, since the repulsion between phenyl rings is minimized and the concentration of surfactants at interface is increased by their proximity [30]. The most effective nonionic surfactant blend, Figure 5, appears to be good with an HLB 8 to 10, having long hydrophobic chains and long polyoxyethylene chains. So the maximum dispersion power was arranged in sequence dispersant 1 > dispersant 2 > dispersant 3.

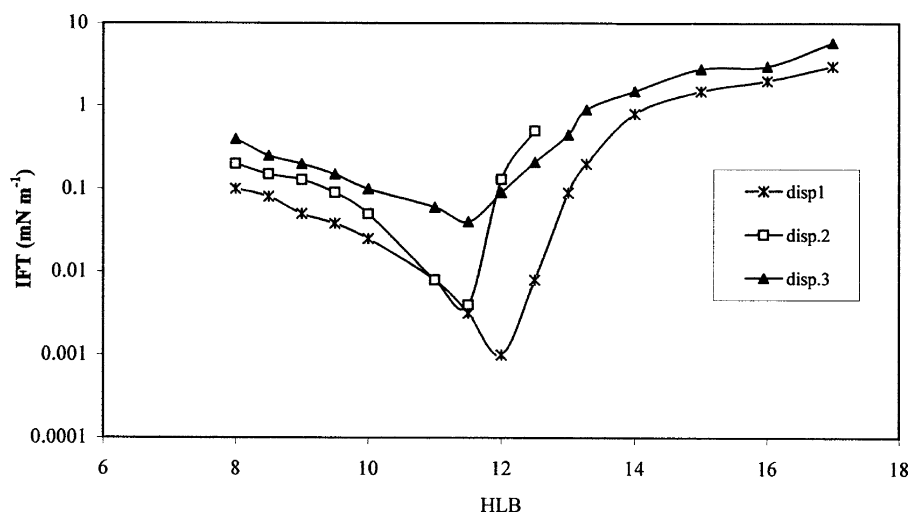


Figure 5. Relation between HLB of surfactant blends and their IFT values at SOR (1:5).

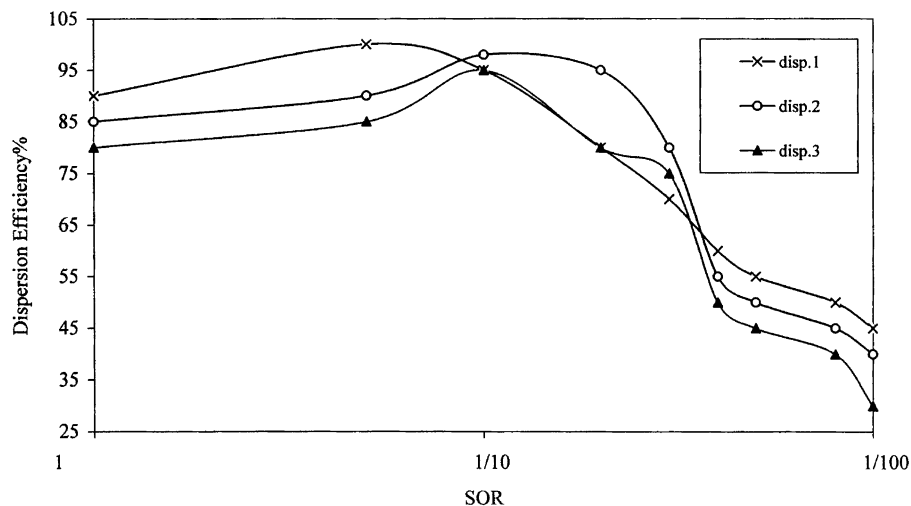


Figure 6. Relation between dispersion efficiency of surfactant blends and their SOR.

Conclusions

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

1. The PET waste could be depolymerized with excess of DEA or TEA at temperature less than 210 °C.
2. The extent of depolymerization was increased with increasing amount of DEA or TEA. The incorporated percentages of DEA or TEA in the produced oligomers are varied from 10 to 14%.
3. Dispersion capability of individual surfactants shows maximum efficiency (95%) for GT1-EO22 surfactant at SOR from (1:1 to 1:20).
4. Nonionic surfactants having HLB (9-12.2) show good dispersion efficiency.
5. Surfactants based on TEA show good dispersion efficiency than those based on DEA.
6. Nonionic surfactants having HLB below 10 show maximum dispersion efficiency at SOR (from 1:1 to 1:5).
7. Maximum dispersion efficiency depends on the greater reduction of IFT values below 0.1 mN/m.
8. The blending of GT1-EO22, GD1-EO9, GT3-EO9 (at HLB = 12) increases the dispersion efficiency to about 100%.

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