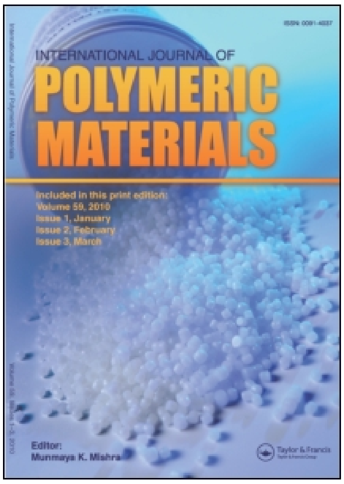

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Synthesis and Characterization of Novel Crude Oil Dispersants Based on Ethoxylated Schiff Base

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Schiff base prepared from salicylaldehyde and diethylene triamine was ethoxylated by poly (ethylene glycol) of different molecular weights, namely 200, 600, 1000 and 2000, by using β,β-dichlorodiethyl ether as a linking agent. The ethoxylation reaction took place at both ends of the base upon using poly(ethylene glycol) (PEG) 200 and 600, whereas at one end when PEG 1000 and 2000 were used. The chemical structure of the prepared compounds was confirmed by using IR and ^{1}HNMR spectroscopy. Thermodynamic parameters for micellization and adsorption or the prepared compounds were measured based on the surface tension of their solutions at different temperatures. Then, the compounds under investigation were tested as oil spill dispersants according to different standard test methods. It was found that the compounds with lower molecular weights of PEG showed the best dispersancy.

Keywords: ethoxylation, oil spill dispersants, salicylaldehyde, Schiff base

INTRODUCTION

The petroleum industry generates a high amount of oily wastes during storage, refining and processing operations. Over several decades, petroleum products have become very common pollutants in the environment as considerable amounts of petroleum compounds are discharged into the environment through industrial effluents. Marine oil spills

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have become more common as offshore oil production and transport increased over the last few decades [1,2]. Oil spill occurrences may result in loss of habitat for economically important species of fishes, other marine animals, and damage to sensitive wetlands along the coast. Recovery of the environment from an oil spill can take years, so there is considerable incentive to quickly clean up these areas after a spill, but the efforts can be expensive and themselves destructive. One oil-spill response tactic is the use of dispersants.

Dispersants are designed to chemically disperse an oil slick so that the oil enters the water phase, minimizing opportunities to be stranded on shorelines. As wave energy is added to chemically dispersed oil (CDO) at sea, the slick breaks up into small oil droplets that disperse into the water phase. Rapid dispersal of an oil slick in open waters is almost always less costly from an economic standpoint than mechanical shoreline cleanup once the oil reaches land [3]. Dispersants may enhance oil bioavailability by creating more surface area in terms of multiple small oil droplets, allowing for increased biodegradation of the oil [4]. Dispersant use has raised questions about their effects on the ecosystem. Many of these concerns are in response to the high toxicity of first-generation dispersants, though the newer formulations are generally more effective and less toxic [5]. Nowadays, there is a large number of dispersants and dispersant blends differing in chemical structure and in efficiency [4–7]. Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. They found numerous applications in different industries [8,9], but very little uses as surfactants. It is the aim of this investigation to prepare different ethoxylated Schiff bases and apply them as crude oil spill dispersants to alleviate the pollution resulting from spilled oil.

EXPERIMENTAL

Materials

Diethylene triamine, salicylaldeyhde, poly(ethylene glycol) 200, 600, 1000 and 2000, β,β-dichlorodiethyl ether were all of analytical grade and used as received from Aldrich. Double-distilled water was used throughout this study in the surface tension measurements. All organic solvents were thoroughly dried and freshly redistilled before use.

Synthesis

Synthesis of Schiff base

A mixture of diethylene triamine (20.634 g, 0.2 mol) and salicylaldehyde (48.848 g, 0.4 mol) in methanol (100 mL) was stirred at room temperature for 1 h to give a yellow liquid. After evaporation of the methanol, the pure Schiff base A (67.4 g, 97.00%) was obtained.

Ethoxylation of Schiff Base Using β,β′-Dichlorodiethyl Ether and Polyethylene Glycol

Four different molecular weights of PEG, namely, PEG 200, 600, 1000 and 2000 g/mol were reacted with compound A and β,β′-dichlorodiethyl ether in presence of NaOH as a catalyst to produce the dispersants by the following procedure: in a 250 ml three-neck round-bottom flask, fitted with a condenser, mechanical stirrer and thermometer were added 0.1 mole of A, 0.1 mole β,β′-dichlorodiethyl ether, 0.1 mole PEG and 0.2 mole NaOH in case of ethoxylating one end of the base. The ratios were doubled when both ends of the base were ethoxylated. The reactants were agitated and slowly heated to a temperature of 343 K. The reaction mixture was maintained at this temperature for 5 h. The progress of the reaction was followed by determining the NaCl content which 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 then 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 a constant weight. Different molecular weights and Hydrophil/Lipophil Balances (HLB)s were obtained by using different molecular weights of PEG. The prepared surfactants were designated as A200, A600, A1000 and A2000 according to the molecular weight of the poly(ethylene glycol) incorporated.

MEASUREMENTS

Infrared Spectroscopic Analysis

The purified synthesized compounds were analyzed using ATI Mattson Genesis Series FTIR spectrophotometer. The samples were investigated as thin film between two KBr discs.

Nuclear Magnetic Resonance Spectroscopic Analysis

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 structure and the HLB by comparing integral trace of different peaks.

TABLE 1 Specifications of Land Belayim Crude Oil

Test	Method	Value
API gravity at 60 F	Calculated	21.7
Viscosity at 60 F (C.S.T)	IP71	762.8
Specific gravity at 60 F	IP 160/87	0.843
Asphaltenes Contents (WT%)	IP 143/84	8.8

Surface Tension Measurements

Water-soluble polymers 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. Doubly distilled water ($\gamma = 72$ dyne/cm) was used for preparing the concentrated stock solutions of the samples. Several concentrations were prepared by diluting the stock solution with doubly distilled water to the appropriate concentration to be used in the determination of critical micelle concentration (CMC). The diluted solutions were allowed to stand for 24 h before the surface tension measurements were performed.

Particle Size Distribution

Particle size of oil droplets was measured using LISST-100X oil droplet size distribution for an emulsion prepared from 100 ppm of A200 in 10% crude in toluene. The specification of the crude used in this work (land Belayim crude oil) is supplied in Table 1.

Evaluation of Prepared Surfactants as Oil Spill Dispersants: Laboratory Dispersions Test

The Egyptian land Belayim crude oil was used throughout this study for testing the efficiency of the prepared surfactants. The specifications of land Belayim crude oil are listed in Table 1. The Environmental Protection Agency [EPA] test method [10] 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 detected at 260 nm. The absorbance for each concentration was determined at this wavelength and the absorbance values for all concentrations were utilized for constructing the calibration curve. Then, an 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 1 min, energy was 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. This procedure was repeated for each dispersant.

RESULTS AND DISCUSSION

Synthesis of Nonionic Surfactants from Schiff Base

The extensive shipping of crude oil and its products over oceans has increased concerns about the effects of accidental spillage of petroleum hydrocarbons in the marine environment. Major marine oil spills highlight the need for cost-effective and environmentally responsible mitigation technologies. Since the early days of contingency planning for marine oil spills, chemical dispersants have been widely used to combat oil spills at sea. Nevertheless, dispersants still play an important role in oil spill contingency planning in many countries, leading to continuous research into the effectiveness, limitations, and application techniques of dispersants. Dispersion toxicity is among the most important factors that control their use. Amines and polyoxyethylenes are known for their very low toxicity. D. R. McCoy introduced a group of surface active agents as the condensation products of an aldehyde or ketone of from 9 to 20 carbon atoms with a polyoxyalkyleneamine which is an amine terminated block copolymer of oxyethylene and oxypropylene groups. such Schiff bases are characterized by their low toxicity and their relative low effectiveness [11].

Breen and Towner [12] have introduced polymer compositions made by reacting a polyol with an aromatic hydrocarbon containing only a single reactive functionality to be used as oil spill dispersants. The aromatic hydrocarbon had at least one aryl group and only one reactive hydroxyl group. The present work deals with ethoxylated Schiff base as nonionic surfactants. It is well-known [13] that nonionic surfactants are not affected by any change in pH of the medium but are affected by the temperature. Table 2 shows that the prepared compounds have

TABLE 2 CMC Data of the Investigated Surfactants at Different Temperatures

					Temperature (K)		
Designation	Cloud point	n	HLB	Surface Property	298	308	318
A200	76°C	9	11.48	*CMC × 10^4	6.56	6.04	5.51
				**γCMC	33.5	33.15	32.9
A600	83°C	27	16.03	*CMC × 10^4	4.35	4.025	3.7
				**γCMC	36.6	36.45	36.2
A1000	81°C	22.7	15.42	*CMC × 10^4	1.375	1.2	1.16
				**γCMC	38.4	37.75	35.8
A2000	92°C	45.5	17.4	*CMC × 10^4	7.64	7.075	6.51
				**γCMC	36.25	35.45	34.95

*CMC × 10^4 in (mol dm^{-3}).
**γCMC in (mNm^{-1}).

relative high cloud points so that they don't phase out of the solution, which is a good parameter for their efficiency.

Confirmation of the Structure

The structures of the produced surfactants were confirmed by using IR spectroscopy. It was observed that the spectra of all the investigated compounds are nearly identical. For brevity, the IR charts of the prepared surfactants are not supplied here. The stretching bands at 3450 cm^{-1} and 3200 cm^{-1} are for N–H and primary and secondary amines respectively. The band at 810 cm^{-1} in the IR spectrum of A200 is assigned to C–H out-of-plane bending for *o*-substituted aromatic whereas that at 1100 cm^{-1} is assigned for C–N. The imine bond appears at 1650 cm^{-1}.

Further confirmation for the structure of surfactants was accomplished by ^{1}HNMR spectroscopy. The ^{1}HNMR spectra of the prepared compounds are also the same, so will not be presented herein. The peaks appearing in these spectra are the protons of oxyethylene units at $\delta = 3.6$ ppm, –OH proton of PEG at $\delta = 2.5$ ppm, N–H proton at 3.8, and those at 8 ppm represent *o*-substituted phenyl group. The ^{1}HNMR spectroscopic analysis was used previously for determining the propylene oxide/ethylene oxide ratio for the PO-EO block copolymers [14–16]. In the present investigation the ^{1}HNMR spectroscopic analysis was used for determining the change in the ratio between the oxyethylene units in the hydrophilic moiety and the phenyl rings in the hydrophobic moiety, (EO/phenyl ratio). In this respect, two signals were considered. The first is 3.6 ppm signal (assigned to CH_2

group protons of oxyethylene units), whereas the second is at 7–8 ppm signal (assigned to ortho-substituted aromatic ring).

Solubility and Surface Activity of the Prepared Surfactants

It is well-known that the modification of surfactants' backbone yields different chain flexibility and solubility due to the difference of inter- and intramolecular interactions. Accordingly, the selection of the proper surfactant depends to a large extent on the type and quantity of the branches attached to the backbone. In this respect, the prepared surfactants are soluble in cold water, isopropanol and most organic solvents.

The solubility of the prepared surfactants depends on their hydrophil/lipophil balance (HLB). The solubility in water of the prepared nonionic surfactants, based on PEG, depends on the content and molecular weight of PEG. For instance, it was found that the nonionic surfactant containing PEG with molecular weight 400 is of a lower water solubility. The amount of PEG in the final nonionic surfactants can be controlled by variation of molar ratios between the reactants during the synthesis process. The HLB values were calculated by using the general formula fornonionic surfactants [17], $HLB = [M_H/(M_H + M_L)] \times 20$, 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. HLB values of the surfactants were calculated and listed in Table 2.

It has been mentioned [18] that when the surfactants are dissolved in a solvent, materials that contain a lyophobic grouping together with a lyophilic group in the same molecule distort the structure of the solvent and therefore increase the free energy of the system. On the other hand, when they concentrate at the surface and orient their lyophobic groups away from the solvent, the free energy of the solution is minimized. However, there are some other means of minimizing the free energy in the systems. The distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by the aggregation of the surface-active molecules into clusters (micelles) while their hydrophilic groups pointing toward the solvent. The micellization is therefore a mechanism alternative to adsorption at the interfaces for removing the lyophobic groups from contact with the solvent, thereby reducing the free energy of the system. The micellization and adsorption of surfactants are based on the critical micelle concentrations (CMC), which was determined by the surface balance method. The CMC values of the prepared polymeric surfactants were determined at 298, 308 and 318 from the change in the slope of the plotted data of surface tension (γ) vs. the natural logarithm of the solute concentration.

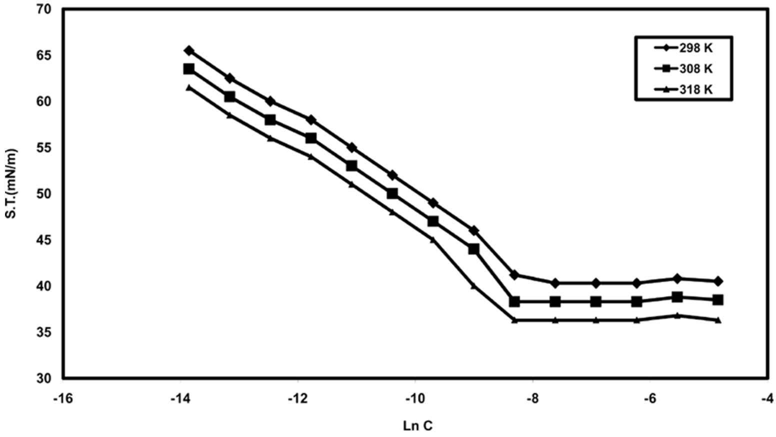

FIGURE 1 Surface tension–concentration isotherm of A200.

Some representative plots for surface tension-concentration isotherm of A200 and A2000 are illustrated respectively in Figures 1 and 2. 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 of the purity of the prepared surfactants. The obtained values of CMC for nonionic and ionic surfactants at different temperatures are tabulated in Table 2, together with values for the surface tension at CMC. Generally,

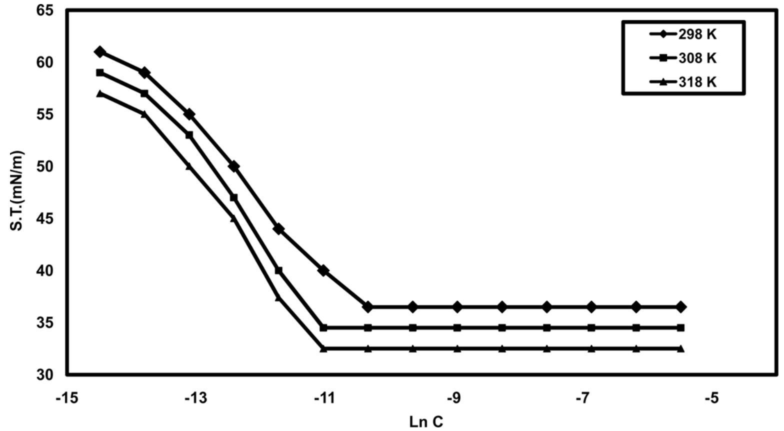

FIGURE 2 Surface tension–concentration isotherm for A2000.

increasing the number of ethylene oxide units increases CMC values [18,19] due to the increased hydrophilicity and solubility of the surfactants in water. Such improved solubility lowers the tendency for the surfactant to form micelles. Some investigators [20,21] found that increasing the EO units decreases CMC as in our case. However, these surfactants have very long hydrophobic tails (at least 16 carbons) or bulk hydrophobic nucleus. It may be possible in these cases that the low water solubility of these surfactants is due to the hydrophobic nucleus and 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 [22–26] 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 the decrease in the number of oxyethylene groups in the molecule. This can be attributed to the hydrophobic interaction between benzene rings which increases coiling of terminated polyethylene oxide. So, the solubility of surfactants in water is controlled by the structure of the hydrophobic groups.

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 solubility of the molecule as a result of increased temperature [27,28]. The same results can be obtained from measuring the cloud temperatures of the prepared surfactants in water. It was established that aqueous solutions of polyoxyethylenated nonionics 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 phases appear 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 2. 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.

When comparing the performance of different surfactants at interfacial phenomena, as in most phenomenon, it is usually necessary to distinguish between the amount of surfactant required to produce a given amount of change in the phenomenon under investigation and the maximum change in the phenomenon that the surfactant can produce, regardless of amount used. The former parameter is the efficiency of the surfactant and the latter is its effectiveness. These two parameters do not necessarily run in parallel to each other in surfactants and, in fact, in many cases run counter to each other. 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. This interface can readily be calculated as a surface excess concentration, $\Gamma_{\max}$. The surface excess concentration of surfactant at the interface may therefore be calculated from surface or interfacial tension γ data by using the following equation:

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

where $(-\partial\gamma/\partial \ln c)_T$ is the slope of the plot of γ versus ln c at a constant temperature (T), and R is the gas constant in $\mathrm{J\,mol^{-1}\,K^{-1}}$. 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 which adsorption can attain.

The $\Gamma_{\max}$ values were used for calculating the minimum area $A_{\min}$ at the aqueous-air interface. The area per molecule at the interface provides information on the degree of the packing and the orientation of the adsorbed surfactant molecules, when compared with the dimensions of the molecule as obtained by use of models. From the surface excess concentration, the area per molecule at interface is calculated using Eq. (2).

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

where N is Avogadro's number.

The effectiveness of surface tension reduction, $\prod_{\mathrm{CMC}} = \gamma_{\mathrm{o}} - \gamma_{\mathrm{CMC}}$, where γ_{o} is the surface tension of water and γ_{CMC} is the surface tension of solution at CMC [30], was determined at different temperatures. The $\gamma_{\max}$, $A_{\min}$ and $\prod_{\mathrm{CMC}}$ values were calculated and are listed in Table 3.

The data listed in Table 3 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 nonionics [31,32]. The $A_{\min}$ of nonionic surfactants that contain PEG in their molecular structureincreases with the number of oxyethylene units [33]. This can

TABLE 3 Surface Properties of the Prepared Surfactants at Different Temperatures

		Temperature (K)		
Sample	Surface property	298	308	318
A200	$\prod$CMC (mNm – 1)	43	44	45
	Amin (nm^2/molecule)	0.612	0.597	0.568
	Γmax 10^{10}cm^{-2}	1.63	1.67	1.74
A600	$\prod$CMC (mNm – 1)	43	43	45
	Amin (nm^2/molecule)	0.567	0.561	0.510
	Γmax 10^{10}cm^{-2}	1.764	1.79	1.81
A1000	$\prod$CMC (mNm – 1)	40	41	39
	Amin (nm^2/molecule)	0.540	0.533	0.491
	Γmax 10^{10}cm^{-2}	1.832	1.875	2.007
A2000	$\prod$CMC (mNm – 1)	48	46	44
	Amin (nm^2/molecule)	0.480	0.398	0.389
	Γmax 10^{10}cm^{-2}	2.071	2.511	2.538

be attributed to the behavior of surfactants with hydrophilic groups at opposite ends of the molecule, which show large area per molecule at theinterface 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} indicate the dependence of the effectiveness of adsorption at the aqueous solution/air interfaces on the structure of surfactants.

The nature of the hydrophilic group has a major effect on the effectiveness of adsorption. In general, A_{min} appears to be determined by the cross-sectional area of the hydrated hydrophilic group at the interface. In nonionic polyoxyethylenated compounds, effectiveness appears to increasing with increase in length of the hydrophobic group [34]. In polyoxyethylenated nonionics the lack of significant temperature effect may result from two compensating effects:

- Decrease in A_{min} at the surface due to increaseddehydration of the hydrophilic group at higher temperature.
- Increase in A_{min} as a result of enhanced molecular motion at higher temperature [35].

In the present system it was found that the minimum area per molecule also decreases with an increase in temperature, which may be a result of breaking of hydrogen bonding by temperature.

The effectiveness of adsorption, however, may increase, decrease or show no change with an increase in the length of the hydrophobic group, depending on the orientation of the surfactant at interface. If the 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 [36].

This is because the cross-sectional area occupied by the chain oriented perpendicular to the interface does not change with an 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 increased length of hydrophobic group, resulting from greater Van der Waals attraction and consequent closer packing of longer chains [37].

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 increased chain length, due to increased cross-sectional area of the molecule on the surface. Thus saturation of the surface may be accomplished by a smaller number of molecules [37,38]. Nonionic surfactants with short PEG chains show a lowering of both efficiency and effectiveness with increased length of PEG [39].

Thermodynamic Parameters of Micellization and Adsorption

The ability for micellization processes depends on thermodynamic parameters, (enthalpy, ΔH, entropy, ΔS, and free energy, ΔG) of micellization. The thermodynamic parameters of micellization are the standard free energies ΔG_{mic}, enthalpies ΔH_{mic}, and entropies ΔS_{mic}, of micellization for nonionic surfactants.

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

Values of ΔS_{mic} were obtained from Eq. (4) by invoking the values of ΔG_{mic} at 298, 308 and 318,

$$\frac{\partial \Delta G_{mic}}{\partial T} = -\Delta S_{mic} \tag{4}$$

In addition, ΔH_{mic}, was calculated from $\Delta\ G_{mic}$ and ΔS_{mic} by applying Eq. (5).

TABLE 4 Thermodynamic Parameters of Micellization for Surfactants at Different Temperatures

	Thermodynamic parameters at different temperatures*						
	298 K		308 K		318 K		ΔS_{mic} kJ mol^{-1} K^{-1}
Sample	ΔG_{mic}	ΔH_{mic}	ΔG_{mic}	ΔH_{mic}	ΔG_{mic}	ΔH_{mic}	
A200	20.59	54.53	−23.06	52.07	−25.64	49.49	0.2521
A600	−24.80	42.70	−26.51	42.36	−29.30	41.91	0.2366
A1000	−25.26	37.42	27.85	34.83	−33.56	32.13	0.2070
A2000	−27.32	12.793	−30.00	11.45	−34.08	9.720	0.1346

*$-\Delta G_{mic}$ and ΔH_{mic} in kJ mol^{-1}.

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

The thermodynamic parameters values of adsorption, ΔG_{ad}, ΔH_{ad} and ΔS_{ad} were calculated via Eqs. (6)–(8), respectively [40].

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

$$\frac{\partial \Delta G_{ad}}{\partial T} = -\Delta S_{ad} \tag{7}$$

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

The obtained values are listed in Table 4. Detailed discussion for the data recorded in these tables will be provided below.

Thermodynamic Parameters of Micellization

The values of ΔG_{mic}, ΔH_{mic} and ΔS_{mic} for the prepared nonionic surfactants were calculated and are listed in Table 4. Analyzing the thermodynamic parameters of micellization indicates that the process is spontaneous ($\Delta G_{mic} < 0$). The data show that ΔG_{mic} values are more negative with increasing number of ethylene oxide units in the chains. This indicates that the increase of hydrophilic groups favors the micellization process, thus covering the most important requirement for surfactant detergency.

The data listed in Table 4 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 aqueous environment. The decrease of positive ΔS_{mic}

value with increasing the number of oxyethylene units in the surfactant molecule has been observed by other investigators [40,41]. This may be because longer PEG Chains lead to increasing solubility of the molecules which allows them more free motion. The dissolution of the oxyethylene units has been stated [40,41] 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 listed previously [42]. It was reported that negative ΔH_{mic} values were obtained at 298 K for p-tert-octylphenoxypoly(ethylenoxy ethanol)s containing less than four oxyethylene units. By such increasing the number of oxyethylene units in the molecule the values of ΔH_{mic} decrease. This is in accord with the observations of other investigators [43,44] indicating that a greater solubility is obtained as a result of lengthening ethylene oxide chains.

Thermodynamic Parameters of Adsorption

The values of ΔG_{ad}, ΔH_{ad} and ΔS_{ad} for the investigated surfactants are calculated and presented in Table 5. 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. It is apparent that the work of transfer, which measures the ease of adsorption to form a monolayer at zero surface pressure relative to ease of micellization, shows appreciable change with temperature in the range 298–318 K, but increases with the increase in the number of oxyethylene units in the molecule. The values of ΔS_{ad} are all positive and have greater values than ΔS_{mic}

TABLE 5 Thermodynamic Parameters of Adsorption for Surfactants at Different Temperatures

	Thermodynamic parameters at different temperatures*						
	298 K		308 K		318 K		
Sample	ΔG_{ad}	ΔH_{ad}	ΔG_{ad}	ΔH_{ad}	ΔG_{ad}	ΔH_{ad}	ΔS_{ad}
A200	−22.5968	61.800	−25.0577	62.104	−26.6388	62.288	0.2765
A600	−25.2701	47.322	−27.5105	45.509	−30.333	44.771	0.2521
A1000	−27.8028	40.011	−29.855	39.576	−35.560	39..322	0.2171
A2000	−30.3189	27.3189	−35.0105	20.6862	−37.083	19.25951	0.1614

*−ΔG_{ad}, ΔS_{ad} and ΔH_{ad} in kJ mol^{-1}.

for nonionic surfactants based on Schiff base. This may reflect the greater freedom of motion of the hydrophobic moieties at the planar air-aqueous solution interface compared to that in the relatively cramped interior inside the convex surface of the micelle.

Evaluation of the Prepared Surfactants as Oil Spill Dispersants

The use of dispersants generally is preferred over the other options if there is insufficient time for prior mechanical recovery of the oil. If use of dispersants will prevent environmental damage, dispersion of the spilled oil should be strongly considered. Also, if dispersion of oil can reduce or eliminate hazardous conditions, use of dispersants is also recommended.

The use of chemical dispersants as a countermeasure to accidental oil spills at sea is now a technique accepted worldwide. In recent years, the commercial availability of dispersants, containing less toxic chemicals and more efficient surfactants, has renewed interest in basic studies on dispersant effectiveness and on the fate of dispersed oil in the marine environment [45–47].

Dispersants effectiveness is defined as the amount of oil that the dispersants put into the water phase versus that which remains on the surface. There are many factors that influence dispersant effectiveness: sea energy, oil composition, state of oil weathering, rate of dispersants application, dispersant type, temperature, and salinity of the water. The most important factor for dispersants' effectiveness is the composition of the oil, followed very closely by sea energy and amount of dispersant applied. Effectiveness of dispersants is relatively easy to measure in the laboratory however, there are many nuances in testing procedures.

In this respect, the dispersion capability of individual nonionic surfactants (ethoxylated Schiff base) was tested on asphaltenic crude oil. The surfactant to oil ratio (SOR) was in a range from 1:5 to 1:30. The relation between SOR and dispersion efficiency for all prepared surfactants were thoroughly studied at 25°C and presented in Figure 3. The data reveal that A200 has the maximum efficiency (95%) at SOR from 1:10 to 1:20. The obtained results can be correlated with the thermodynamic data of micellization and adsorption which indicate the dependence of adsorption process on the chemical structure of surfactants. It was found above that the prepared surfactants favor adsorption over micellization which is sensitive to the molecular weight of PEG. The data of dispersion capabilities of the prepared surfactants can also be correlated with HLB values of these surfactants. Typically the HLB of common commercial dispersants ranges from 9 to 12 [47].

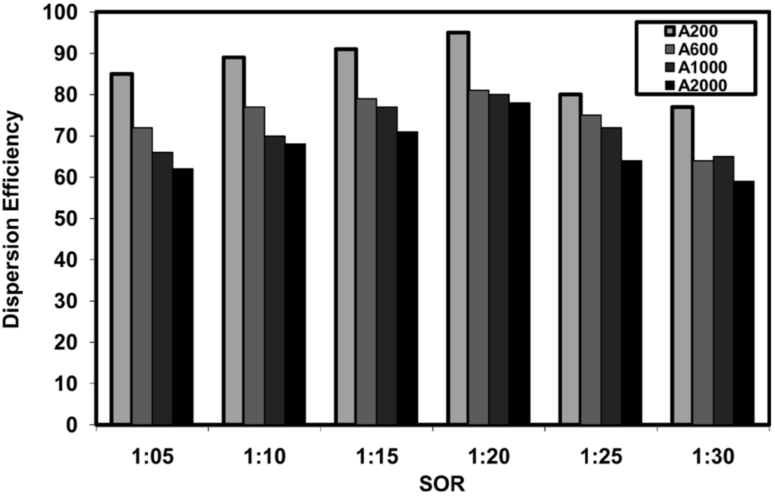

FIGURE 3 Dispersion efficiency at different SOR for the prepared surfactants.

Particle Size Distribution

Figure 4 shows particle size distribution of an oil emulsion (10% oil in toluene agitated for 30 min) in absence and presence of 100 ppm of A200.

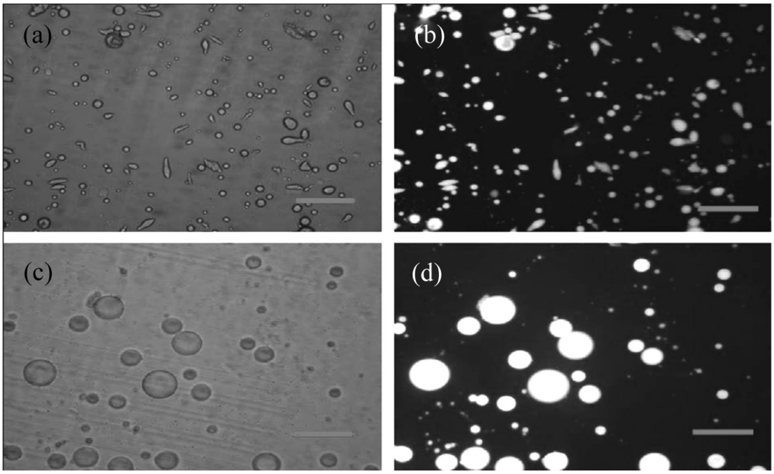

FIGURE 4 Images of oil droplet formation under the inspection of epifluorescent microscope: oil particles formed in the presence (a and b) and absence (c and d) of dispersant from the observation under transmitted light (a and c) or epifluorescent (b and d) light illumination. Samples taken for imaging were diluted by a factor of 20 before microscopy. Bars shown are 100 lm.

The chemically dispersed emulsion (with the dispersant) appeared to have predominantly uniform structures in morphology, whereas the physically dispersed emulsion was largely spherical (unstable emulsion). Enumeration of the dispersed oil particles under the microscope indicated that chemical dispersant dramatically increased the particles number per unit volume.

CONCLUSIONS

The following conclusions can be drawn:

- Four nonionic surfactants based on ethoxylated Schiff base were prepared.
- The thermodynamic properties for micellization and adsorption were calculated for all the prepared surfactants, based on measuring the surface tension of different solutions at three temperatures.
- It was found that the prepared surfactants favor micellization rather than adsorption.
- The investigated compounds were tested as crude oil dispersants by standard test method.

It was found the A200 shows maximum dispersancy (95%) at SOR from 1:10 to 1:20.

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