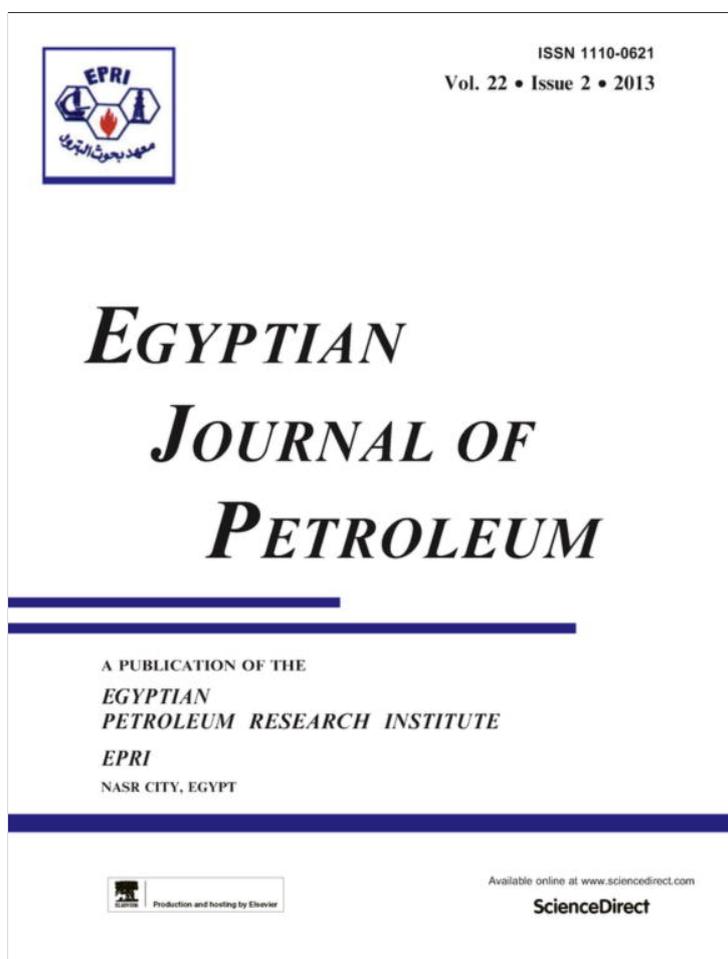


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Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

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FULL LENGTH ARTICLE

Synthesis of new surface-active ammonium-type complexes based on palmitic acid for removing thin petroleum films from water surface

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KEYWORDS

Palmitic acid;
Nitrogen-containing compounds;
Complex;
Dispersing agent;
Collecting agent;
Propylene oxide

Abstract Complexes based on palmitic acid and nitrogen-containing compounds (monoethanolamine and triethylenetetramine) were synthesized. The synthesized complexes were taken to react with different moles of propylene oxide (1, 2 and 3) to form propoxylated compounds (surfactants). Some of physico-chemical indices of the prepared compounds such as solubility, acid and amine numbers as well as electrical conductivity have been determined. Surface-active properties (interfacial tension) of the obtained complexes were investigated by the stalagmometric method. Surface properties studied included critical micelle concentration (CMC), maximum surface excess (Γ_{\max}), and minimum surface area (A_{\min}). Free energies of micellization ($\Delta G_{\text{mic}}^{\circ}$) and adsorption ($\Delta G_{\text{ads}}^{\circ}$) were calculated. Petroleum-collecting and dispersing properties of the synthesized and propoxylated complexes in diluted (5 wt.% aq. solution) and undiluted form in waters of varying salinity have been studied. FTIR spectra, C^{13} and H^1 NMR spectra confirm the compound structure.

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Abbreviations: PMEa, palmitic acid and monoethanolamine complex; PTETA, palmitic acid and triethylenetetramine complex; POPMEa1, PMEa added 1 mol propylene oxide; POPMEa2, PMEa added 2 mol propylene oxide; POPMEa3, PMEa added 3 mol propylene oxide; POPTETA1, PTETA added 1 mol propylene oxide; POPTETA2, PTETA added 2 mol propylene oxide; POPTETA3, PTETA added 3 mol propylene oxide; CMC, critical micelle concentration

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1. Introduction

Oil pollution is a significant hazard for the marine environment. Sources of such pollution include oil exploration and production operations, natural seeps, atmospheric input, tanker accidents, industrial discharge, and urban run-off [1]. Increasing demand for petrochemicals has led to increased levels of petroleum hydrocarbons in marine, coastal and estuarine environments.

Oil in the sea can occur as dispersed oil droplets, as an emulsion (water in oil or oil in water), bound to solid particles, or solubilized in water. Chemical dispersants and collectors are used as cleaning agents to alter the normal behavior of petroleum hydrocarbons by increasing their functional water solubility, resulting in increased bioavailability and altered interactions between dispersant, oil, and biological membranes [2–6].

The use of chemical dispersants is still restricted by many governmental regulations and controlled by guidelines in field application [7–9]. This situation is mainly due to the bad reputation of the first generation of dispersants developed in the early 1970s, which were, in some cases, so toxic to the marine environment that adverse effects of the dispersed oil were much greater than the effects of untreated oil [10].

Oil spill dispersants and collectors reduce the interfacial tension in the oil–water interface to very low values. It therefore takes only a small amount of mixing energy to increase the surface area and break the oil slick into droplets stabilized by oil spill surfactant [11–16]. The behavior of a surfactant is affected by its hydrophilic-lipophilic balance (HLB).

The main target of this work is to prepare ecologically safe and better petroleum-collecting and dispersing agents based on palmitic acid and monoethanolamine, as well as triethylenetetramine to form surface active complexes. The synthesized complexes are reacted with different moles of propylene oxide to form propoxylated complexes (highest petro-collecting and dispersing properties). Surface properties including the CMC, the maximum surface excess (Γ_{\max}), the minimum surface area (A_{\min}) and effectiveness (Π_{CMC}) were determined. Petro-collecting and dispersing properties of synthesized complexes were thoroughly studied.

2. Experimental

2.1. Materials

Propylene oxide was used as an industrial product of the factory “Organic Synthesis” (Sumgait, Azerbaijan). It had a purity of 99.97%. Triethylenetetramine was from the “Kazanorgsintez” Joint Stock Company (Russia) and was used without further purification. Palmitic acid was from Moscow’s “Component-Reactant” Joint Stock Company (Russia) production. Monoethanolamine was of Russian Federation production (95% purity) (see Table 1).

2.2. Instrumentation

^1H NMR and ^{13}C -NMR spectra were recorded on a Bruker TOP SPIN 300.13 MHz and 75.46 MHz spectrometer with chemical shift values (δ) in ppm downfield from TMS using CDCl_3 , acetone- d_6 and CCl_4 as solvents. IR spectra were recorded on a model FT-IR, Spectrum BX spectrometer using KBr disks. Acid and amine numbers are determined according to procedures given in [17]. Electrical conductivity for the prepared complexes was measured using a Conductivity Meter apparatus, type OK-102/1, made in Hungary.

2.3. General procedure for the reactions of palmitic acid with monoethanolamine and triethylenetetramine

Palmitic acid (0.01 mol) was taken at equimolar ratio separately with monoethanolamine and triethylenetetramine. The

components of reactions were mixed, closed well and placed in a thermostat at a temperature ranging from 55 and 60 °C for a period between 20 and 25 h. The obtained complexes are generally viscous liquids and solids. Their colors vary from yellow to blackish-brown.

2.4. Propoxylation of the synthesized complexes

The synthesized complexes were mixed at different mole ratios with propylene oxide (1:1, 1:2 and 1:3). The reaction mixture was heated in an autoclave at temperature of 120–130 °C on a sand bath for 25–30 h, and then cooled. The propoxylated product was obtained by moderate evaporation of unreacted propylene oxide. Conversion of propylene oxide was found by gravimetric method. The number of propylene oxide moles for PTETA is 0.96, 1.72 and 2.81 and for the PMEA 0.95, 1.85 and 2.78.

2.5. Evaluation methods of surface active properties

2.5.1. Interfacial tension measurements

Measurements of the interfacial tension were carried out using deionized water to make the solutions. The solutions kept at the desired temperature were measured 45 s after transfer to the thermostated measuring dishes. The actual temperature within the dishes was controlled prior to and after the measurement by means of a thermocouple. Deviations from the desired temperature were ± 0.3 °C. The interfacial tension as a function of concentration was measured at 20 °C using a drop volume stalagmometer. Interfacial tension values from the three measurements varying by no more than 0.3 mN/m were averaged and reported.

2.5.2. Determination of critical micelle concentration

Critical micelle concentration values of the prepared compounds were determined using interfacial tension techniques, i.e., the interfacial tension measurements were plotted against the \ln of the surfactant complex concentration. As is usual, the abrupt change in the curve slope is taken as the CMC.

2.5.3. Effectiveness

Effectiveness (Π_{CMC}) is the difference between the surface tension of pure water (γ_0) and the surface tension of the surfactant solution (Π_{CMC}) at the CMC:

$$\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \quad (1)$$

2.5.4. Maximum surface excess

The values of the maximum surface excess (Γ_{\max}) were calculated from surface or interfacial data by the use of Gibbs equation [18]:

$$\Gamma = 1/RT(\delta\gamma/\delta\ln C)_T \quad (2)$$

where:

Table 1 The general characterization of the sea water.

Density	pH	Cations				Anions	
		Sodium	Calcium	Potassium	Magnesium	Chloride	Sulfate
1.0098 g/mL	7.7	2.99 g/kg	0.34 g/kg	0.09 g/kg	0.70 g/kg	5.18 g/kg	2.98/kg

Γ Surface excess in mole/cm²

R Universal gas constant 8.31 J mole⁻¹ K⁻¹

T Absolute temperature

γ Surface pressure in mN/m

C Surfactant concentration

$(\delta\gamma/\delta\ln C)T$ is the slope of a plot interfacial tension versus ln concentration curves below CMC at constant temperature.

2.5.5. Minimum surface area

The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule. The average minimum surface area (A_{min} ; in square Angstrom) occupied by each molecule adsorbed on the interface [19] is given by:

$$A_{min} = 10^{16} / \Gamma_{max} N_A \quad (3)$$

where:

N_A is Avogadro's number.

2.5.6. Thermodynamic parameters of micellization and adsorption

The thermodynamic parameters of adsorption and micellization of the synthesized complexes were calculated according to Gibbs adsorption equations as follows [20]:

$$\Delta G_{mic}^{\circ} = RT \ln C_{CMC} \quad (4)$$

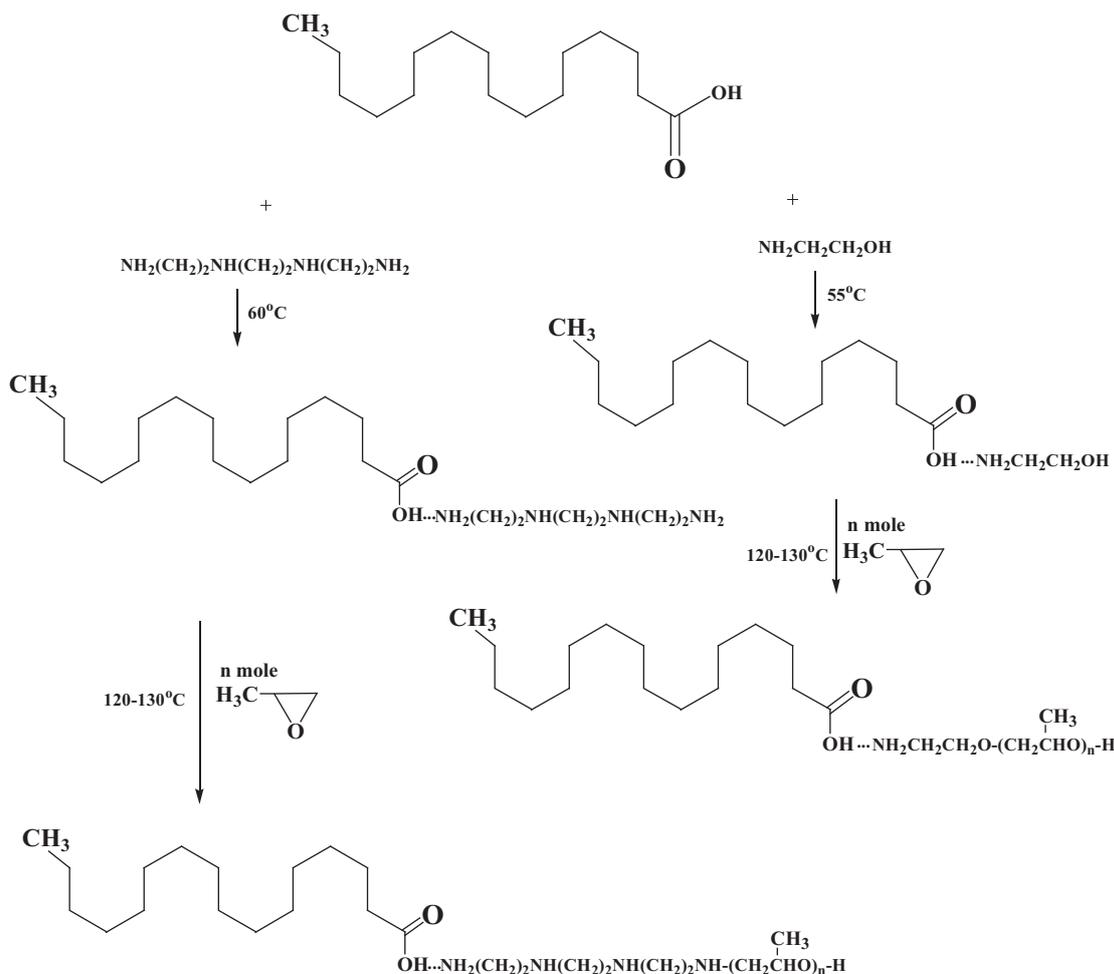
$$\Delta G_{ads}^{\circ} = \Delta G_{mic}^{\circ} - 6.023 \times 10^{-1} \times A_{min} \times \Pi_{CMC} \quad (5)$$

2.5.7. The interfacial activity (I_{activ})

I_{activ} is expressed by physico-chemical parameter $\Delta G_{ads}^{\circ} / A_{min}$, where ΔG_{ads}° is the standard free energy of adsorption of the surfactant at the air-solution interface and A_{min} is the minimum cross-sectional area of the surfactant.

2.6. Procedure for studying petroleum-collecting and petroleum-dispersing capacities

Petroleum-collecting properties of the synthesized compounds (in the pure state and in the form of 5 wt.% aq. solution) have been mainly studied on the example of Ramany crude oil (density and kinematic viscosity at 20 °C are respectively 0.86 g/cm³ and 0.16 cm²/s) from the oil field in the Absheron peninsula (Azerbaijan). The surfactant (0.02 g) or its solution was added to a thin film (thickness 0.16–0.17 mm) of this petroleum on the surface of distilled water, fresh water and the Caspian Sea water (Table 1) (separately) in Petri dishes. The maximum values of the petroleum collecting coefficient (K) are calculated using



Where n is 1, 2 and 3 mole

General scheme For preparation of palmitic acid complexes and propenoxylation of the synthesized complexes.

the formula $K = S_0/S$, where S_0 is an area of the surface of initial petroleum film and S is an area of the surface of accumulated petroleum (as a thickened spot). Since the moment of the surfactant application observations are carried out with measurement of the spot surface area and determination of the K values at fixed time intervals. When the crude oil film is dispersed, the percentage of the water surface cleaning (k_d) is found at the appropriate times of measurements. K_d is calculated using the ratio of the surface area of the oil at the peripheral part of the dish and the surface area of the initial oil slick.

3. Results and discussion

3.1. Synthesis and propoxylation of palmitic acid complexes

The synthesis complexes and their propoxylation can be illustrated by the following reaction scheme.

3.2. Measurements of physico-chemical indices of synthesized complexes and propoxylated compounds

Such physico-chemical indices as solubility in different solvents (water, ethyl alcohol, CCl_4 , toluene, kerosene), electro-conductivity, acid and amine numbers were determined. It is noted from Table 2 that the obtained complexes are generally viscous liquids and solids. Their colors vary from yellow to blackish-brown color. Measurements of the electrical conductivity of the complexes 0.5% aqueous solutions proved their polarity. Measurements of the acid and amine numbers for all complexes were done.

3.3. Results of FTIR, ^{13}C and ^1H NMR data

PTETA is a yellowish-brown wax, insoluble in water. IR showed an absorption band at the $1555.4\text{--}1595.4\text{ cm}^{-1}$ region character-

istic for $\delta\text{ COO}^-$ stretches, in addition to $2847.8\text{--}2917.1\text{ cm}^{-1}$ for aliphatic CH, 3210.5 cm^{-1} for NH (amine groups). This proves formation of the target complexes. ^1H NMR (300.13 MHz, CDCl_3), δ (ppm): 0.82 (t, 3H, $\text{CH}_3\text{--CH}_2$), 1.1–1.3 (m, 22H, CH_2 chain), 1.51 (t, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$), 2.2 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$), 2.52 (t, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$), 2.51 (q, 2H, $\text{CH}_2\text{CH}_2\text{NH}$), 2.87 (q, 6H, $(\text{CH}_2)_2\text{NHCH}_2$), 2.92 (t, 1H, $\text{NH}(\text{CH}_2)_2$), 3.53 (s, 1H, $\text{H}\dots\text{NH}_2$), 5.3 (m, 4H, $(\text{CH}_2)_2\text{NH}$), 5.31 (s, 2H, $(\text{CH}_2)_2\text{NH}_2\dots\text{H}$), 5.34 (m, 1H, NHCH_2), 2.5 (m, 2H, $(\text{CH}_2)_2\text{NH}_2$). $^{13}\text{C}\text{--}\{^1\text{H}\}$ NMR (75.46 MHz, CDCl_3) δ (ppm): 13.1 ($\text{CH}_3\text{--CH}_2$), 20–40 (saturated alkyl chain 20CH_2), 182 (COO). IR of propoxylated compounds showed the appearance of absorption bands at $3103\text{--}3200.4\text{ cm}^{-1}$ region characteristic for the terminal OH group and at $1040\text{--}1110\text{ cm}^{-1}$ which is intrinsic for C–O of the desired compounds. ^1H -NMR (300.13 MHz, CDCl_3), δ (ppm): 3–3.5 (m, 3H, $\text{CH}_2\text{CH--O}$), 1.3 (d, 3H, $\text{CH}_2\text{CH}(\text{CH}_3)\text{--O}$) of the propylene oxide group beside the other protons of the original compound. ^{13}C -NMR (75.46 MHz, CDCl_3) δ (ppm): 15.2 ($\text{CH}_2\text{--CH}(\text{CH}_3)\text{O}$), 38.3 ($\text{CH}_2\text{--CH--O}$), 36.1 ($\text{CH}_2\text{--CH--O}$) beside the other carbons of the original compound.

3.4. Surface properties of the prepared surfactant complexes

3.4.1. Interfacial tension measurements

Interfacial tension at the kerosene–water border in the presence of prepared complexes and propoxylated compounds was measured and shown in Figs. 1 and 2. From Table 3 it is noted that PMEAs has good surface-active properties. Also as the length of the polyoxypropylene chain of the nonionic portion increases it leads to a higher surface activity.

3.4.2. Critical micelle concentration

CMC values of the prepared complexes were determined by plotting the interfacial tension (γ) of surfactant solutions

Table 2 Some physico-chemical characteristics of synthesized complexes and products of their propoxylation.

Complex	External view of the complex	Acid number, mg. KOH/gm	Amine number, mg HCl/gm	Solubility of the complexes	Electrical conductivity 0.5 wt.% of aqueous solution, $\text{Ohm}^{-1}\text{ m}^{-1}$
PMEA	Solid of yellowish–brown color	–	5.0	Turbid solution was obtained in water, toluene, CCl_4 and kerosene; readily soluble in ethyl alcohol	0.048700
POPMEA1	Solid of muddy-brown color	9.1	–	Insoluble in water; readily soluble in ethyl alcohol, toluene and CCl_4 ; soluble in kerosene	0.0000116
POPMEA2	Semi-solid of blackish-brown color	20.4	–	Turbid solution was obtained in water; readily soluble in ethyl alcohol, toluene, CCl_4 and kerosene at $70\text{ }^\circ\text{C}$	0.001740
POPMEA3	Viscous liquid of blackish-brown color	8.9	–	Turbid solution was obtained in water at $60\text{ }^\circ\text{C}$, readily soluble in ethyl alcohol, toluene, CCl_4 and kerosene at $70\text{ }^\circ\text{C}$	0.001550
PTETA	Semi-solid of yellowish-brown color	–	6.1	Turbid solution was obtained in water; readily soluble in ethyl alcohol, toluene, CCl_4 ; soluble in kerosene	0.000262
POPTETA1	Viscous liquid of yellow color	1.6	–	Readily soluble in water, ethyl alcohol, toluene, CCl_4 and kerosene	0.001740
POPTETA2	Viscous liquid of yellow color	3.2	–	Readily soluble in water, ethyl alcohol, toluene, CCl_4 and kerosene	0.001240
POPTETA3	Semi-solid of brown color	5.9	–	Readily soluble in water, ethyl alcohol, toluene, CCl_4 and kerosene	0.008940

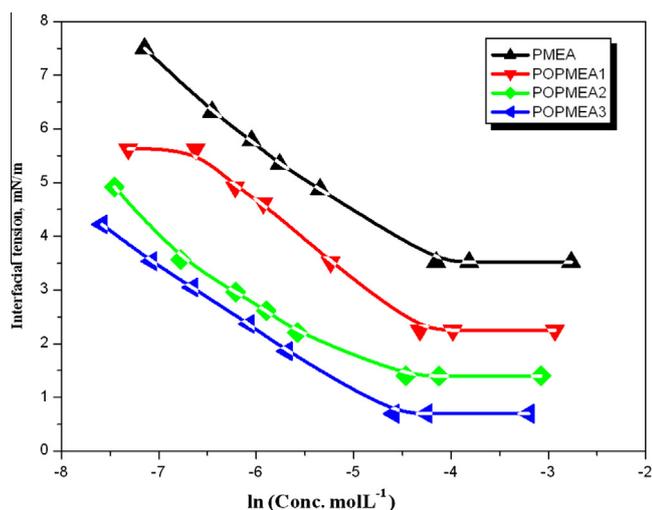


Figure 1 Interfacial tension versus concentration of PMEa complex and products of its propoxylation in aqueous solution at 20 °C.

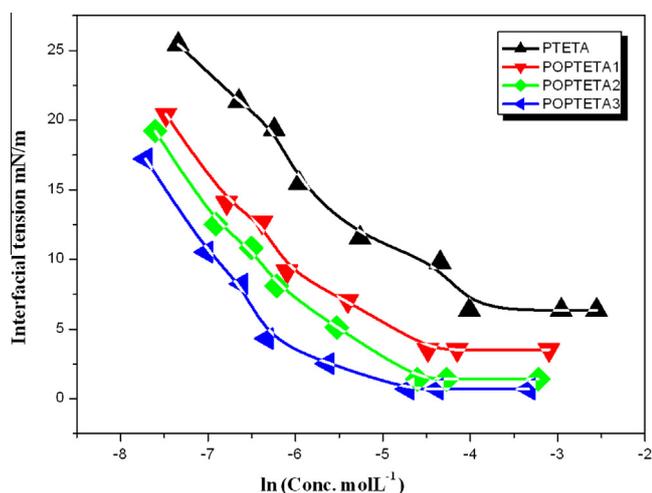


Figure 2 Interfacial tension versus concentration of PTETA complex and products of its propoxylation in aqueous solution at 20 °C.

versus their bulk concentrations in mole/L at 20 °C. The CMC values listed in Table 3 show a decrease in CMC with increase in the length of the polyoxypropylene chain of the nonionic portion that corresponds to the results described in [21].

3.4.3. Effectiveness (Π_{cmc})

The effectiveness (Π_{cmc}) is determined by the difference between interfacial tension values at CMC (γ_{cmc}) and measured for pure water at the appropriate temperature (γ_0). From the results in Table 3 it is noted that PMEa and products of its propoxylation compounds are the most effective ones.

3.4.4. Maximum surface excess

The number of surfactant molecules at the kerosene-water interface at the CMC at 20 °C is expressed by Γ_{max} . A substance lowering the surface energy is thus present in excess at or near the surface, i.e., when the interfacial tension decreases with increasing activity of surfactant, Γ_{max} is positive. It can be noted from Table 3 that PTETA and propoxylated compounds derived from it have higher Γ_{max} values than other complexes. Also, as the length of the oxypropylene chain of the nonionic portion increases, this leads to an enhance in the migration of molecules to the water-kerosene interface, causing a consequent increase in Γ_{max} values.

3.4.5. Minimum surface area

The minimum surface area is defined as the area occupied by surfactant molecules at the kerosene-water interface when the solution is at equilibrium. The results given in Table 3 indicate that the higher values of Γ_{max} lead to crowding at the interface, which results in smaller A_{min} values.

3.4.6. Standard free energies of micellization and adsorption

From Table 3, it is evident that the values of the standard free energies of micellization and adsorption (ΔG_{mic}^{deg} and ΔG_{ads}^{deg}) are always negative, indicating that these two processes are spontaneous; however, there is a greater increase in the negative value of ΔG_{ads}^{deg} compared to those of micellization. This suggests the tendency of the molecules to be preferentially adsorbed at the interface.

3.5. Petroleum-collecting and dispersing properties of the synthesized complexes and propoxylated compounds

Petroleum-collecting and petroleum-dispersing properties of the synthesized surfactants were studied using as an example thin films of Ramany crude oil on the surface of distilled, fresh and sea waters, the surfactant being taken in undiluted form and as 5% wt. aq. solutions. In Tables 4 and 5 results of studies of petroleum-collecting and petroleum-dispersing ability of the synthesized surfactants are presented. From Table 4 it can be noted that POPMEa1 in diluted form exhibits a better petroleum-collecting action in distilled water ($K_{max} = 35.8$, $\tau = 52.5$ h), a good effect in sea water ($K_{max} = 27.6$,

Table 3 Surface properties of the synthesized complexes and products of their propoxylation.

Complex	CMC $\times 10^{-3}$, mol L $^{-1}$	γ_{cmc} , mN/m	Π_{cmc} , mN/m	$\Gamma_{max} \times 10^{-11}$, (mol cm $^{-2}$)	$A_{min} \times 10^2$, (nm 2)	ΔG_{mic}° , kJ/mol	ΔG_{ads}° , kJ/mol	$\Delta G_{ads}^{\circ}/A_{min}$ kJ/mol.nm 2
PMEa	15.75	3.5	42.9	5.3	3.11	-10.1	-90.6	-29.1
POPMEa1	13.30	2.2	44.2	5.9	2.79	-10.5	-89.7	-32.1
POPMEa2	11.00	1.4	45.1	6.0	2.75	-10.9	-85.7	-31.1
POPMEa3	10.00	0.7	45.8	6.1	2.71	-11.2	-85.9	-31.7
PTETA	18.00	6.4	40.1	22.7	0.73	-9.8	-27.4	-37.6
POPTETA1	11.27	3.5	42.9	23.3	0.71	-10.9	-29.3	-41.3
POPTETA2	9.97	1.4	45.1	23.6	0.70	-11.2	-30.2	-43.2
POPTETA3	8.90	0.7	45.8	28.1	0.60	-11.5	-28.1	-46.7

Table 4 Petroleum-collecting and petroleum dispersing properties of PMEOA complex and products of its propoxylation.

Surfactants	Undiluted product						5 wt.% solution					
	Distilled water		Fresh water		Sea water		Distilled water		Fresh water		Sea water	
	τ (h)	k	τ (h)	k	τ (h)	k	τ (h)	k	τ (h)	k	τ (h)	k
PMEA	0	24.3	0	2.6	0–169	No effect	0	22.5	0	1.7	0	2.8
	1.5	17.4	1	3.8			1.5	1.8	1.5	Spilling	19.0	2.6
	19.0	9.3	43	3.0			19.0	1.8			49.5	2.9
	25.5	2.2	49	2.8			25.5	Spilling			67.0	Spilling
	73.5	Spilling	139	3								
POPMEA1	0	1.5	0	1.7	0	2.8	0	24.3	0	17.5	0	17.4
	4.5	4.4	22	4.6	22.0	8.1	4.5–28.5	30.4	4.5–22	20.3	22	21.7
	22.0	8.6	70	6.0	28.5	9.2	46.0	34.7	28.5–46	24.3	28.5	24.3
	28.5	9.2	76.5	6.3	46–52.5	66.9%	52.5	35.8	52–76	26.4	46–52.5	25.4
	96–166	10.1	96–166	8.1	70–166	82.6%	76.5	26.4			70–76	27.6
POPMEA2	0–2.5	2.9	0–140	91.1%	0–2.5	30.4	0–2.5	91.1%	0–2.5	No effect	0–2.5	No effect
	20–140	24.3			20–140	40.5	20–74.5	40.5	20	3.8	20	2.2
							140	88.9%	26.5–50.5	4.2	26.5	3.1
									68–74.5	4.8	44–74.5	2.4
									140	2.4	140	Spilling
POPMEA3	0–2.5	2.1	0–2.5	2.2	0–2.50	2.2	0–2.5	10.1	0–2.5	20.3	0–2.5	91.1%
	20	2.9	20–26.5	13.5	20–26	3.8	20–74.5	24.3	20–26.5	30.4	20–140	88.9%
	26.5	6.3	74.	10.6	44	2.5	140	8.7				
	140	8.7	140	Spilling	50–140	2.4						

K is collecting coefficient; k_d is water surface cleaning percentage; τ is fixed time interval.

Table 5 Petroleum-collecting and petroleum dispersing properties of PTETA complex and products of its propoxylation.

Surfactants	Undiluted product						5 wt.% solution					
	Distilled water		Fresh water		Sea water		Distilled water		Fresh water		Sea water	
	τ (h)	k	τ (h)	k	τ (h)	k	τ (h)	k	τ (h)	k	τ (h)	k
PMEA	0–22	No effect	0–5.50	No effect	0–5	91.7%	0	20.3	0	78.6%	0–5	15.2
	95	7.6	22–239	91.7%	22–239	95.5%	22–77	24.3	5.5–166	95.5%	22–29	71%
	101	10.1					95	20.3			46–101	75%
	166	95.5%					101	17.4			166	94%
POPMEA1	0	8.7	0–2	91.1%	0	7.6	0	10.1	0	88.9%	0–165	86.8%
	2	20.3	19.5–165	95.5%	2	86.8%	2	15.2	2	91.1%		
	19.5–165	95.5%			19.5–165	95.5%	19.5–165	95.5%	19.5–165	95.5%		
POPMEA2	0	10.4	0–5	91.1%	0	9.3	0	12.4	0	88.9%	0–165	91.1%
	2	25.4	19.5–165	95.5%	2	86.8%	2	18.5	2	91.1%		
	19.5–165	95.5%			19.5–165	95.5%	19.50–165	95.5%	19.5–165	95.5%		
POPMEA3	0	8.7	0–5	91.1%	0	12.6	0	12.8	0–5	91.1%	0–165	95.5%
	19.50–165	95.5%	19.5–165	95.5%	5–165	91.1%	5–165	91.1%	52–165	95.5%		

K is collecting coefficient; k_d is water surface cleaning percentage; τ is fixed time interval.

$\tau = 70–76$ h) and in fresh water ($K_{max} = 26.4$, $\tau = 52–76$ h). But in undiluted form it gave a good petroleum-dispersing effect in sea water ($K_d = 82.6\%$, $\tau = 70–166$ h) and moderate petroleum-collecting effect ($K_{max} = 10.1$, $\tau = 96–166$ h). POPMEA2 in undiluted form gave a very high petroleum-collecting effect in sea water ($K_{max} = 40.5$, $\tau = 20–140$ h), a good petroleum-collecting effect in distilled water ($K_{max} = 24.3$, $\tau = 20–140$ h) and a better petroleum-dispersing effect in fresh water ($K_d = 91.1\%$, $\tau = 0–140$ h). In diluted form POPMEA2 exhibits a good petroleum-dispersing effect in distilled water ($K_d = 88.9\%$, $\tau = 140$ h). POPMEA3 in diluted form exhibits the highest petroleum-collecting property in fresh water ($K_{max} = 30.4$, $\tau = 20–26.5$ h), a good petroleum-collecting

effect in distilled water ($K_{max} = 24.3$, $\tau = 20–74.5$ h) and a good petroleum-dispersing effect in sea water ($K_d = 88.9\%$, $\tau = 20–140$ h). But in undiluted form POPMEA3 gave a good petroleum-collecting effect in fresh water ($K_{max} = 13.5$, $\tau = 20–26.5$ h). From all results it can be observed that all the propoxylated compounds gave higher effect than PMEAs themselves. Also POPMEA2 is the best compound toward the petroleum-collecting and dispersing properties so that POPMEA2 can be used as a petroleum-collecting agent in distilled and fresh waters.

From the results given in Table 5 it is seen that PTETA and its propoxylated derivatives can be used mainly as petroleum-dispersing agents in waters of varying salinity (fresh and sea waters). Petroleum-collecting is observed mainly in distilled

water. As the number of propylene oxide units increase in case of undiluted product petroleum-collecting in sea water at the initial time becomes more effective whereas PTETA itself in this water is a dispersant. In fresh water propoxylated products are more effective dispersants than PTETA itself. In the case of diluted products petroleum-dispersing in sea water occurs more effectively (especially the first 4 days) when propoxylated compounds are used.

4. Conclusion

In this study, the palmitic acid complexes and oxypropylated compounds were prepared and characterized by physico-chemical indices. The prepared compounds were identified by FTIR, ^{13}C and ^1H NMR spectra. It was found that all the synthesized complexes have high surface activities particularly PMEAC complex and its propoxylation products. From the results of studying the petroleum-collecting and dispersing properties of the synthesized complexes, we found that all the synthesized compounds have better petro-collecting and dispersing effects. POPMEA2 can be used as petroleum-collecting agent in sea water and petroleum-dispersing agent in fresh water. Also PTETA and its propoxylated compounds can be used as petroleum-dispersing agent in diluted or undiluted form in waters of varying salinity (distilled, fresh and sea waters).

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