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RESEARCH ARTICLE - CHEMISTRY

Synthesis of New, Ecologically Safe and Efficient Oil Slick-Collecting and Dispersing Agents Based on Oleic Acid and Its Propoxylation Products

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Abstract In this study, the complexes synthesized by reactions of oleic acid separately with ethylenediamine and triethylenetetramine were reacted with different moles of propylene oxide to form propoxylated compounds. The obtained propoxylated compounds were characterized by a number of physico-chemical methods. The physical properties of the synthesized surfactants including interfacial tension and critical micelle concentration were determined. From these measurements, the maximum surface excess concentration and the minimum area per molecule at the water solution/ kerosene interface and the standard thermodynamic parameters of adsorption and micellization were calculated. Petroleum-collecting and dispersing properties of the synthesized propoxylated complexes in diluted and undiluted form in waters of varying salinity have been studied. FTIR spectra, C^{13} and H^1-NMR spectra confirm these complex structures.

Keywords Oleic acid · Propoxylated compounds · Surfactant · Collecting agent · Dispersing agent · Propylene oxide

الخلاصة

تم الحصول في هذه الدراسة على مركبات تعتمد على تفاعل حمض الأوليك مع الايثلين داى امين والترای ايثلين تترامين مع مولات مختلفة من أوكسيد البروبلين لكي تعطي مشتقات مركبات البروبكسيل. وتم تعيين خواص هذه المراكبات المكونة عن طريق بعض الطرق الفيزيوكيميائية. وتم كذلك تحيد الخواص الفيزيائية التي تشمل التوتر السطحي البيني والتركيز الحرج لتكوين المايسل (CMC). ومن هذه القياسات تم تحديد التركيز الأعلى الزائد على السطح والمساحة الأقل للجزء عند السطح الفاصل بين الماء والكيروسين، وتم إلى جانب ذلك تحديد عوامل الامتزاز والديناميكا الحرارية القياسية لتكوين المايسل. وتم دراسة الخواص التجمعية والتشتتية للبترول للمركبات التى تم الحصول عليها فى الحالة المخففة بالماء وغير المخففة وكذلك في أنواع ملوحة مختلفة. وتم أخيراً إثبات شكل المركبات باستخدام طيف الاشعه الحمراء وبروتون وكربون الرنين المغناطيسي.

Abbreviations

OEDA	Oleic acid and ethylenediamine complex
OTETA	Oleic acid and triethylenetetramine complex
POOEDA1	OEDA added 1 mol propylene oxide
POOEDA2	OEDA added 2 mol propylene oxide
POOEDA3	OEDA added 3 mol propylene oxide
POOTETA1	OTETA added 1 mol propylene oxide
POOTETA2	OTETA added 2 mol propylene oxide
POOTETA3	OTETA added 3 mol propylene oxide
CMC	Critical micelle concentration

1 Introduction

Pollution of water basins with crude oil and oil products is one of the principal problems facing mankind currently. Due to various reasons, including accidents in oil tankers and oil pipelines, a huge amount of crude oil enters the hydrosphere. After removing thick oil films by mechanical

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means on the water surface there always remains a thin oil film which is ecologically hazardous. Such thin films may be liquidated only using colloid-chemical methods that include an application of petroleum-collecting and petroleum-dispersing reagents [1–9].

Ionic and complex surfactants are strong emulsifiers which are very soluble in water and partially soluble in oil so such surfactants are usually used to remove the water from any oil present. Though such products disappear rapidly in the water column, they are readily available at a reasonable price. Therefore, some ionic surfactants are proposed for use as dispersants. These agents are better classified as surface-washing agents [10–18].

The purpose of this work is the investigation of the surface properties for the new synthesized propoxylated compounds. Also, we study their application as petroleum-collecting and petroleum-dispersing agents.

2 Experimental

2.1 Materials

Triethylenetetramine was obtained from "Kazanorgsintez" Joint Stock Company (Russia) and was used without further purification. Ethylenediamine was obtained from Russian Federation. Propylene oxide was used as an industrial product of the factory "Organic Synthesis"(Sumgait, Azerbaijan). It has a purity of 99.97 %. Oleic acid was from Moscow's "Component-Reactant" Joint Stock Company (Russia) production (Table 1).

2.2 Instrumentation

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker TOP SPIN 300.13 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 FTIR, Spectrum BX spectrometer using KBr disks. Acid and amine numbers were determined according to procedures given in [18]. Electrical conductivity for the prepared complexes were measured using conductivity meter apparatus, type OK-102/1, made in Hungary.

2.3 General Procedure for Synthesis of Oleic Acid Complexes

Equimolar amount of oleic acid (0.01 mol) was taken separately with ethylenediamine and triethylenetetramine. The components of reactions were mixed, closed well and placed in a thermostat at a temperature ranging between 50 and 55 °C for a period ranging between 20 and 25 h. The obtained complexes are generally very viscous liquids. Their colors vary from brown 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 120–130 °C on 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 mole equivalents of propylene oxide moles added to OTETA were 0.94, 1.81 and 2.70 and to OEDA were 0.96, 1.75 and 2.81.

2.5 Evaluation Methods of Surface-Active Properties

2.5.1 Interfacial Tension Measurements

All the interfacial tension measurements were carried out using distilled water to make the solutions. The solutions were kept at the desired temperature using 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 ±0.2 °C. The interfacial tension as a function of concentration was measured at 25 °C using a drop volume stalagmometer. Interfacial tension values from the three measurements varying by no more than 0.2 mN/m were averaged and reported. Critical micelle concentration (CMC) values of surfactants were determined according to the break points in plots of the interfacial tension versus logarithm of molar concentration of surfactants.

2.5.2 Colloidal-Chemical Parameters

Effectiveness (Π), maximum surface excess (Γ_{max}), minimum surface area (A_{min}), thermodynamic parameters of micellization (ΔG^0_{mic}) and adsorption (ΔG^0_{ads}) as the interfacial activity (I_{activ}) were calculated according to [11,20].

2.6 Procedure for Studying Petroleum-Dispersing Capacities

Petroleum-dispersing 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/cm^3 and 0.16 cm^2/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 (separately) in Petri dishes.

Table 1 The general composition of the sea water [19]

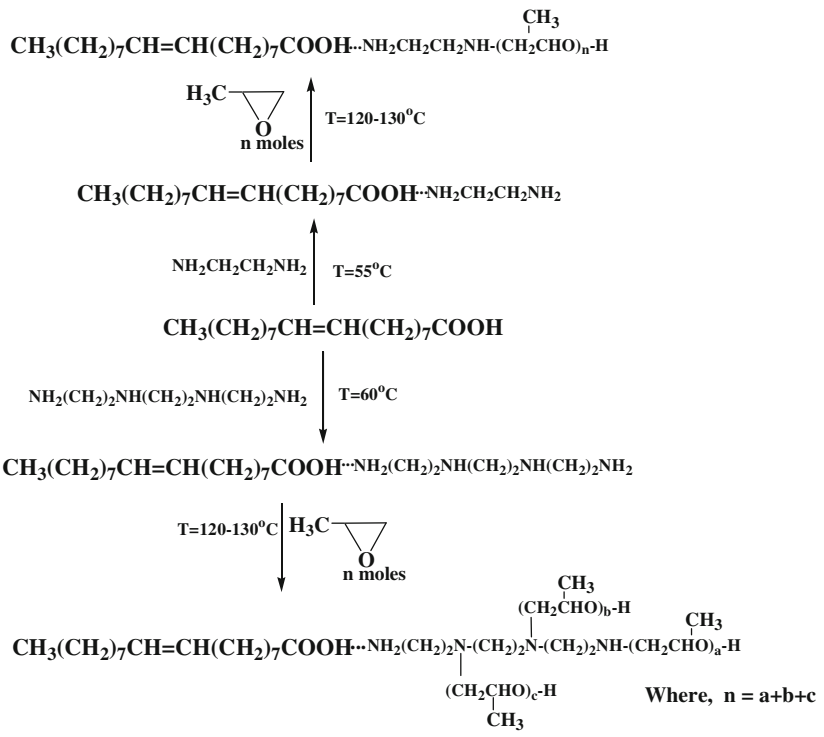
Density (g/mL)	pH	Cations				Anions	
		Sodium (g/kg)	Calcium (g/kg)	Potassium (g/kg)	Magnesium (g/kg)	Chloride (g/kg)	Sulfate (g/kg)
1.0098	7.7	2.99	0.34	0.09	0.70	5.18	2.98

The maximum values of the petroleum-collecting coefficient (K) are calculated using the formula $K = S_o/S$, where S_o is area of the surface of initial petroleum film and S is 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 as 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 Oleic Acid Complexes

Synthesis of oleic acid complexes and its propoxylation products can be illustrated by the following reaction scheme:



Where n is 1, 2 and 3

3.2 Measurements of Physico-Chemical Parameters of Propoxylated Compounds

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

3.3 Results of FTIR, ^{13}C and ^{1}H-NMR Spectroscopy

OEDA is a yellowish-brown wax, soluble in water. IR showed an absorption band at the 1,554.4–1,593.1 cm^{-1} region characteristic for COO^- stretches, in addition to 2,847.8–2,917.1 cm^{-1} for aliphatic CH, 3,210.5 cm^1 for NH (amine groups).

Table 2 Some physico-chemical characteristics of the propoxylated compounds

Propoxylated complex	External view of the complex	Amine number, mg HCl/g	Solubility of the complexes	Electrical conductivity of 0.5 % wt. aqueous solution, $Ohm^{-1}\ m^{-1}$
POOEDA1	Viscous liquid of blackish-brown color	1.66	Readily soluble in water, ethyl alcohol, toluene, CCl_4, kerosene	0.00164
POOEDA2	Viscous liquid of dark brown color	1.02	Readily soluble in water, ethyl alcohol, toluene, CCl_4, kerosene	0.00124
POOEDA3	Very viscous liquid of blackish-brown	0.40	Turbid solution was obtained in the water; readily soluble in ethyl alcohol, toluene, CCl_4, kerosene	0.00130
POOTETA1	Viscous liquid of blackish-brown	0.76	Readily soluble in water, ethyl alcohol, toluene, CCl_4, kerosene	0.00159
POOTETA2	Very viscous liquid of blackish-brown	0.60	Readily soluble in water, ethyl alcohol, toluene, CCl_4, kerosene	0.00132
POOTETA3	Very viscous liquid of blackish-brown	0.38	Readily soluble in water, ethyl alcohol, toluene, CCl_4, kerosene	0.00143

For OEDA: ^{1} H-NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.0 (t, 3H, CH_3–CH_2), 1.4–1.5 (m, 26H, CH_2 chain), 1.51 (t, 2H, CH_2COO), 5.4–5.6 (m, 2H, CH=CH), 2.5–2.7 (m, 4H, CH_2CH_2NH), 3.53 (s, 1H, H…NH_2), 5.31 (s, 2H, $(CH_2)_2$ NH_2...H), 2.34 (t, 2H, CH_2NH_2). ^{13}C– {^{1}H} NMR (75.46 MHz, $CDCl_3$) δ (ppm): 14.1 (CH_3–CH_2), 20–34 (saturated alkyl chain 14CH_2), 180 (COO), 38 ($NH_2CH_2CH_2NH_2$), 130–132(CH=CH). IR of propoxylated compounds showed the appearance of absorption bands at 3,050–3,100 cm^{-1} region characteristic for terminal OH group and at 1,040–1,110 cm^{-1} which is characteristic for C–O bond of the desired compounds. For propoxylated compound (POOEDA1) ^{1}H-NMR (300.13 MHz, $CDCl_3$), δ (ppm): 3–3.5 (m, 3H, CH_2CH–O), 1.3 (d, 3H, $CH_2CH(CH_3)$–O) of propoxy group beside the other protons of the original compound. ^{1}3C–{^{1}H} NMR (75.46 MHz, $CDCl_3$) δ (ppm): 15.2 (CH_2–CH (CH_3)O), 37.8 (CH_2–CH–O), 36.1 (CH_2–CH–O) beside the other carbons of the original compound.

3.4 Surface Properties of the Synthesized Propoxylated Compounds

3.4.1 Interfacial Tension Measurements

Interfacial tension at the kerosene–water border in the presence of propoxylated compounds is shown in Figs. 1, 2, 3, 4. From Table 3, it is noticed that POOEDA2 and POOTETA3 have good surface-active properties. Also, in the case of propoxylated OTETA and OEDA elongation of the polyoxypropylene chain of the nonionic portion leads to higher surface activity as shown in Figs. 1, 2, 3, 4.

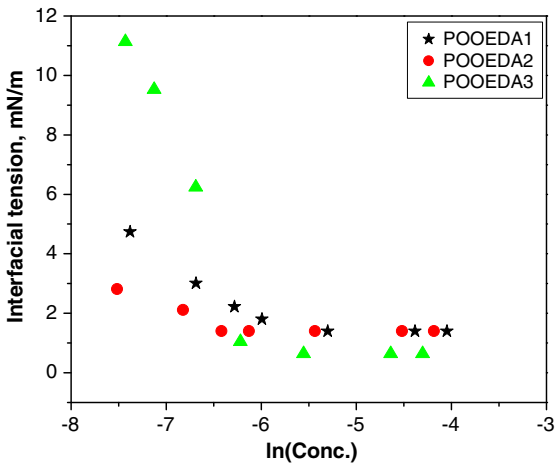


Fig. 1 Interfacial tension at the kerosene–water border versus concentration of propoxylated OEDA complex in aqueous solution at 25 °C

3.4.2 Critical Micelle Concentration

Critical micelle concentration values of the prepared complexes were determined by plotting the interfacial tension (γ) of surfactant solutions versus their bulk concentrations in mol/L at 25 °C. The CMC values listed in Table 3 show POOEDA2 and POOTETA3 have very low CMC (1.6 and 1.7×10^{-3} mol/L) and in case of propoxylated OTETA complex a decrease in CMC with increase in the length

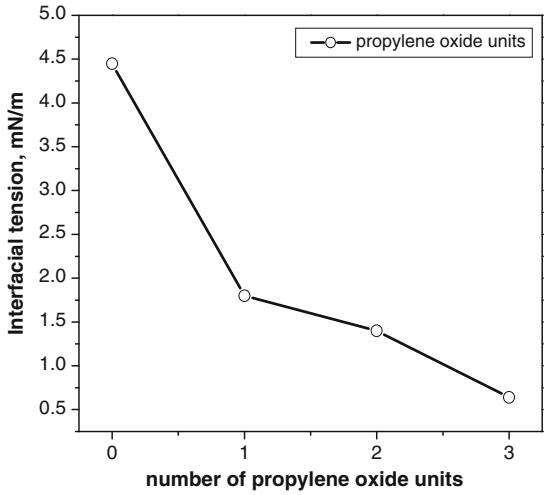


Fig. 2 Interfacial tension versus different moles of propylene oxide added to OEDA complex at 0.1 % mass concentration

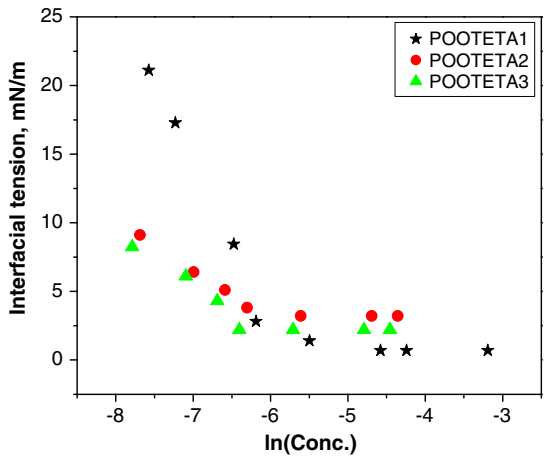


Fig. 3 Interfacial tension at the kerosene–water border versus concentration of propoxylated OTETA complex in aqueous solution at 25 °C

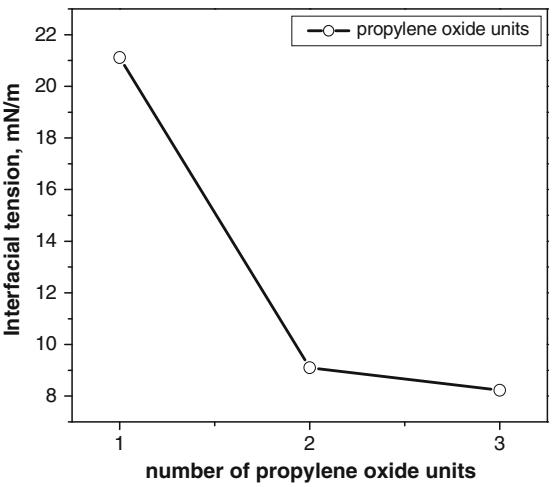


Fig. 4 Interfacial tension versus different moles of propylene oxide added to OTETA complex at 0.0025 % mass concentration

of the polyoxypropylene chain of the nonionic portion is observed.

3.4.3 Effectiveness ($\prod_{cmc}$)

The effectiveness ($\prod_{CMC}$) is determined by the difference between interfacial tension values at CMC (γ_{CMC}) and the interfacial tension values measured for pure water at the appropriate temperature (γ_o). The most effective one is that which gives the greatest lowering of interfacial tension for a given CMC. From the results in Table 3, it is noticed that POOEDA3 and POOTETA1 are the most effective ones. But POOEDA1 and POOEDA2 have a moderate effectiveness compared to the other compounds.

3.4.4 Maximum Surface Excess

It can be noticed From Table 3 that POOTETA1 has higher Γ_{max} value (5.2×10^{-10} mol cm^{-2}) than the other complexes. POOTETA3, POOTETA2 and POOEDA3 have good levels of Γ_{max} (1.7, 1.5 and 1.5×10^{-10} mol cm^{-2}, respectively).

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} and ΔG°_{ads}) are always negative, indicating that these two processes are spontaneous; however, there is a greater increase in the negative value of ΔG°_{ads} compared to those of micellization. This suggests the tendency of the molecules to be preferentially adsorbed at the interface.

3.5 Petroleum-Dispersing Properties of Propoxylated Compounds

Petroleum-dispersing properties of the propoxylated compounds were studied using as an example thin films of Ramany crude oil. In Table 4, results of studies of petroleum-dispersing ability of the synthesized surfactants are presented and also from all results in Table 4 when the best (maximum values) of petroleum-dispersing action for all synthesized complexes is taken and drawn them with the length

Table 3 Surface properties of the propoxylated compounds

Propoxylated complex	CMC $\times 10^{-3}$ (mol L^{-1})	γ_{CMC} (mN/m)	$\prod_{CMC}$ (mN/m)	$\Gamma_{max} \times 10^{-10}$ (mol cm^{-2})	A_{min} (nm^2)	ΔG°_{mic} (kJ/mol)	ΔG°_{ads} (kJ/mol)	ΔG°_{ads}/ A_{min} (kJ/mol nm^2)
POOEDA1	4.9	1.4	45.1	0.9	1.9	−13.1	−65.6	−33.9
POOEDA2	1.6	1.4	45.1	0.5	3.3	−15.9	−106.1	−31.9
POOEDA3	3.9	0.6	45.9	1.5	1.1	−13.8	−43.9	−40.2
POOTETA1	10.2	0.7	45.8	5.2	0.3	−11.2	−20.07	−62.71
POOTETA2	3.7	3.2	43.3	1.5	1.1	−13.8	−42.43	−38.57
POOTETA3	1.7	2.2	44.3	1.7	1.0	−15.7	−41.84	−42.69

Table 4 Petroleum-collecting and petroleum-dispersing properties of propoxylated compounds

Surfactants	Undiluted product						5 %wt. Solution					
	Distilled water		Fresh water		Sea water		Distilled water		Fresh water		Sea water	
	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)	τ (h)	K (k_d)
POOEDA1	0	20.3	0	88.9 %	0–2	91.1 %	0	17.4	0	88.9 %	0–165	95.5 %
	2	24.3	2–26	91.1 %	19.5–165	95.5 %	2	91.1 %	2–165	91.1 %		
	19.50–26	26.4	43–165	95.5 %			19.50–165	95.5 %				
	43.50–165	95.5 %										
POOEDA2	0	17.1	0	13.5	0	88.4 %	0	16.4	0	88.4 %	0	86.8 %
	4–20	20.5	4–20	91.1 %	4–100	91.1 %	20–100	91.1 %	20–100	91.1 %	20–100	91.1 %
	26–100	26.2	26–100	88.4 %								
POOEDA3	0	8.7	0	10.1	0	86.8 %	0	9.4	0–100	91.1 %	0–100	91.1 %
	4	10.1	4–100	78.6 %	4	82.6 %	20–100	91.1 %				
	20	20.0			20–100	78.6 %						
	26–100	26.5										
POOTETA1	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 %		
	19.50–165	95.5 %			19.5–165	95.5 %	19.50–165	95.5 %	19.5–165	95.5 %		
POOTETA2	0	9.4	0	80.6 %	0	91.1 %	0	82.6 %	0	91.1 %	4–100	91.1 %
	4	65.1 %	4	86.8 %	4	82.6 %	4–100	86.8 %	4–50	95.5 %		
	20–100	91.1 %	20–100	78.6 %	20–100	91.1 %			60–100	91.1 %		
POOTETA3	0	10.6	0–4	78.6 %	0	82.6 %	0	9.2	0–4	82.6 %	0	86.8 %
	4	78.6 %	20–100	86.8 %	4–100	91.1 %	4	86.8 %	20–100	91.1 %	4–100	91.1 %
	20–100	86.8 %					20–100	91.1 %				

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

of fatty chain as shown in Figs. 5 and 6. So, from all results in Table 4 and Figs. 5 and 6, it can be noticed that POOEDA1 and POOEDA2 undiluted or diluted form exhibit a better petroleum-dispersing action and K_d is ranging from 91.1 to 95.5 %, τ = 165 h (in distilled, fresh and sea waters). POOEDA3 in undiluted form gave a good petroleum-collecting property in distilled water (k = 26.5, τ = 26–100 h). In diluted form it exhibits a very good petroleum-dispersing in all waters of varying salinity (K_d = 91.1 %, τ = 0–100 h). POOTETA1 in undiluted or diluted form exhibits a strong petroleum-dispersing action and K_d is 95.5 %, τ = 165 h (in distilled, fresh and sea waters) and a good effect in sea water in diluted form (K_d = 86.8 %, τ = 0–165 h). POOTETA2 in undiluted form gave a high petroleum-dispersing effect in distilled and sea waters (K_d = 91.1 %, τ = 20–100 h) and a moderate effect in fresh water (K_d = 78.6 %, τ = 20–100 h). But POTETA2 in diluted form exhibits a better petroleum-dispersing action in fresh and sea waters (K_d = 91.1 %, τ = 4–100 h) and also a moderate effect in distilled water (K_d = 86.8 %, τ = 4–100 h). In undiluted form POOTETA3 gave only a good petroleum-dispersing property in sea water (K_d = 91.1 %, τ = 4–100

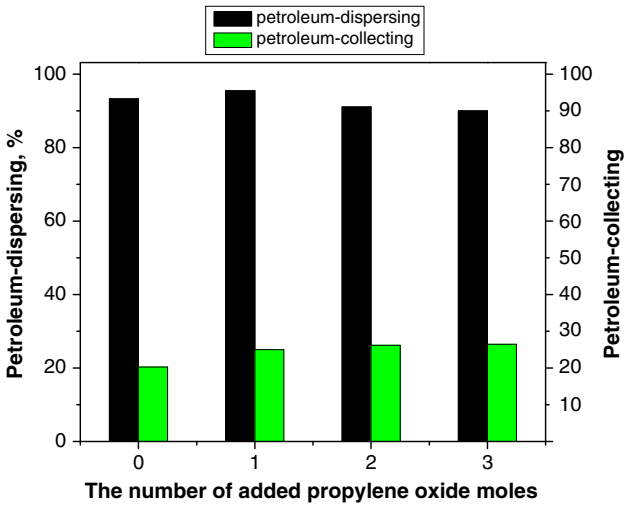


Fig. 5 Petroleum-dispersing and petroleum-collecting capacity of OEDA complex added different moles of propylene oxide

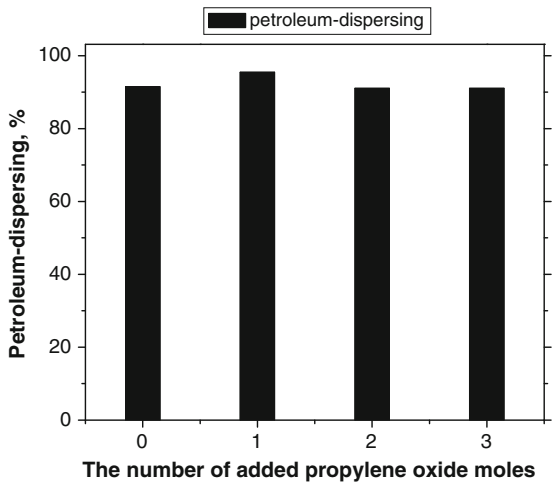


Fig. 6 Petroleum-dispersing capacity of OTETA complex added different moles of propylene oxide

h) and a moderate effect in distilled and sea waters (K_d = 86.8 %, τ = 20–100 h). Also in diluted form POOTETA3 exhibits a very good petroleum-dispersing effect in distilled, fresh and sea waters (K_d = 91.1 %, τ = 4–100 h). From all the showed results it is noticed that all propoxylated compounds can be used as a good petroleum-dispersing agents, particularly POOEDA1, POOEDA2, POOTETA1 and POOTETA2.

4 Conclusion

We prepared novel complexes surfactants based on oleic acid and ethylenediamine, triethylenetetramine. The propoxylated compounds were synthesized by reaction of synthesized complexes with different moles of propylene oxide. Some of the obtained complexes and propoxylated compounds were investigated by FTIR spectra, ^{13}C and ^{1}H-NMR spectra. From all obtained results it is noticed that POOEDA2 and POOTETA3 have good surface-active properties. In the case of propoxylated OTETA and OEDA elongation of the polyoxypropylene chain of the nonionic portion leads to higher surface activity. The results showed that all propoxylated compounds can be used as good petroleum-dispersing agents, particularly POOEDA1, POOEDA2, POOTETA1 and POOTETA2.

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