

Petroleum-Collecting and Dispersing Complexes Based on Oleic Acid and Nitrogenous Compounds as Surface-Active Agents for Removing Thin Petroleum Films from Water Surface

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Abstract: Petroleum-collecting and dispersing complexes were synthesized on the basis of oleic acid and nitrogen-containing compounds. Surface-active properties (interfacial tension) of the obtained complexes were investigated by stalagmometric method. Petroleum-collecting and dispersing properties of the oleic acid complexes in diluted (5% wt. water or alcoholic solution) and undiluted form have been studied in waters of varying salinity (distilled, fresh and sea waters). Some of physico-chemical indices of the prepared compounds such as solubility, acid and amine numbers as well as electrical conductivity have been determined. The ability of oleic acid complex with ethylenediamine as petro-collecting and dispersing agent towards different types of petroleum has been studied. The influence of thickness and "age" of the petroleum slick on collecting and dispersing capacity of this complex has been clarified. 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.

Key words: Oleic acid, nitrogen-containing compounds, complex, dispersing agent, collecting agent, interfacial tension. Abbreviations

1 INTRODUCTION

Accidents leading to oil spill pollution in the big ocean and coastal environments are not rare. One of the processing techniques is the application of oil spill collecting and dispersants on oil slicks. The collectors and dispersants¹⁻⁸⁾ used for this purpose are surfactants. Collectors herd the oil into a spot whereas dispersants enhance the rate of natural dispersion of oil and its removal from the contaminated surface. The application of collectors and dispersants minimizes the impact of oil spills on marine birds⁹⁻¹⁸⁾ and surfactants are widely used for removing such thin petroleum films from the water surface.

The purpose of any oil spill response is to minimize the damage that could be caused by the spill. Collectors and dispersants are ones of a limited number of practical responses that are available to liquidate oil spills on the surface sea. When oil is spilled at sea, a small portion of it will be naturally dispersed by the mixing action caused by waves. This process can be slow and proceeds to only a

limited extent for most situations. Dispersants are used to accelerate the removal of oil from the surface of the sea by greatly enhancing the rate of natural dispersion of oil and thus prevent it from coming ashore. Dispersed oil will also be more rapidly biodegraded by naturally occurring microorganisms. The rationale for dispersant use is that the dispersed oil is likely to have less overall environmental impact than oil that persists on the surface of the sea, which drifts and eventually contaminates the shoreline.

OTETA	oleic acid and triethylenetetramine complex
OEDA	oleic acid and ethylenediamine complex
OU	oleic acid and urea complex
OAm	oleic acid and ammonium hydroxide complex
OMn	oleic acid and morpholine complex
OPn	oleic acid and pyridine complex
OPPn	oleic acid and piperidine complex
ODEA	oleic acid and diethyl amine complex
OTEA	oleic acid and triethyl amine complex
CMC	Critical Micelle Concentration

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The development of modern collectors and dispersants began after the Torrey Canyon oil spill in 1967. Many lessons have been learned since that spill, and consequently the modern dispersants and application techniques in use today have become an effective way of responding to an oil spill. For example, the dispersant response to the Sea Empress spill in 1996 demonstrated that dispersants can be very effective and prevent a much greater amount of environmental damage from being caused^{19, 20}.

Collectors and dispersants are blends of surfactants (surface-active agents) and solvents, designed to herd the oil into a thickened spot or to hasten breakup of oil slicks into fine droplets that disperse naturally in the sea. The surfactants, which are the active components, are 'soap-like' molecular structures that have both water-seeking hydrophilic and oil seeking lipophilic sections.

Surfactants are commonly used in the cosmetic and food industries also. Because of their dual nature, the surfactant molecules in oil spill collectors and dispersants reach their lowest energy state by positioning themselves at oil-water interfaces, thereby lowering the oil-water interfacial tension. Collectors act due to their high surface pressure whereas dispersants significantly lower the energy required to generate oil droplets in water. In addition, droplets generated with dispersants are typically much smaller than would otherwise form by the natural energy of the sea²¹.

The main aim of the presented work was to produce new, ecologically safe and efficient oil slick-collecting and dispersing agents based on oleic acid through their interaction with various nitrogen-containing bases to form surface active complexes. Surface-active properties as well as petro-collecting and dispersing properties of synthesized complexes were thoroughly studied.

2 EXPERIMENTAL

2.1 Chemical Reagents

Ethylenediamine, triethylenetetramine, ammonium hydroxide, urea, morpholine, piperidine and pyridine were from the "Kazanorgsintez" Joint Stock Company (Russia) and were used without further purification. Oleic acid was from Moscow's "Component-Reactant" Joint Stock Company (Russia) production. Triethylamine were of analytical grade (Merck, Germany, 98% purity). Diethylamine was of Russian Federation production (98% purity). The Ramany oil, Neft Dashlary, May 28 and Dubandy crude oils were obtained from different oil companies located in Azerbaijan. Kerosene was purified from aromatic compounds by treatment with sulfuric acid up to a surface tension of 24 mN/m. Sea water was the Caspian sea water having the following physico-chemical characteristics and composition²²: $\rho_{20} = 1.0098$ g/mL, pH = 7.7, contents of ions and other species (g/kg): $\text{Na}^+ 2.99$; $\text{K}^+ 0.09$; $\text{Ca}^{2+} 0.34$;

$\text{Mg}^{2+} 0.70$; $\text{Cl}^- 5.18$; $\text{SO}_4^{2-} 2.98$.

2.2 Synthesis of oleic acid complexes

2.2.1 General Procedure for the reactions of Oleic acid with nitrogen containing compounds

Oleic acid (0.01 mol) was taken at equimolar ratio with ethylenediamine, triethylenetetramine, ammonium hydroxide, urea, morpholine, piperidine, pyridine, triethylamine and diethylamine. The components of reactions were mixed, closed well and placed in a thermostat at a temperature ranging between 50 and 60°C for a period ranging between 15 and 20 hours. The obtained complexes are generally viscous liquids and solids. Their colors vary from light-yellow to dark-brown.

2.3 Methods of analysis and instruments

Acid and amine numbers are determined according to procedures given in²³.

Electrical conductivity for the prepared complexes were measured using Conductivity Meter apparatus, type OK-102/1, made in Hungary.

Infrared spectra for the synthesized complexes were measured at a model FT-IR, Spectrum BX spectrometer using KBr disks. The measurements were carried at Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan.

2.4 Evaluation methods of surface active properties

2.4.1 Interfacial tension measurements

All the interfacial tension measurements were carried out using kerosene 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 $\pm 0.2^\circ\text{C}$. The interfacial tension as a function of concentration was measured at 19°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.

2.4.2 Determination of critical micelle concentration

The CMC 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.

2.4.3 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.

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

2.4.4 Maximum surface excess

The values of the maximum surface excess (Γ_{\max}) were calculated from surface or interfacial data by the use of Gibbs equation²⁴⁾.

$$\Gamma_{\max} = 1/RT(\delta\gamma/\delta\ln C)_T \quad (2)$$

Where:

- Γ_{\max} maximum surface excess in mole/cm²
- R universal gas constant 8.31 Joule mole⁻¹ K⁻¹
- T absolute temperature
- $\delta\gamma$ 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.

2.4.5 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 interface²⁵⁾ is given by:

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

- Γ_{\max} maximum surface excess in mole/cm²
- N Avogadro's number

2.4.6 Thermodynamic parameters of micellization and adsorption

The thermodynamic parameters of adsorption and micellization of the synthesized complexes were calculated according to Gibb's adsorption equations as follows²⁶⁾:

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

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

2.4.7 The interfacial activity (I_{activ})

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

2.5 Procedure for Studying Petroleum-Collecting and Petroleum-Dispersing Capacities

Petroleum-collecting properties of the synthesized complexes (in the pure state and in the form of 5% wt. water or ethanolic 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) as well as Neft Dashlary (in the Caspian Sea, $\rho^{20} = 0.887$ g/mL, $\nu^{20} = 15.7$ cSt), May 28 (in the Caspian Sea, $\rho^{20} = 0.856$ g/mL, $\nu^{20} = 9.7$ cSt) and Dubandy (in the Caspian sea, $\rho^{20} = 0.861$ g/mL, $\nu^{20} = 15.7$ cSt) crude oils from the oil fields 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. The maximum values of the petroleum collecting coefficient (K) are calculated using 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 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 of oleic acid complexes

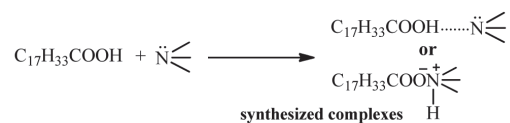
The complexes were synthesized on the basis of oleic acid and nitrogenous compounds at 60-70°C for 15-20 hours. The synthesized complexes can be illustrated by the following reaction scheme:

3.2 Measurements of physico-chemical indices of synthesized complexes

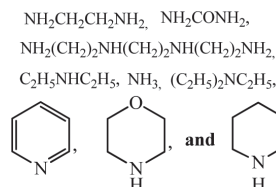
The studied physico-chemical indices are solubility in different solvents (distilled water, ethyl alcohol, CCl₄, toluene, kerosene), electro conductivity, acid and amine numbers. From Table 1, it is noted that the obtained complexes are generally viscous liquids and solids. Their colors vary from yellow 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 data

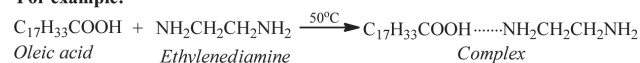
The chemical structures of oleic acid complexes with piperidine and morpholine were identified by FT-IR spectroscopy.



where $\ddot{N} \begin{array}{l} \diagup \\ \diagdown \end{array}$ may be



For example:



Scheme 1 Reactions scheme of the synthesis of oleic acid complexes.

Table 1 Some physico-chemical characteristics of oleic acid complexes.

Complex	External view of the complex	Acid number, mgKOH/g	Amine number, mgHCl/g	Solubility of the complexes	Electrical conductivity of 0.5% wt aqueous solution $\text{Oh}^{-1} \cdot \text{m}^{-1}$
OTETA	Dark-brown semi-solid	41.5	–	Insoluble in water, readily soluble in ethyl alcohol, toluene, CCl_4 , kerosene.	0.0020200
OEDA	Muddy-brown viscous liquid	–	5.1	Readily soluble in water, ethyl alcohol, toluene, CCl_4 , kerosene.	0.0018700
OU	Muddy-brown solid	105.0	–	Slightly soluble in water, readily soluble in ethyl alcohol, toluene, CCl_4 , kerosene	0.0015000
OAm	Muddy yellowish – brown solid (past shaped)	–	2.9	Readily soluble in water, ethyl alcohol, toluene, CCl_4 , kerosene.	0.0000120
OMn	Clear-brown, viscous liquid	80.0	–	Readily soluble in water, ethyl alcohol, toluene, CCl_4 , kerosene	0.0000107
OPn	Clear-brown, viscous liquid-	–	0.5	Readily soluble in water, ethyl alcohol, toluene, CCl_4 , kerosene.	0.0000126
OPPn	Yellow, low viscous liquid	173.3	–	Insoluble in water, readily soluble in ethyl alcohol, toluene, CCl_4 , kerosene	0.0000123
ODEA	Blackish-brown, low-viscous liquid	–	0.8	Readily soluble in water, ethyl alcohol, turbid solution was obtained in toluene, CCl_4 , kerosene.	0.0018600
OTEA	Blackish-brown, low-viscous liquid	–	0.5	Readily soluble in water, ethyl alcohol, toluene, CCl_4 , kerosene.	0.0018600

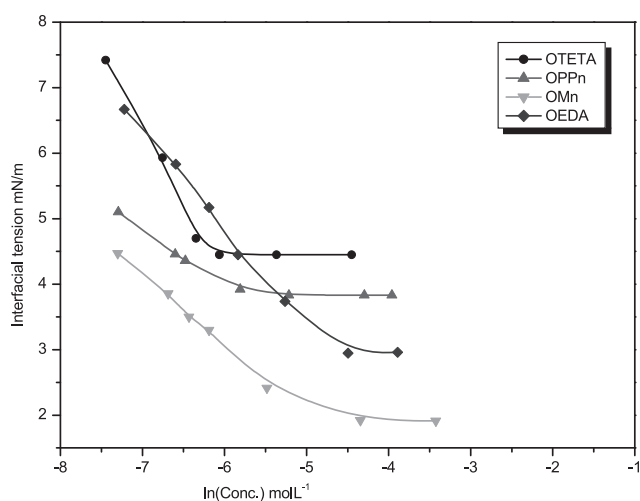


Fig. 1 Interfacial tension versus concentration of OTETA, OPPn, OMn and OEDA complexes in kerosene solution at 19°C.

copy. The FT-IR absorption spectra for both complexes showed an absorption band at the 1555.4-1595.4 cm^{-1} region characteristic for δCOO^- stretches. This proves formation of the target complexes.

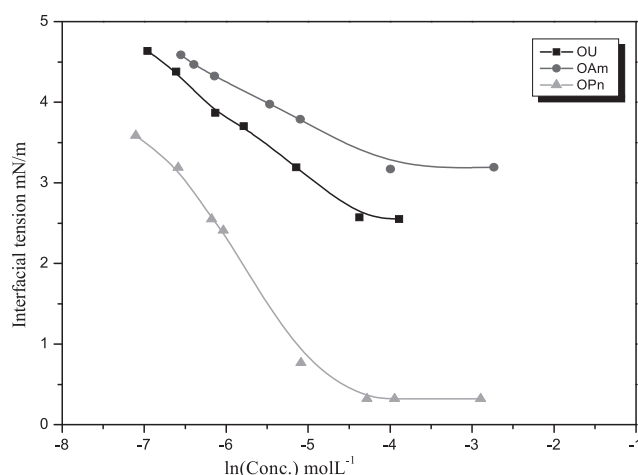


Fig. 2 Interfacial tension versus concentration of OU, OAm and OPn complexes in kerosene solution at 19°C.

3.4 Surface properties of the prepared surfactants complexes

3.4.1 Interfacial tension measurements

Interfacial tension at the kerosene-water border in the presence of prepared oleic acid complexes was measured and shown in **Figs. 1, 2 and 3**. From the figures it is clear that the synthesized complexes (OTETA, OMn, OEDA, OU,

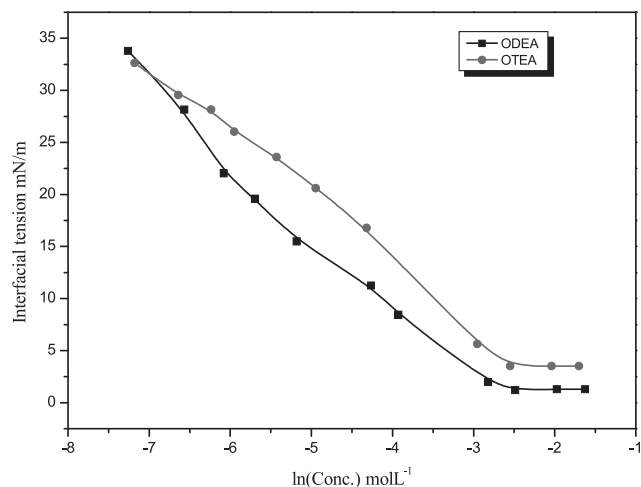


Fig 3 Interfacial tension versus concentration of ODEA and OTEA complexes in kerosene solution at 19°C.

OPPn, OPn, OTEA, ODEA and OAm) have good surface-active properties. Particularly OPn, OMn, OU, OEDA should be mentioned.

3.4.2 Critical micelle concentration

CMC values of the prepared complexes were determined by plotting the surface tension (γ) of surfactant solutions versus their bulk concentrations in mole/L at 19°C. The results in **Table 2**, **Figs. 1, 2** and **3** showed that all the synthesized complexes have small values of CMC, particularly OTETA and OPPn. These complexes have very low values of CMC, i.e., micellization process takes place spontaneously, occurring very easily. Increasing the number of hydrophobic chains (decrease in polarity, in other words, decrease of portion of polar groups), decreases the solubility and consequently increases the free energy change of the system leading to concentrating the surfactant molecules at the surface and easier formation of micelles that means a decrease of CMC value.

3.4.3 Effectiveness (Π_{cmc})

The effectiveness (Π_{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_0). The most effective one is that which gives the greatest lowering of interfacial tension for a given CMC. OPn was found to be the most effective one (**Table 2**) because it revealed the maximum reduction of the interfacial tension at CMC. Also ODEA and OMn exhibited a good effectiveness if compared with the rest of complexes that gave a moderate effectiveness.

3.4.4 Maximum surface excess

The number of surfactant molecules at the kerosene-water interface at the CMC at 19°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 surface tension decreases with increasing activity of surfactant, Γ_{max} is positive. From **Table 2**, it can be noted that ODEA, OTEA and OTETA have highest Γ_{max} values (27.6×10^{-11} , 26.4×10^{-11} and 10.6×10^{-11} mol.cm⁻² respectively). Γ_{max} has the largest values in the case of ODEA and OTEA, these complexes being formed by relatively strong bases of smaller dimensions.

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 2** 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 2**, it is evident that the values of the standard free energies of micellization and adsorption ($\Delta G_{\text{mic}}^{\circ}$ and $\Delta G_{\text{ads}}^{\circ}$) are always negative, indicating that these two processes are spontaneous; however, there is a greater increase in the negative value of $\Delta G_{\text{ads}}^{\circ}$ compared to those of micellization. This suggests the tendency of the molecules to be adsorbed at the interface.

Table 2 Surface properties of the synthesized oleic acid complexes.

Complex	CMC $\times 10^3$ molL ⁻¹	γ_{CMC} mN/m	Π_{CMC}	$\Gamma_{\text{max}} \times 10^{11}$ mol cm ⁻²	$A_{\text{min}} \times 10^2$ nm ²	$\Delta G_{\text{mic}}^{\circ}$ kJ/mol	$\Delta G_{\text{ads}}^{\circ}$ kJ/mol	$\Delta G_{\text{ads}}^{\circ}/A_{\text{min}}$ kJ/(mol)(nm) ²
OAm	18.4	3.2	43.3	6.3	2.6	- 9.7	- 78.9	- 29.8
ODEA	83.7	1.2	45.3	27.6	0.6	- 6.0	- 22.4	- 37.3
OEDA	11.2	2.9	43.6	7.8	2.2	- 10.9	- 55.7	- 25.7
OMn	13.0	1.9	44.6	7.3	2.3	- 10.5	- 71.8	- 31.5
OPPn	5.5	3.8	42.7	3.3	5.1	- 12.6	- 75.9	- 15.0
OPn	13.8	0.3	46.2	5.8	2.9	- 10.4	- 91.6	- 31.4
OTETA	2.3	4.4	42.0	10.6	1.6	- 14.7	- 54.3	- 34.8
OTEA	52.3	3.5	43.0	26.4	1.6	- 7.2	- 48.1	- 30.4
OU	12.6	2.6	43.9	4.9	3.4	- 10.6	- 93.7	- 27.5

3.5 The prepared surface-active complexes as oil slicks collection agents or dispersing agents:

3.5.1 Petroleum-collecting and dispersing properties of surface active complexes based on oleic acid and nitrogen-containing compounds complexes

In this work, petroleum-collecting and petroleum-dis-

persing properties of the 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. alcoholic or water solutions. In **Table 3** results of studies of petroleum-collecting and petroleum-dispersing ability of the synthesized

Table 3 Petroleum-collecting and petroleum dispersing properties of oleic acid and nitrogen-containing 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)
OA	30	5.1	0	2.2	0-166	No effect	0	5.6	0	1.9	0-166	No effect
	166	2.1	5	spilling			70	13.5	70	6.7		
							96	spilling	166	7.6		
OTETA	0	12.2	0	15.2	0	10.1	0	12.2	0	84.7%	0-166	91.5%
	4.5	91.7%	4.5	82.6%	4-28	82.6%	4-166	91.5%	4-166	91.7%		
	28	91.5%	166	91.7%	52	84.7%						
	166	95.5%			166	91.7%						
OEDA	0	10.1	0	13.5	0	13	0-4	15.2	0	15.2	0	15.2
	52	91.7%	4	86.8%	4	86.8%	76	20.3	4.5	88.9%	4.5	84.7%
	166	95.5%	166	91.7%	166	88.9%			28.5	91.7%	22	86.8%
OU									166	93.3%	166	91.7%
	4.5	8.6	4.5	5.1	0	3.8	0	7.1	4.50	6.3	0	78.6%
	28.5	3.7	76.5	3.6	22	59.7%	76.5	11.4	22	7.1	52.5	86.8%
OAm	96	spilling	166	3.2	28.5	spilling	166	9.9	166	7.6	166	91.7%
	22	13.5	0	10.1	0	5.5	1	11	1	5.4	1	78.6%
	76.5	10.6	4.5	11	4.5	15.2	18	14.6	24.5	9.8	48.5	84.7%
OMn	166	9.8	166	12.1	22	spilling	138	9.8	138	12.4	138	12.2
	4.50	15.2	0	80.6%	0	80.6%	1	9.4	18	9.4	0	89.7%
	52.5	16.4	28.5	76.6%	28.5	78.6%	18-42	18.5	24.5	10.7	1-138	91.7%
OPn	76.5	17.4	166	76.5%	166	82.6%	138	20.5	138	11.5		
	4.5	13.5	4.5	8.7	28.5	68.8%	4.5	12.2	4.5	5.6	22	88.9%
	22	11.4	70	65.1%	76.5	82.6%	52.5	10.6	76.5	9.2	28.5	91.5%
OPPn	76.5	8.1	76.5	78.6%	166	86.8%	166	4.4	166	10.1	166	93.3%
	0	5.7	0	2.9	0	2.9	22	13.4	4.5	6.7	4.5	91.7%
	4.5	1.3	52.5	2.1	4.5	spilling	46-70	19.4	28.5	5.9	22	84.7%
ODEA	22	spilling	166	2.			76.5	21.4	46	4.8	166	91.7%
	0	3.4	0-5.5	83.9%	2.5	7.1	0	3.7	0	2.4	0	5.4
	5.5	3.7	53.5	9.4	53.5	10.1	5.5	3.9	5.5	2.8	5.5	6.4
OTEA	53.5	7.1	119	spilling	119	spilling	119	6.4	119	5.4	119	89.7%
	19.5	23.9	2	6.7	2	13.5	2	12.1	26	14.6	2	88.9%
	26	26.8	26	16	26	17.4	26-165	13.4	74	17.6	74	15.2
	74	30.2	165	17.6	165	20.7			165	21.45	165	17.4

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

surfactants complexes based on oleic acid and nitrogenous compounds are presented. From **Table 3** it can be noted that OTETA and OEDA in undiluted or diluted form exhibit a better petroleum-dispersing action than the other complexes. K_d is ranging from 91.5 to 95.5%, $\tau = 166$ h (in distilled, fresh and sea waters). In undiluted and diluted form the OTEA shows a better petroleum-collecting effect than the other surfactants in diluted form (in undiluted form $K_{max} = 30.2$ in distilled water, $\tau = 74$ h and $K_{max} = 20.3$ in the sea water, $\tau = 165$ h, in diluted form $K_{max} = 21.4$ in fresh water, $\tau = 165$ and in sea water $K_{max} = 17.4$, $\tau = 165$ h). In the sea water, OMn in diluted form exhibits high petro-dispersing properties ($K_d = 91.7\%$, $\tau = 138$ h). In distilled water it also exhibits good petro-collecting properties ($K_{max} = 20.5$, $\tau = 138$ h) and moderate effect in fresh water $K_{max} = 11.5$, $\tau = 138$ h. In diluted form OPPn shows its highest petroleum-collecting effect in distilled water ($K_{max} = 21.4$, $\tau = 76.5$ h) and petroleum-dispersing effect in the sea water ($K_d = 91.7\%$, $\tau = 166$ h). The other complexes gave a moderate effect showing petro-dispersing properties especially in diluted form. From these results it can be said that OTETA, OEDA and OMn may be used as dispersing agents especially in the sea water. Finally all of the prepared complexes gave higher effect than oleic acid itself in regard to petro-dispersing and petro-collecting properties.

3.5.2 Petroleum-collecting and dispersing properties of OEDA toward different types of petroleum oils

From **Table 4** it can be seen that OEDA is effective

towards different types of petroleum. It gave the highest effect as a petro-collecting agent against Dubandy crude oil ($K_{max} = 40.5$, $\tau = 50$ h in distilled and fresh water) and highest effect as a petro-dispersing agent against the same petroleum ($K_d = 95.5\%$, $\tau = 18$ h in the sea water).

3.5.3 Petroleum-collecting and dispersing properties of OEDA toward petroleum slicks of different thickness

From **Table 5** including the results of studying the effect of OEDA toward the petroleum slick of different thicknesses (0.165-1.650 mm), it may be noted that OEDA has a strong effect in the case of relatively thin (0.165-0.995), this effect gradually decreasing with increasing the thickness.

3.5.4 Petroleum-collecting and dispersing properties of OEDA toward petroleum slicks of varying "age"

From **Table 6** it is noted that OEDA in the sea water is efficient even against a slick of a month's "age". But the effect is larger in the first 20 days. In the case of "soft" waters (distilled and fresh) OEDA acts strongly against the "aged" slicks only in undiluted form.

Conclusion

In the present work, the oleic acid complexes were prepared and characterized by physico-chemical indices. It was found that all the synthesized complexes are surface-active (particularly OPn, OMn, OU, and OEDA). Most of

Table 4 Petroleum-collecting and petroleum-dispersing properties of oleic acid and ethylenediamine complex toward different types of petroleum.

Different types oils	Undiluted product						5% wt. water 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)
Ramany	0	10.1	0	13.5	0	13	0-4.5	15.2	0	15.2	0	15.2
	52.5	91.7%	4.50	86.8%	4.5	86.8%	76.5	20.3	4.5	88.9%	4.5	84.7%
	166	95.5%	166	91.7%	166	88.9%			166	93.3%	166	91.7%
Dubandy	0-1	24.3	25	91.1%	0-1	91.1%	0-1	17.4	0-1	82.6%	0-1	88.9%
	139	30.4	49	20.3	18	93.3%	49-139	40.5	18	86.8%	18	95.5%
			139	83.7%	68	95.5%			25	91.1%	139	91.1%
May 28	0	20.3	0	20.3	0	20.3	1.5	24.3	0	17.4	0-25	17.4
	1-25	24.3	1	82.6%	18-25	86.8%	43-49	30.2	1-25	20.3	43-73	15.2
	43-73	26.8	18-25	17.4	68-145	17.4	68-73	26.8	164	15.2	145	17.4
	139-145	22.5	68-164	13.5	164	15.2	139-145	24.3			164	20.3
Neft	49.5	13.5	0-25	2	0-1	91.1%	0-1.5	30.4	18-25	20.3	0-1.5	84.7%
	68-73	20.3	43-49	12.2	18-25	93.3%	18	23.9	43-49	13.5	25.5-145	86.8%
Dashlary	139-145	26.4	68-164	15.2	43-164	95.5%	25-49	24.3	139-145	12.2	164	10.1
	164	20.3					68-164	20.3	164	7.6		

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 oleic acid and ethylenediamine complex toward Ramany crude slicks of different thicknesses.

Thickness of petroleum slick, mm	Undiluted product						5% wt. water 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)
0.165	0	12.2	0	15.2	0	10.1	0-1	11	0	82.6%	0-48	86.8%
	4.5	91.7%	4	82.6%	4-28	82.6%	18	20.3	1-138	91.7%	68-138	15.2
	22-28	91.5%	22-166	91.7%	46-52	84.7%	24-42	22.5				
	46-166	95.5%			70-166	91.7%	48	23.4				
0.330	0-2	10.13	0-2	8.1	0	78.6%	2	6.1	0-2	78.6%	0-2	74.6%
	19-146	86.8%	19	82.6%	2-146	86.8%	19	10.6	19	74.6%	19	6.1
			26-146	86.8%			26-50	11.4	26	78.6%	26	6.7
							59-74	12.2	146	78.6%	44-146	4.7
0.495	0-17	75.6%	0	7.6	0-1	6.1	0-1	4.4	0-1	78.6%	1	78.6%
	43-49	7.6	1	8.1	17-25	74.6%	17	7.1	17	7.6	17-25	72.6%
	68-73	7.1	17-25	84.7%	43-73	78.6%	25	7.6	25	8.1	43-49	70.7%
	139-145	6.7	43-73	82.6%	139-145	65.1%	43-49	81	43-49	6.1	68-73	66.9%
0.660	0	7.1	0	4.4	0	5.1	0-1	5.64	0	4.4	0	6.4
	1	5.4	1	76.3%	1	76.3%	17-23	7.4	1	76.3%	1-23	72.7%
	17-23	65.7%	17-23	3.7	17-23	72.7%	42-119	8.3	17-23	64%	42-119	55.8%
	42-119	4.16	42-119	2.6	42-119	64%			42-119	4.2		
0.825	0-1	59.7%	0-49	82.6%	0-49	52.9%	0-5	3.1	0	2.6	1	70.7%
	20-49	70.7%	69-73	80.6%	69-73	66.9%	43-49	6.3	1	3	20-25	2.8
	69-97	66.9%	91-97	6.1	91-97	43.4%	69-73	5.6	91-97	3.2	91-97	2.1
	163-189	63.3%	163-189	2.1	163-189	32.3%	91-97	4.8	163-189	2.4	163-189	2
0.990	1	2.5	20-25	63.3%	0-25	1.7	1	2.4	0-1	2.78	0-49	2.3
	20-25	56.2%	49	74.6%	43-49	1.2	20-25	4.4	20-25	3.4	69-73	1.9
	43	54.5%	69-73	78.6%	69	spilling	43-73	3.8	43-73	2.9	91-97	1.6
	91-97	46.5%	91-97	66.9%			163	spilling	91-97	2.8	163-189	1.3
1.155	0	2.9	0	2.8	0	46.5%	0	2	0-5	63.3%	0-5	56.2%
	47-53	2.8	25-29	2.6	5.50-29	43.4%	5	2.6	47-53	59.7%	25-29	3.2
	119-125	2.2	119-125	2.4	47-53	46.5%	25-53	2.7	119-125	57.9%	119-125	3
	143	2.2	143	2.2	119-125	39%	119-125	2.1	143	43.4%	143	2.9
1.650	0	29.7%	0-2	1.4	0-140	No effect	0	1.4	0-2	1.4	0	40.5%
	2	spilling	20-50	1.9			2	1.3	20-26	1.6	2	28.5%
			68-140	1.9			68-74	1.3	44	spilling	20-50	37.6%
							140	spilling			68-140	32.3%

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

complexes show high petro-collecting and dispersing effects. From the results of studying the petro-collecting and dispersing properties of ODEA towards different types of petroleum, thickness and "age" of oil slick, it was found that ODEA has a high effect in the case of all crude oils, the thickness of slick being less than 0.5 mm. OTETA and PPPn have very lower values of CMC than the others complexes. OPn was found to be the most effective (high Π_{cmc} value), ODEA, OTEA and OTETA have highest Γ_{max} values. The values of ΔG_{ads}^0 for all synthesized complexes confirmed that all complexes have ability to be adsorbed at the

kerosene-water interface.

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Table 6 Petroleum-collecting and petroleum dispersing properties of OEDA toward of Ramany crude oil slicks of varying "age"

"Age"of petroleum slick	Undiluted product						5% wt. water 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)
10 days	0-98	13.5	0-26	91.1%	0-2	91.1%	0-2	3.6	0-2	2.4	0-26	86.8%
	164	17.4	164	40.5	20	93.3%	26	8.7	20-26	7.6	92-98	13.5
					164	91.1%	92-98	11	92-98	10.1	164	70.7%
20 days							116	7.6	116	8.1		
	0	86.8%	0-102	82.6%	0-102	93.3%	0	10.1	0	2.1	0-102	91.1%
	6-102	91.1%					6	4.3	6.5	2.8		
30 days							24-102	13.5	24	66.9%		
	0	72.6%	0	1.2	0	70.7%	0	No effect	0	No effect	0-144	70.7%
	6-30	86.8%	6-30	6.7	6-30	76.6%	6-126	1.41	6-144	2.8		
	96	88.9%	96	8.7	96	88.9%	144	spilling				

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

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