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THE PHYSICAL-COLLOIDAL PROPERTIES OF COMPLEXES FORMED COMPLEXES FORMED BY OCTADECANOIC ACID WITH MONOETHANOLAMINE, DIETHANOLAMINE AND TRIETHANOLAMINE

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ABSTRACT

The article presents the results of the study of the surface activity substances, physical-colloidal parameters, and elemental composition calculated using the tensiometer of the complexes formed by the monobasic saturated carboxylic acid octadecanoic acid with monoethanolamine, diethanolamine, triethanolamine with different concentrations. As a result of surface tension measurements, parameters such as critical micelle formation density, surface pressure, minimum surface area per molecule, and micelle formation and adsorption Gibbs free energy were calculated based on electrical conductivity values. These measurements provided important information about the properties of the synthesized materials. Finally, experiments were conducted on three different water samples with different mineral content to investigate the effectiveness of the synthesized surfactants in removing oil spills from the water basin, oil collection and oil dispersing properties.

1. Introduction

Like other water bodies around the world, the Caspian Sea also faces unique challenges, such as the pollution of its water reservoir and the resulting deterioration of its ecological condition.

Currently, the main causes of pollution in the Caspian Sea are accidents that occur during oil extraction from oil fields and the transportation of oil.

The characteristic features of pollution by oil and its products include contamination of environmental components, their dispersion across large water areas, accumulation in sediments at the seabed, and other forms of pollution. Oil spills degrade water quality and negatively impact oxygen levels, disrupting the balanced interaction between the upper water layers and the atmosphere, which leads to a disturbance in the overall ecological regime.

Oil-based films that reflect sunlight prevent the absorption of energy by the water, which is essential for the life activities of marine organisms. The Caspian Sea is home to many species of fish, including 95% of the world's sturgeon population, making the removal of such oil spills particularly crucial for their survival.

After the accident on the crude oil platform in the Gulf of Mexico, urgent safety measures were implemented in the oil fields of the Caspian Sea, one of the largest centers of hydrocarbon resources. Among these measures, addressing the consequences of such incidents holds great importance. During mechanical cleaning of spilled oil, some of it remains on the water surface in the form of slicks. These slicks can only be removed through certain physico-chemical methods, using dispersants and collectors.

Surfactants (SAMs) used to remove thin oil films from the water surface are categorized into oil dispersants and oil collectors [1-10].

2. Materials And Experimental Methods

Octadecanoic acid, with the chemical formula $C_{17}H_{35}COOH$, is a saturated monobasic carboxylic acid that appears as white, crystalline, odorless solid. It is insoluble in water but soluble in ether. Its relative molecular mass is 284.5 g/mol, with a melting point of 69.6°C and a boiling point of 361°C.

Monoethanolamine (MEA) is a strong base with a molar mass of 61.1 g/mol. It is a colorless, transparent substance that can mix with water in any proportion.

Diethanolamine (DEA) is a strong base with a molar mass of 105.2 g/mol. It is a colorless, transparent substance that can mix with water in any proportion.

Triethanolamine (TEA) is a weak base with a molar mass of 149.19 g/mol. It is a colorless, transparent substance with an ammonia-like odor.

Infrared spectra were identified in the wavenumber range of 400-4000 cm^{-1} using a BIO-RAD FTS 3000 MX spectrometer (Germany).

The surface tension values were defined at the air-water interface via a du Nouy tensiometer with a ring method (KSV Sigma 702, Finland). [11].

The petro-collecting and dispersing properties of the synthesized surfactants were performed according to the methodology given in [12].

The petro-collecting properties were characterized by the collecting coefficient (K) (the ratio of the initial surface area of the petroleum film to the surface area of the thickened petroleum spot formed under the influence of the reagent) and the duration effect (τ) of the collected petroleum.

3. Results and Discussion

The reaction between octadecanoic acid and monoethanolamine (MEA) was conducted under laboratory conditions at a 1:1 molar ratio, with intensive stirring at a temperature of 70-75°C over the course of one day.

The reaction scheme is as follows:

$C_{17}H_{35}COOH + NH_2C_2H_4OH \rightarrow [\ C_{17}H_{35}COO^-\ N^+\ H_3\ C_2H_4OH]$

The relative molecular mass of the obtained complex is 345.6 g/mol. Based on the calculation method, the mass fractions of the elements in the quaternary ammonium salt formed from octadecanoic acid and MEA are as follows:

- Carbon (C): 69.5%
- Hydrogen (H): 12.7%
- Oxygen (O): 13.8%
- Nitrogen (N): 4%

These percentages reflect the distribution of each element's mass in the complex.

The reaction between octadecanoic acid and diethanolamine (DEA) was conducted under laboratory conditions at a 1:1 molar ratio, with intensive stirring at a temperature of 70-75°C over the course of one day.

The reaction scheme is as follows:

$C_{17}H_{35}COOH + NH(C_2H_4OH)_2 \rightarrow [\ C_{17}H_{35}COO^-\ N^+\ H_2(C_2H_4OH)_2]$

The relative molecular mass of the obtained complex formed from the reaction between octadecanoic acid and diethanolamine (DEA) is 433.4 g/mol.

Based on the calculation method, the mass fractions of the elements in the quaternary ammonium salt formed from octadecanoic acid and diethanolamine (DEA) are as follows:

- Carbon (C): 67.8%
- Hydrogen (H): 12.1%
- Oxygen (O): 16.5%
- Nitrogen (N): 3.6%

These percentages indicate the distribution of each element's mass in the complex.

The reaction between octadecanoic acid and triethanolamine (TEA) was conducted under laboratory conditions at a 1:1 molar ratio, with intensive stirring at a temperature of 70-75°C over the course of one day.

The reaction scheme can be represented as follows:

$C_{17}H_{35}COOH + N(C_2H_4OH)_3 \rightarrow [\ C_{17}H_{35}COO^-\ N^+\ H(C_2H_4OH)_3]$

The relative molecular mass of the obtained complex formed from the reaction between octadecanoic acid and triethanolamine (TEA) is 433.7 g/mol. Based on the calculation method, the mass fractions of the elements in the quaternary ammonium salt are as follows:

- Carbon (C): 66.4%

- Hydrogen (H): 11.8%

- Oxygen (O): 18.5%

- Nitrogen (N): 3.3%

these percentages indicate the distribution of each element's mass in the complex.

The octadecanoic acid with MEA was identified by IR-spectroscopy (Fig. 1). Spectral results are listed below: Stretching vibrations of N–H and O-H bonds at 3293 cm^{-1}, 2915 və 2848 cm^{-1} stretching vibration of C-H bond in CH_3 and CH_2 groups, stretching vibration of C=O bond at 1639 cm^{-1}, stretching vibrations of N-H bond at 1554 cm^{-1}, 1464, 719 cm^{-1} stretching vibration of C-H bond in CH_3 və CH_2 groups.

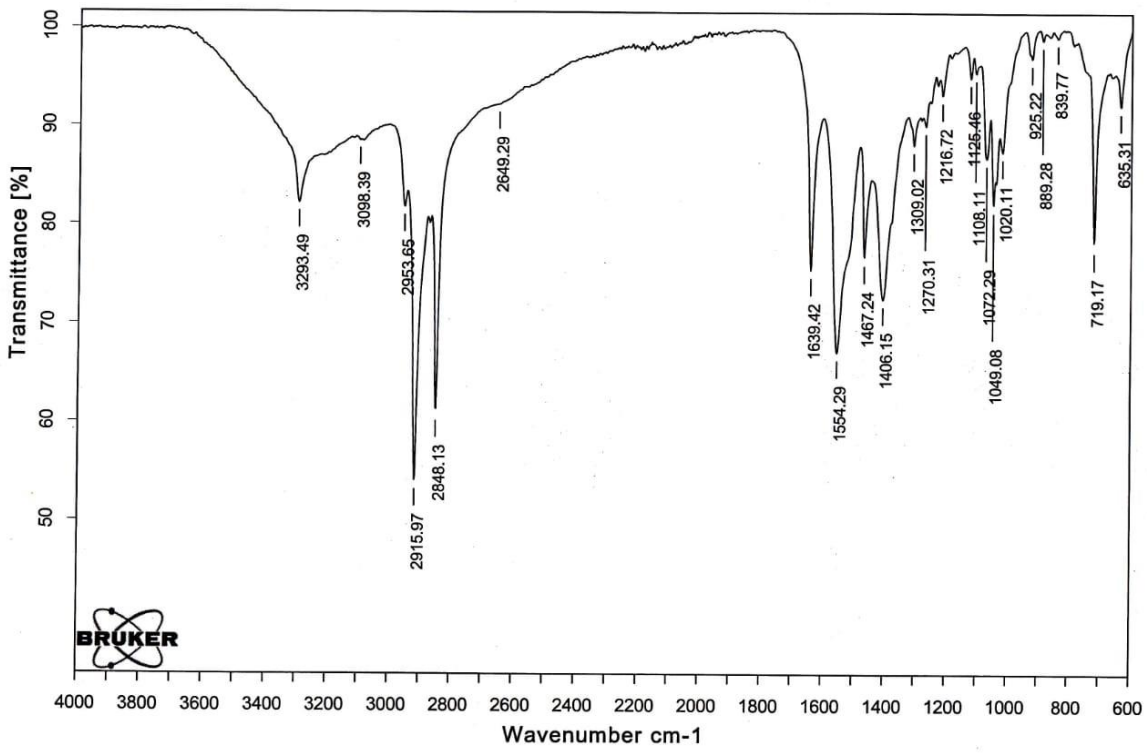

Fig. 1. FTIR spectra of octadecanoic acid with MEA

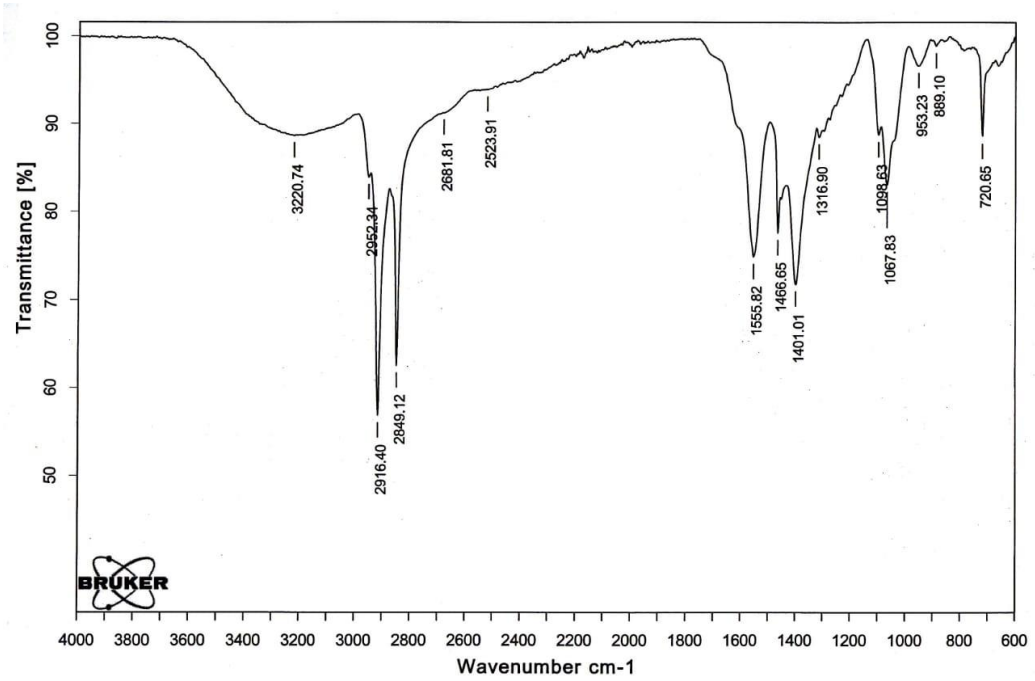

Fig. 2. FTIR spectra of octadecanoic acid with DEA

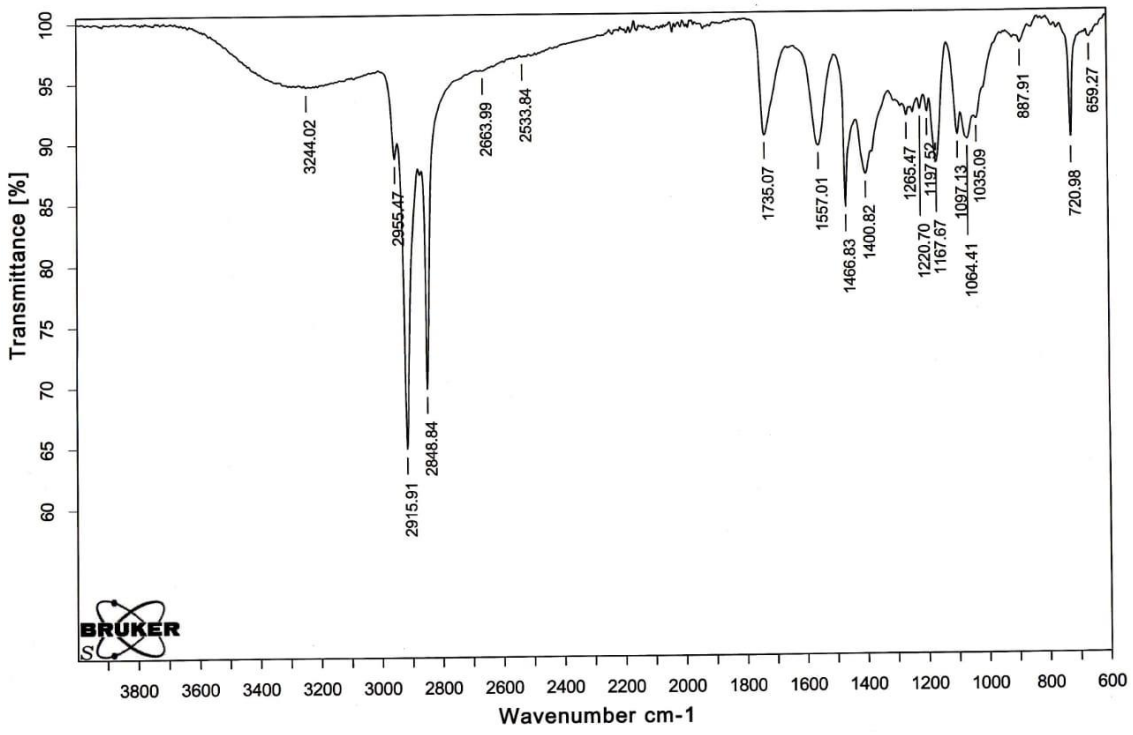

Fig. 3. FTIR spectra of octadecanoic acid with TEA

Identification of the structure of complexes formed by octanoic acid with MEA, DEA and TEA by IR spectroscopic method also proves that the reactions proceed according to the above scheme (Figure 1, 2,3).

Based on the measured surface tension values obtained using the tensiometric method, surface tension isotherms were established (Figure 4).

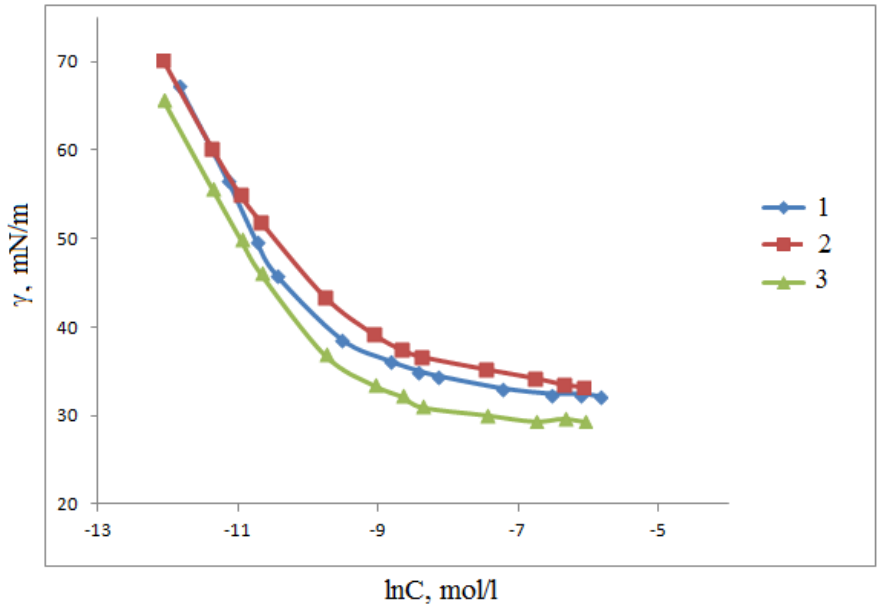

Figure 4. The surface tension isotherms of the salts formed by octadecanoic acid with MEA (1), DEA (2), and TEA (3).

Based on this figure, the value of *γ–lnC* was determined graphically [13]. In the absence of reagents, the surface tension at the air-water interface is equal to 72.0 mN·m^{-1}. The stabilization of the surface tension values for the salts formed by octadecanoic acid with MEA, DEA, and TEA occurs at approximately 32.5, 33.5, and 29.4 mN·m^{-1}, respectively.

According to the figure, the value of d/dlnC was determined graphically. By putting this value into the Gibbs equation, the adsorption value – G is calculated:

$$\Gamma_{max} = -\frac{1}{nRT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_T$$

where d/dlnC – surface activity (tangent of the slope of the dependence on lnC at constant temperature T); R – universal gas constant (8.314 J·/mol K).

The minimum cross-sectional area of the polar group of the synthesized surfactants was calculated using the formula:

$$A_{\min} = \frac{1}{\Gamma_{max} N_A},$$

where N_A is Avogadro's number (6.023·1023).

The value of efficiency (pC20), characterizing the concentration at which surface tension decreases by 20 mN/m, was calculated using the equation:

$$pC_{20} = -\lg C_{(-\Delta\gamma=20)}.$$

Surface pressure or efficiency (π_{CMC}) of aqueous solutions of synthesized substances at the water-air interface is determined by the formula:

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC}$$

where γ_0 is the surface tension in the absence of a surfactant, γ_{CMC} is the surface tension of the solution with CMC.

It is known from the literature that for nonionic surfactants, the thermodynamic parameters of micellization, namely the change in the Gibbs free energy, are calculated using the equation

$$\Delta G_{mis} = (2-\alpha)RT \ln CMC$$

where lnKKM is the surfactant concentration at the CMC point.

The value of ΔG_{ad} was calculated using the equation [13]

$$\Delta G_{ad} = (2-\alpha)RT \ln CMC - \pi_{CMC} A_{CMC.}$$

The colloid-chemical parameters of the synthesized surfactants (SAMs) were calculated based on the equations provided in [13], and the results are presented in Table 1.

Table 1– Colloid-chemical parameters of the new surfactants formed by octadecanoic acid with MEA, DEA, and TEA.

Surfactants	*CMC×10^{-3}, mol·dm^{-3}*	*G_{max}×10^{-10}, mol·sm^{-2}*	*A_{min}×10^{-2}, nm^2*	*γ_{CMC}, mN·m^{-1}*	*π_{CMC}, mN·m^{-1}*	*pC_{20}*	*ΔG_{mis}, kJ/mol^{-1}*	*ΔG_{ad}, kJ/mol^{-1}*
1	1.45	1.78	93.6	32.5	39.5	4.73	-25.89	-48.14
2	1.73	2.46	67.6	33.5	38.5	4.65	-25.44	-41.13
3	1.15	2.19	75.80	29.4	42.6	4.82	-26.23	-45.68

Note:

- CMC – Critical micelle concentration (CMC)

- γ_{CMC} – Surface tension of the solution at CMC

- G_{max} – Maximum adsorption

- A_{min}– Minimal surface area of the polar group

- π_{CMC} – Surface pressure or effectiveness

- pC_{20} – Efficiency value

- ΔG_{mis}– Enthalpy change during micelle formation

- ΔG_{ad} – Enthalpy change during the adsorption process.

Table 2 Research results of oil collection and oil dispersing ability of complexes formed by octanoic acid with MEA, DEA and TEA (Balakhana oil; thickness 0.17 mm)

Surfactants	The case of giving the reagent to the surface of the oil	Distilled water		Drinkable water		Sea water	
		τ, saat	K(K_D,%)	τ, saat	K(K_D,%)	τ, saat	K(K_D,%)
Octadecanoic acid +MEA	Undiluted product	0-24 48-72 72-96	Disp 66.2% Disp 78.6% Disp 86.6%	0-24 48-72 72-96	Disp 79.9% 12.2 Disp 86.6%	0-24 48-72 72-96	Disp 66.2% Disp 78.6% Disp 86.6%
	5% aqueous dispersion	0-24 48-72 72-96	Disp 66.2% Disp 78.6% Disp 86.6%	0-24 48-72 72-96	Disp 79.9% 12.2 Disp 86.6%	0-24 48-72 72-96	Disp 69.2% Disp 87.6% Disp 81.1%
Octadecanoic acid +DEA	Undiluted product	0 1.0-4.0 21.0-76.0	Disp 70.9% Disp 78.6% Disp 82.6%	0 1.0-4.0 21.0-76.0	Disp 70.9% Disp 78.6% Disp 82.6%	0 1.0-4.0 21.0-76.0	
	5% aqueous dispersion	0 1.0-4.0 21.0-76.0	Disp 60.9% Disp 68.6% Disp 72.6%	0 1.0-4.0 21.0-76.0	Disp 60.9% Disp 88.7% Disp 82.9%	0 1.0-4.0 21.0-76.0	Disp 73.5% Disp 78.6% Disp 72.6%
Octadecanoic acid +TEA	Undiluted product	1.0-5.0 21.0-76.0	Disp 78% Disp 86.8%	1.0-5.0 21.0-76.0	Disp 63.7% Disp 75%	1.0-5.0 21.0-76.0	Disp 72.6% Disp 65.9%
	5% aqueous dispersion	1.0-5.0 21.0-76.0	Disp 75% Disp 79.2%	1.0-5.0 21.0-76.0	Disp 72% Disp 82.4%	1.0-5.0 21.0-76.0	Disp 78.6% Disp 86.8%

As can be seen from Table 2, the complex of ocadecanic acid and MEA, DEA, TEA exhibits the ability to disperpsed oil in seawater for both application forms of the reagents.

4. Conclusion

Based on the results of the research, it was found that the complex formed by octadecanoic acid with MEA increased the surface tension from 72.0 mN/m to 32.5 mN/m at that boundary, and the complex formed by octadecanoic acid with DEA increased the surface tension from 72.0 mN/m to 33.5 mN/m, at that the complex formed by octadecanoic acid with TEA shows high surface activity by reducing the surface tension from 72.0 mN/m to 29.4 mN/m at that limit.

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