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A comparative study of the quaternary ammonium salts of enanth and undecanoic acids treated with triethanolamine

Abstract

At present, the wide application of surfactants in various fields such as detergents, foam and emulsion stabilizers, fluorogens, hydrophobizers, and corrosion inhibitors makes their synthesis one of the urgent issues. In the article, the results of the study of oil-collecting and oil-dispersing properties of the quaternary ammonium salt formed by triethanolamine (TEA) of enanthic acid, which is a monobasic carbonic acid, in distilled, drinking, and seawater contaminated with Balakhani oil are given. The surface activity property of the products of different concentrations of this complex was calculated using a tensiometer, and the element content was calculated using the calculation method. The complex formed by enanthic acid with TEA shows high surface activity by reducing the surface tension from 71.98 mN/m to 26.3 mN/m at that boundary.

The complex of enanthic acid and TEA exhibits the ability to accumulate oil in seawater, both in the pure and 5% forms of the reagent.

The complex formed by undecanoic acid with TEA shows high surface activity by reducing the surface tension from 71.98 mN/m to 23 mN/m at that boundary.

Keywords: *oil accumulation, oil dispersion, surface tension, surfactant, carbonic acid*

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. 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.

The use of chemical dispersants is still restricted by many governmental regulations and controlled by guidelines in field application. 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.

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. The behavior of a surfactant is affected by its hydrophilic-lipophilic balance (HLB).

Currently, like other water basins of the world, the pollution of the reservoir of the Caspian Sea and the related deterioration of the ecological situation here are considered urgent issues. Examples of sources of pollution of this sea include tankers carrying oil, accidents during oil extraction and transportation.

Oil spills degrade water quality and disrupt the balanced relationship of the upper water layers with the atmosphere, leading to a disruption of oxygen to living organisms.

Oil-based films that reflect the sun's rays prevent the energy from being absorbed by the water. Thremoval of such spots is especially necessary for the life of marine inhabitants, because more than a hundred species of fish, 95% of the world's sturgeon population live in the Caspian Sea.

Surfactants (SAMs) used to remove thin layers of oil from the water surface are divided into oil dispersants and oil collectors (Asadov, Ahmadova, Rahimov, Mammadova, 2011: 1012-1017; Asadov, Nasibova, Poladova, Rahimov, Asadova, 2012: 175-178; Asadov, Tantawy, Zarbaliyeva, Rahimov, 2012: 2; Asadov, Akhmedova, Aga-Zadeh, Nasibova, Zarbaliyeva, Bagirova, Ragimov, 2012:1916-1927; Asadov, Salamova, Eyyubova, Yolchuyeva, 2020: 388-398; Asadov, Rahimov, Salamova, 2012: 505-511; Asadov, Tantawy, Zarbaliyeva, Rahimov, 2012: 199-200; Asadov, Tantawy, Zarbaliyeva, Rahimov, Ahmadova, 2012: 136-145; Asadov, Tantawy, Zarbaliyeva, Rahimov, 2012: 621-630; Asadov, Tantawy, Zarbaliyeva, Rahimov, 2013: 261-267; Penfold, Thomas, 2024: 8084-8102; Jiang, Liu, Tan &Lin, 2019: 11-23; Jiang, Fu, Xie &Lin, 2014: 1799-1805; Asadov, Tantawy, Azizov, Zarbaliyeva, Rahimov, 2013: 13-23; Asadov, Zarbaliyeva, Rahimov, Salamova, Eyyubova, Ahmadova, Asadova, 2014: 205-214).

The presented article is dedicated to the study of the oil-collecting and oil-dispersing properties of the complex formed by enanthic acid with TEA.

Research

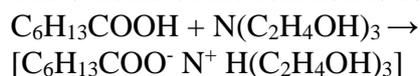
Enanthic acid is insoluble in water, relative molecular mass 130.2 g/mol, an oily, colorless liquid with a general formula of $C_6H_{13}COOH$, boiling point $223^{\circ}C$, sparingly soluble in water but well soluble in ethanol, has an unpleasant oily odor. is a saturated monobasic carbonic acid. Undecanoic acid is a monobasic saturated carbonic acid with the formula $C_{10}H_{21}COOH$, well soluble in methanol, ethanol, acetone, chloroform, molar mass 186.3 g/mol, melting point $28-30.5^{\circ}C$, boiling point $284^{\circ}C$ in the form of a white powder at room temperature.

Triethanolamine (TEA) is a colorless, transparent, ammonia-smelling liquid with a molar mass of 149.19 /mol-1, a density of 1.124 g/ml-1, a solidification point of $22^{\circ}C$, a boiling point of $335^{\circ}C$, and a refractive index of 1.4850 ($20^{\circ}C$).

IR-spectra of salts of undecanoic and tetradecanoic acids formed with TEA were recorded on FT-IR, Spectrum BX and ALPHA (Bruker) spectrometers using a KBr disk. The surface activity of substances was determined at the air-water interface using a KSV Sigma 702 (Finland) tensiometer using a Du Nui ring.

The reaction between enanthic acid and TEA was carried out under laboratory conditions in a 1:1 molar ratio at room temperature with vigorous stirring.

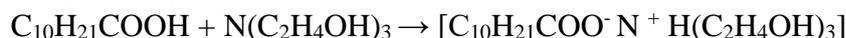
The scheme of the reaction is as follows:



The quaternary ammonium salt obtained on the basis of enanthic acid and TEA has a relative molecular mass of 279.4 g/mol, dissolves in 0.75%, 0.1% solutions in water by forming a colloidal solution, and is well soluble in ethyl and isopropyl alcohols.

According to the results of the element composition research by calculation method, the mass share of carbon in the quaternary ammonium salt of enanthic acid with TEA is 55.9%, the mass share of hydrogen is 10.5%, the mass share of oxygen is 28.6%, and the mass share of nitrogen is 5%.

The reaction between undecanoic acid and TEA was carried out in laboratory conditions in a 1:1 mol ratio at $34^{\circ}C$ for 3-4 hours with intensive stirring. The general scheme of reactions can be shown as follows:



Relative molecular mass of the salt formed by undecanoic acid with TEA

335.5 g/mol, ethyl and isopropyl alcohol are well soluble. Based on the calculation, the element composition of this salt was calculated and it was determined that the mass share of carbon is 60.9%, the mass share of hydrogen is 11.2%, the mass share of oxygen is 23.4%, and the mass share of nitrogen is 4.5%, respectively.

The surface activity property of the complex formed by enanthic and undecanoic acids with TEA were determined using a tensiometer at the water-air interface at a temperature of $21^{\circ}C$ (Table 1).

The surface activity property of the complex formed by undecanoic and enanthic acids with TEA was determined using a tensiometer at the water-air interface at a temperature of 21°C (Table 1).

item name	Density of SAM (% by mass)											
	0.00025	0.0005	0.00075	0.001	0.0025	0.005	0.0075	0.01	0.025	0.05	0.075	0.1
	Values of surface tension at the air-water boundary, $\text{mN}\cdot\text{m}^{-1}$											
Undecanoic acid+TEA	48.4	39.5	35.8	33.1	28.6	26.8	25.8	25.2	23.6	23.1	23.2	23.0
Enanthic acid +TEA	71.6	58.7	61.9	56.8	51.9	50.6	45.5	45.4	33.3	28.1	27.5	26.7

The complex formed by enanthic acid with TEA shows high surface activity by reducing the surface tension from 71.98 mN/m to 26.3 mN/m at that boundary.

Complexes formed by enanthic acid with TEA were studied as an oil collector and oil dispersant in cleaning the water surface clouded with an oil layer with a thickness of 0.17 μm . The effectiveness of this reagent was studied in the laboratory on waters with different degrees of mineralization using the Balakhani light oil sample. The reagent was used both in its pure form and in the form of a 5% aqueous solution. The reduction of the area of the initial oil layer due to the penetration of the reagent into oil-contaminated waters determines its effectiveness. The oil accumulation coefficient is a quantity that characterizes this effect. K is calculated as the ratio of the initial area of the oil layer to the area of the oil spot formed by the effect of the reagent.

Table 3. Research results of the oil collection and oil dispersing ability of the TEA complex of enanthic acid (Balakhani oil; thickness 0.17 μm)

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	$K(K_D, \%)$
Undiluted product	0-24 48-72 72-96	Dispersed	0-24 48-72 72-96	Dispersed	0-24 48-72 72-96	Dispersed
5% aqueous dispersion	0-24 48-72 72-96	4 Dispersed	0-24 48-72 72-96	5 Dispersed	0-24 48-72 72-96	Dispersed

As can be seen from Table 2, the complex of Enanthic acid and TEA exhibits the ability to accumulate oil in seawater for both application forms of the reagent.

Table 3. Research results of the oil collection and oil dispersing ability of the TEA complex of undecanoic acid (Balakhani oil; thickness 0.17 μm)

The case of giving the reagent to the surface of the oil	Distilled water		drinkable water		Sea water	
	τ , hour	$K(K_D, \%)$	τ , hour	$K(K_D, \%)$	τ , hour	$K(K_D, \%)$
Undiluted product	0-24 48-72 72-96	15.1 8.7 12.2	0-24 48-72 72-96	10.3 8.7 7.6	0-24 48-72 72-96	Dispersed
5% aqueous dispersion	0-24 48-72 72-96	15.2 2.6 2.5	0-24 48-72 72-96	12.2 3.5 Dispersed	0-24 48-72 72-96	17.3 15.2 11.1

As can be seen from Table 3, the complex of Undecanoic acid and TEA exhibits the ability to accumulate oil in seawater for the 5% application forms of the reagent.

Conclusion

Based on the results of the study, quaternary ammonium salts formed by undecanoic and enanthic acids with TEA show high surface-activity properties, similar to quaternary ammonium salts formed by TEA of other higher carboxylic acids (Shahverdiyeva, 2024: 21-25; Shahverdiyeva, Salamova, 2024: 34-38).

Solutions of new complexes of undecanoic and tetradecanoic acids synthesized on the basis of TEA in different concentrations have oil-dispersing and oil-collecting properties.

References

1. Asadov, Z.H., Ahmadova, G.A., Rahimov, R.A., Mammadova, Kh.A. (2011). Colloidal-chemical parameters of petroleum-collecting and dispersing surfactants based on vegetable oil acid fractions and 2-(chloromethyl) oxirane. *Journal of the Korean Chemical Society*. Vol. 55, No. 6, pp. 1012-1017.
2. Asadov, Z.H., Nasibova, S.M., Poladova, T.A., Rahimov, R.A., Asadova, A.Z. (2012). Petroleum collecting and petroleum dispersing reagents based on alkyl amine and alkyl iodides. *Materials Research Innovations*. 16: 175–178.
3. Asadov, Z.H., Tantawy, A.H., Zarbaliyeva, I.A., Rahimov, R.A. (2012). Synthesis of surface-active agents based on tridecanoic acid and nitrogenous bases and their petroleum-collecting and dispersing properties. *Al-Azhar Engineering Twelfth International Conference*, December, 25–27, 2012, AEIC 2012. Abstracts book. Cairo, Egypt, Vol.1. Faculty of Engineering, Al-Azhar University, Nasr City. PT02, p. 2.
4. Asadov, Z.G., Akhmedova, G.A., Aga-Zadeh, A.D., Nasibova, Sh.M., Zarbaliyeva, I.A., Bagirova, A.M., Ragimov, R.A. (2012). Ionic Liquid Surfactants. *Russian Journal of General Chemistry*, vol. 82, №12, p. 1916-1927.
5. Asadov, Z.H., Salamova, N.V., Eyyubova, S.K., Yolchuyeva, U.J. (2020). Methyl iodide salts of aminoesters of vegetable oils fatty acids. *Processes of petrochemistry and oil refining*. Vol.21, No.4, pp. 388-398.
6. Asadov, Z.H., Rahimov, R.A., Salamova, N.V. (2012). Synthesis of animal fats ethylolamides, ethylolamide phosphates and their petroleum-collecting and dispersing properties. *J.Amer. Oil. Chem. Soc.*, 89, March, p.505-511.
7. Asadov, Z.H., Tantawy, A.H., Zarbaliyeva, I.A., Rahimov, R.A. (2012). Synthesis of New Surface-Active Ammonium-Type Complexes Based on Palmitic Acid For Removing Thin Petroleum Films From Water Surface. *The 1st Intern.Conference on Science Diplomacy and Developments in Chemistry*, November 24-26, 2012. Book of Abstracts, p.199-200.
8. Asadov, Z.H., Tantawy, A.H., Zarbaliyeva, I.A., Rahimov, R.A., Ahmadova, G.A. (2012). Surfactants Based on Palmitic Acid and Nitrogenous Bases for Removing Thin Oil Slicks from Water Surface. *Chemistry Journal*. Vol. 02, Issue 04, p. 136-145.
9. Asadov, Z.H., Tantawy, A.H., Zarbaliyeva, I.A., Rahimov, R.A. (2012). Petroleum-Collecting and Dispersing Complexes Based on Oleic Acid and Nitrogenous Compounds as Surface-Active Agents for Removing Thin Petroleum Films from Water. *Journal of Oleo Science by Japan Oil Chemists Society*. 27, 61(11), p. 621-630.
10. Asadov, Z.H., Tantawy, A.H., Zarbaliyeva, I.A., Rahimov R.A. (2013). Synthesis of new surface-active ammonium-type complexes based on palmitic acid for removing thin petroleum films from water surface. *Egyptian Journal of Petroleum*. 22, p.261-267.
11. Asadov, Z.H., Zarbaliyeva, I.A., Rahimov, R.A., Salamova, N.V., Eyyubova, S.K., Ahmadova, G.A., Asadova, A.Z. (2014). Petroleum-collecting and dispersing chemicals for cleaning sea surface from thin petroleum slicks. *Bull. Chem. Soc. Ethiop*. 28(2), p.205-214.
12. Asadov, Z.H., Tantawy, A.H., Azizov, A.H., Zarbaliyeva, I.A., Rahimov, R.A. (2013). Synthesis Of New Complexes-Surfactants Based on Fatty Acids and Study of The Effect of

- Length of Fatty Acid Chain on The Petroleum-Collecting and Surface-Active Properties. *Caspian Journal of Applied Sciences Research (Malaysia)*. V.2, №.3, p. 13–23.
13. Jeffrey, P., Robert, T. (2024). The Gibbs and Butler Equations and the Surface Activity of Dilute Aqueous Solutions of Strong and Weak Linear Polyelectrolyte-Surfactant Mixtures: *The Roles of Surface Composition and Polydispersity J, Phys Chem B*. 2024 Aug 22;128(33):8084-8102. <https://doi.org/10.1021/acs.jpcc.4c03541>.
 14. Rong, J., Chang, L., Li, T., Tan & Cuiying L. (2019). Formation of carboxymethylchitosan/gemini surfactant adsorption layers at the air/water interface: *Effects of association in the bulk* Pages 11-23 | Received 23 Jan 2018, Accepted 24 Mar 2018, Published online: 22 Nov 2019 <https://doi.org/10.1080/01932691.2018.1462195>
 15. Rong, J., Lin, F., Fandong, X. & Cuiying L. (2014). Dynamic Surface Elasticity of Polyelectrolyte/Surfactant Adsorption Films at the Air/Water Interface: Carboxymethylchitosan and Cetyltrimethylammonium Bromide Pages 1799-1805 | Received 03 Sep 2014, Accepted 08 Oct 2014, Published online: 26 Jun 2015 <https://doi.org/10.1080/01932691.2015.1022653>
 16. Shahverdiyeva, A. (2024). Comparative study of quaternary ammonium salts formed by cis-9-octadecene and ocradecanoic acids with triethanolamine. *Nature and science* 6(2) 21-25. <https://doi.org/10.36719/2707-1146/41/21-24>
 17. Shahverdiyeva, A, Salamova, N. (2024). Study of the oil detergent and oil dispersing properties of quaternary ammonium salts treated with heptan acid with triethanolamine. *Nature and science* 6 (7), 34- 38 <https://doi.org/10.36719/2707-1146/41/21-24>

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