2024. Volume 8, Number 1 ***Pages 52-58***

UOT:661
https://doi.org/10.30546/2521-6317.2024.108

SYNTHESIS OF SURFACTANTS BASED ON SOYBEAN OIL TRIGLYCERIDES, N-(2-HYDROXYETHYL) ETHYLENEDIAMINE, AND PROPYLENE OXIDE, AND THE STUDY OF THEIR PETRO-COLLECTING AND PETRO-DISPERSING PROPERTIES

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ARTICLE INFO

Article history:

Received:2024-09-23

Received in revised form:2024-10-18

Accepted:2024-10-18

Available online

Keywords:

soybean oil triglycerides;

surface activity;

specific electrical conductivity;

petro-collecting;

petro-dispersing.

ABSTRACT

An aminoamide containing a hydroxyl group was synthesized from the reaction of a soybean oil acid mixture with hydroxyethylethylenediamine. The obtained aminoamide was then oxypropylated with propylene oxide. The composition and structure of the synthesized aminoamide and its oxypropyl derivatives were determined by FTIR spectroscopy. The synthesized products were characterized by their important physico-chemical properties, and conductometric measurements of their aqueous solutions at different concentrations were carried out. The colloid-chemical parameters of the synthesized surfactants were studied, and their adsorption properties were determined experimentally. Simultaneously, the critical micelle concentration, surface pressure, maximum adsorption, minimum surface area of the molecule, adsorption efficiency, and free Gibbs energy of micellization and adsorption were calculated. The petro-collecting and petro-dispersing properties of the obtained products were studied in a thin oil layer on the surface of different types of water.

1. Introduction

It is well-known that one of the main sources of water pollution is oil and petroleum products [1-7]. Oil pollution in marine waters occurs primarily during oil extraction and transportation by tankers. Accidental spills, operational discharges, and leaks during these activities significantly contribute to the presence of oil in the marine environment. The impact of oil pollution on marine life is profound, affecting both the health of aquatic organisms and the overall balance of the ecosystem.

Methods for cleaning water contaminated with oil are carried out in several stages to effectively reduce pollution levels. The first stage usually involves removing the thick layer of oil from the water surface using mechanical methods. These methods include the use of sorbents, skimmers, and booms, which physically separate the oil from the water. For example, sorbents [8,9] absorb or adsorb oil, making it easier to collect and dispose of. Skimmers are used to collect oil from the water surface [10,11], while booms prevent the spread of oil, keeping it from reaching the shoreline and sensitive habitats.

Despite the effectiveness of mechanical methods in removing the bulk of the oil, a thin layer of oil often remains on the water surface. This residual layer is difficult to eliminate, requiring more advanced methods. At this stage, colloidal-chemical methods are used to disperse or break down the thin oil film. These methods include the use of surfactants and dispersants, which reduce the surface tension between the oil and water [12-16].

Ongoing research and development in this field aim to improve the efficiency of these reagents, ultimately leading to cleaner and healthier oceans.

2. Materials and Experimental Methods

Soybean oil was used as a commercial product by the Labinsk branch of LLC "MEZ Yug Rusi" according to GOST R 53510-2009 (Russia). N-(2-hydroxyethyl) ethylenediamine (HEtEDA) – purity 99%, Sigma-Aldrich.Propylene oxide (PO) - purity 99%, Alfa Aesar, Great Britain. The chemical structures of the prepared compounds were confirmed by FT-IR analysis.

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

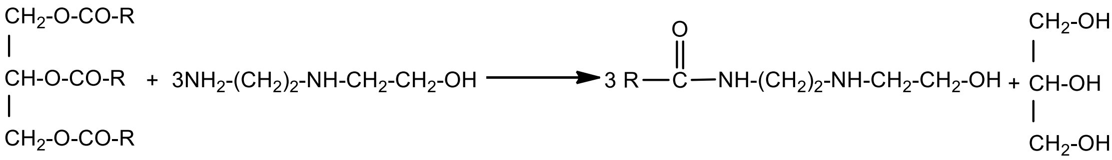
The surface tension values were defined at the air-water interface via a du Nouy tensiometer (KSV Sigma 702, Finland) with a ring method. [17].

The petro-collecting and dispersing properties of the synthesized surfactants were performed according to the methodology given in [18].

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

An aminoamide containing a hydroxyethyl group was synthesized from the reaction of soybean oil triglycerides with HEtEDA. The reaction was carried out at a temperature of 120-130°C in a 1:3 mol ratio of reagents. The reaction time was 24 hours. The total course of the reactions is given in Scheme 1:



(1)

The aminoamide of the obtained soybean oil acid mixture (SOAM) with hexaethylethylenediamine was identified by IR-spectroscopy (Fig. 1). Spectral results are listed below: Stretching vibrations of N–H and O-H bonds at 3295 və 3271 cm^{-1}, stretching vibrations of CH=CH at 3009 cm^{-1}, 2852 və 2921 cm^{-1} stretching vibration of C-H bond in CH_3 and CH_2 groups, stretching vibration of C=O bond at 1640 cm^{-1}, stretching vibrations of N-H bond at 1558 cm^{-1}, 1464, 1397, 1376 və 720 cm^{-1} stretching vibration of C-H bond in CH_3 və CH_2 groups.

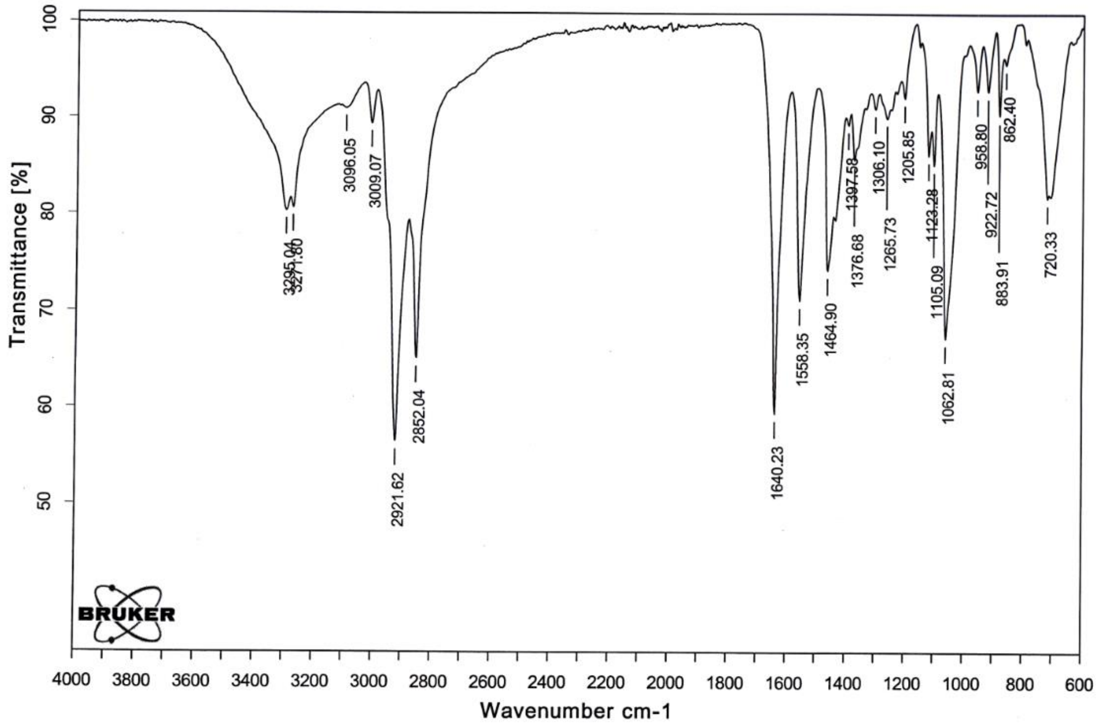
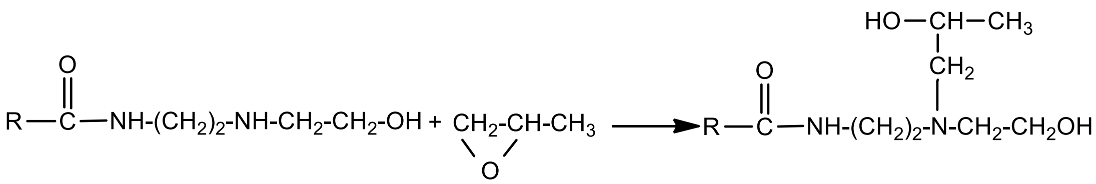


Fig. 1. FTIR spectra of hydroxyethyl aminoamide of SOAM

Synthesis of obtained SOAM aminoamide HEtEDA with PO was carried out and the oxypropyl derivative was synthesized. The reaction was carried out at room temperature in an equimolar ratio of reagents. The reaction lasted 15-16 hours. The general scheme (2) of the reaction is given below:



(2)

The structure of the synthesized oxypropyl derivative of the hydroxyethylethylenediamine aminoamide of SOAM was confirmed by IR-spectroscopy (Fig. 2). Absorption bands belonging to the following groups are observed in the spectrum: stretching vibration of the bond at 3321 cm^{-1}, stretching vibration of CH=CH bond at 3008 cm^{-1}, stretching vibration of C-H bond in CH_3 and CH_2 groups at 2853 and 2923 cm^{-1}, the stretching vibration of the C=O bond of the amide group at 1645 cm^{-1}, the stretching vibration of the N-H bond at 1547 cm^{-1}, the stretching vibration of the C-H bond in the CH_3 and CH_2 groups at 1456 and 1372 cm^{-1}, the stretching vibration of the C–O at 1048 cm^{-1}, vibrations belonging to the alkyl chain at 721 cm^{-1}.

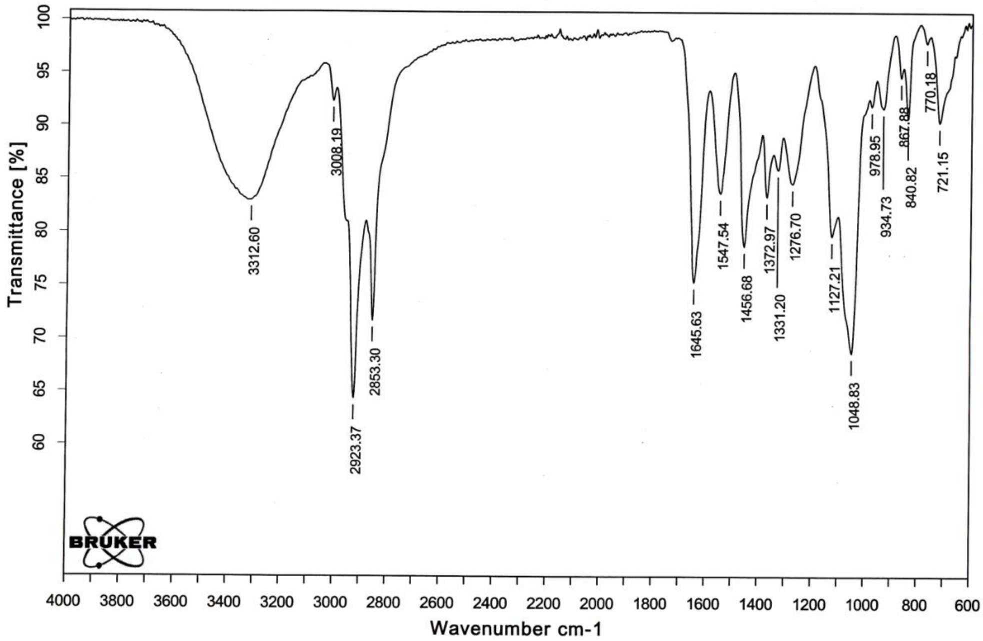


Fig. 2. FTIR spectra of the oxypropyl derivative of the aminoamide of SOAM

Based on the surface tension values of the synthesized SOAM aminoamide and its oxypropyl derivative measured using a tensiometer, surface tension isotherms were constructed in the γ–lnC coordinate (Fig. 3).

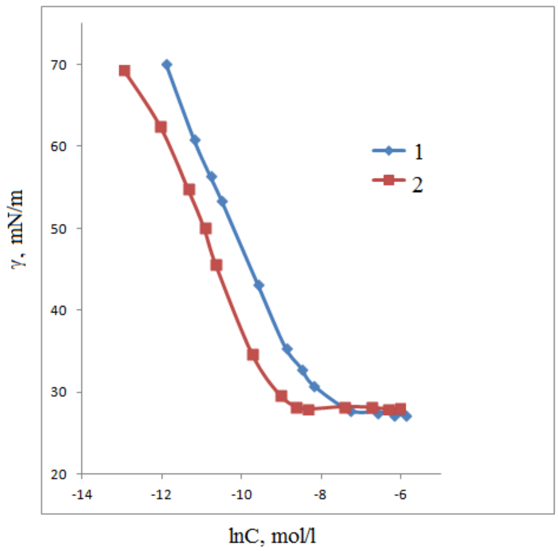


Fig. 3. The surface tension isotherms of the hydroxyethyl aminoamide of SOAM (1) and its oxypropyl derivative (2).

The colloid-chemical parameters of synthesised non-ionic surfactants in Table 1 were calculated according to the equations in reference [19].

Table 1. The colloid-chemical parameters of the hydroxyethyl aminoamide of SOAM (1) and its oxypropyl derivative (2).

Surfactants	CMC×10^{-4}, mol·dm^{-3}	$Γ_{max}$×10^{-10}, mol·cm^{-2}	A_{min}×10^{-2}, nm^2	$γ_{CMC}$, mN·m^{-1}	$π_{CMC}$, mN·m^{-1}	pC_{20}	$ΔG_{mic}$, kJ/mol^{-1}	$ΔG_{ad}$, kJ/mol^{-1}
1	6.82	2.50	66.50	27.8	44.2	4.52	-28.9	-45.9
2	1.77	1.19	139.16	28.3	43.7	4.82	-31.6	-68.2

CMC – critical micelle concentration, $γ_{CMC}$ – the surface pressure at the water; $Γ_{max}$- maximum surface excess, A_{min} – minimum surface area per molecule, $π_{KMQ}$ – surface pressure or effectiveness, pC_{20} – efficiency of absorption, $ΔG_{mic}$ – Gibbs free energy of micellization, $ΔG_{ad}$ – standard Gibbs energy of adsorption

Comparing the colloid-chemical parameters of hydroxyethyl aminoamide of SOAM and its oxypropyl derivative, it is known that the oxypropylation process has a higher effect on CMC and pC_{20}. Thus, the value of CMC for the oxypropyl derivative decreases significantly, while the value of pC_{20} increases.

The research results of petro-collecting and petro-dispersing properties of undiluted and 5% aqueous dispersion surfactants are given in Table 2.

As can be seen from Table 2, hydroxyethyl aminoamide of SOAM shows a petro-collecting effect in fresh and sea water in both diluted and undiluted forms (K_{max} = 13.6 and 16.0). The Oxypropyl derivative of the hydroxyethyl aminoamide of SOAM shows a petro-collecting effect in the first hours in all three applied forms of water and then shows petro-dispersing properties. The maximum petro-dispersing effect shown in distilled, fresh and sea water was 84.7%, 89.0% and 91.1%.

Table 2. Petro-collecting and petro-dispersing properties of the hydroxyethyl aminoamide of SOAM and its oxypropyl derivative (Balakhani oil; thickness ≈ 0.17 mm).

Distilled water		Fresh water		Sea water	
τ, hours	K (K_D, %)	τ, hours	K (K_D, %)	τ, hours	K (K_D, %)
Hydroxyethyl aminoamide of SOAM (Undiluted product)					
0 2.0-27.0 45.0-71.0 109.0	7.4 19.4 86.8% spilling	0 1.0-27.0 45-71 109.0	8.6 12.4 6.7 spilling	0 2.0-13.4 27.0-97.0 109.0	7.7 16.0 8.6 spilling
Hydroxyethyl aminoamide of SOAM (5% wt. aqueous solution)					
0 1.0-5.0 21.0-71.0 109.0	6.7 12.4 91.1% spilling	0 27-69 109.0	8.6 13.6 spilling	0 1.0-5.0 21.0-69.0 109.0	6.7 11.4 8.9 spilling
Oxypropyl derivative of the hydroxyethyl aminoamide of SOAM (Undiluted product)					
0-5.0 23.0-97.5	7.6 78.6%	0-5.0 23.0-97.5	7.6 78.6%	0-2.0 5.0 23.0-89.0 97.5	7.6 91.1% 86.8% spilling
Oxypropyl derivative of the hydroxyethyl aminoamide of SOAM (5% wt. aqueous solution)					
0-2.0 5.0 23.0-97.5	5.1 78.6% 84.7%	0-5.0 23.0-89.0 97.5	5.0 89.0% spilling	0-5.0 23.0-89.0 97.5	86.8% 91.1% spilling

This reagent shows a petro-dispersing effect in the form of a diluted form in seawater. The duration of action of the reagent is ~4 days.

4. Conclusion

Hydroxyethyl aminoamide of a mixture of soybean oil acids, as well as its oxypropyl derivative synthesized using propylene oxide, have been synthesized. Their structures were identified using IR spectroscopy. The research established that the synthesized substances exhibit high surface activity. It should also be noted that the reagents show a high tendency for surface adsorption. It was found that the surface activity properties can vary depending on the structure of the synthesized substances. Furthermore, comparative studies showed that the oxypropyl derivative of hydroxyethyl aminoamide of the mixture of soybean oil acids demonstrates superior properties in dispersing thin oil films on the surface of seawater compared to the original hydroxyethyl aminoamide of the mixture of soybean oil acids.

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