



New Nonionic Surfactants from Renewable Raw Materials-Sunflower Oil Production Waste

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Abstract

From technical vegetable oil – a by-product of sunflower oil production – a mixture of fatty carboxylic acids (FCA) was obtained via alkaline hydrolysis, acid treatment, and extraction. The composition of the extract was analyzed using IR and NMR spectroscopy, as well as mass spectrometry coupled with chromatographic analysis. It was shown that the extracted mixture contains nine types of fatty carboxylic acids. Nonionic surfactants – monoethanolamides (FCA-MEA) and diethanolamides (FCA-DEA) of the fatty carboxylic acids were synthesized by the esterification of acid mixture with monoethanolamine (MEA) and diethanolamine (DEA). The reaction yields were 92% and 95%, respectively. The chemical structures of the synthesized nonionic surfactants were confirmed by IR and NMR spectroscopy. The main adsorption characteristics of the resulting nonionic surfactants at the water/air interface were determined by measuring the surface tension of their aqueous solutions. It was found that FCA-DEA surfactant was more surface-active than FCA-MEA surfactant and the parameters of Π_{CMC} and CMC/C_{20} for the first surfactant were higher than those for second surfactant. It was shown that the synthesized nonionic surfactants were effective foaming agents and stabilizers of oil-in-water (o/w) emulsions. Notably, the FCA-DEA-based surfactants formed relatively more stable foams and emulsions.

Keywords: Sunflower oil production waste; Renewable raw material; Nonionic surfactant; Foaming; Emulsion.

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1. Introduction

Currently, more than half of all commercially available surfactants are derived from petrochemical feedstocks.^[1-3] The production processes that rely on fossil resources are typically accompanied by substantial CO₂ emissions. While carbon dioxide plays a vital role in plant life and in retaining heat within Earth's atmosphere, excessive atmospheric CO₂ concentrations contribute to the greenhouse effect, ultimately driving global warming (e.g., glacier melting and sea-level rise). Global carbon emissions from fossil fuels reached a record high in 2024,^[4] and according to the annual report of the Energy Institute, CO₂ emissions soared to a record 37.4 billion tonnes, driven by high fossil-fuel consumption.^[5]

Another major concern associated with surfactant production from hydrocarbon and coal feedstocks is the slow biodegradation of these molecules in aquatic environments

under microbial action and sunlight.^[6-8] When surfactant concentrations in fresh and marine waters exceed permissible limits, they adversely affect local flora and fauna. Therefore, the synthesis and development of technologies for producing surfactants from environmentally benign, renewable raw materials is an urgent challenge. The creation of biodegradable surfactants can substantially reduce their ecological footprint.^[9,10] Owing to their unique interfacial and solubilizing properties, nonionic surfactants (NIS) play an essential role across a wide range of industries and in daily life. NIS find broad application in the food industry,^[11-13] cosmetics,^[14-16] household cleaning products,^[17-19] agriculture, and pharmaceuticals^[20-25] as well as in oil and gas extraction and processing,^[26-31] among other sectors.

In,^[32] the potential of the obtaining nonionic surfactants from vegetable oil and waste vegetable oil was investigated. Natural sunflower oil (S-1), used sunflower oil (Household, S-2), used sunflower oil (Restaurant, S-4) and rapeseed oil (S-5) were employed as raw materials for the synthesis. Nonionic surfactants were produced via glycerinization of vegetable oil in the presence of a base. It was shown that the saponification number of the studied oils was ~140 mg KOH/g, the water number ranged from of 3.2 to 6.8 cm³/g and the content of

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active ingredients varied from 24.9% to 79.8%. The highest concentration of active ingredients was found in the raw material S-2 and the lowest – in S-1. The tests of emulsion formation in solutions with the synthesized surfactants revealed that stable (lasting for one hour) emulsions at a temperature of 80°C were formed in the solutions of surfactants derived from raw materials S-2 and S-5.

In^[33] the authors synthesized nonionic surfactants using five different fatty acids (lauric acid, myristic acid, palmitic acid, oleic acid and stearic acid) - in reaction with diethanolamine. The reactions were carried out at 160°C and 1 bar for four hours in the presence of a catalyst (KOH). It was found that the physicochemical properties of the synthesized nonionic surfactants depended on the molecular weight, the length of the hydrocarbon chain and the presence of a double bond in the fatty acid structure. For example, an increase in the length of the hydrocarbon chain led to a decrease in the water number, improved solubility in oil and increased the rheological parameters of the surfactant. Meanwhile, the presence of a double bond in the fatty acid structure improved the surfactant's water solubility. An increase in the length of the saturated hydrocarbon chain led to higher values of the interfacial tension of the surfactant. While the lowest value of interfacial tension was observed in a surfactant containing a double bond in its structure.

The review^[34] is devoted to the discussion of environmental problems associated with the use of n-hexane in the traditional method of extracting vegetable oil from seeds and nuts. Despite the effectiveness of n-hexane for the extraction of vegetable oil, its use is currently subject to harsh criticism due to its negative impact on human health and the environment. As an alternative to hexane extraction, more environmentally friendly solvents and extraction methods have recently been developed and tested. Among them, the Surfactant-Aqueous Extraction Process (SAEP) is considered promising. The use of so-called “extended surfactants” allows for the extraction of more than 90% of oil from seeds.^[35, 36]

Several Gemini type nonionic surfactants based on grape seed oil (GPNGS) were synthesized using grape seed oil and polyethyleneglycol monomethyl ether (350; 550; 750) as raw materials.^[37] The critical micelle concentration of GPNGS with different polyoxyethylene chain lengths ranged from 1.4×10^{-4} to 5×10^{-4} mol/L, and the contact angle of GPNGS on polyamide film was approximately 46–49°. GPNGS was also evaluated as an acid leveling agent for nylon 66. It was shown that the addition of 0.2 mmol/L GPNGS, the standard deviation (S(λ)) of nylon 66 dyeing decreased from 0.084 to about 0.036–0.044, indicating a good leveling effect.

The problems associated with the selection and use of

vegetable oils as raw materials for the synthesis of surfactants with predetermined properties are discussed in the review.^[38] According to this review, the selection of vegetable seeds and oils as raw materials involves three stages: 1) selection of seeds and vegetable peels considered as agricultural waste, 2) consideration of the physicochemical properties of vegetable oils, and 3) determination of the surface-active properties, thermal and oxidative stability of surfactants based on vegetable oils. It should be noted that surfactants based on vegetable oils with a high content of monounsaturated fatty acids (such as oleic acid, erucic acid, nervonic acid, and ricinoleic acid) have good surface-active properties and biodegradability,^[39,40] while surfactants with saturated fatty acids have thermal and oxidative stability.^[41,42]

In order to determine the effect of the hydroxyl group present in the hydrocarbon radical of the surfactant on micelle formation in solutions, the authors of^[43] synthesized two types of nonionic surfactants using an esterification reaction: 1) from a mixture of stearic acid (SA) and short-chain polyethyleneglycol (PEG) and 2) from a mixture of 12-hydroxy stearic acid (HSA) and PEG. The 12-hydroxy group in HSA was previously protected to prevent interaction with PEG. The study showed that in aqueous solutions of SA-PEG-SA surfactants, a "star micelle" is formed, while in HSA-PEG-HSA surfactant solutions, a "flower micelle" was formed. In this case, at high concentrations in HSA-PEG-HSA surfactant solutions, flower micelles began to interact with each other by forming bridge-like hydrogen bonds between OH groups at the C₁₂ alkyl chain. Intermicellar hydrogen bonds increased the stability of the hydrophobic core of micelles, consequently, the phase separation threshold was higher for HSA-PEG-HSA surfactants than for SA-PEG-SA.

Thus, the literature review revealed that insufficient attention has been paid to the use of waste sunflower oil for the synthesis of surfactants and the study of the properties of the resulting surfactants. In light of this, the aim of the present study is to synthesize eco-friendly nonionic surfactants from technical vegetable oil – a by-product of sunflower-oil production and to characterize their physicochemical and surface properties.

2. Experimental

2.1 Materials

Technical vegetable oil – a by-product of “Shedevr” sunflower oil production (Almaty, The Republic of Kazakhstan) used as the hydrophobic component for the synthesis of nonionic surfactants.

Monoethanolamine (MEA) and diethanolamine (DEA), both obtained from Sigma-Aldrich, served as the hydrophilic components. The purity of these compounds was no less than 98 wt.%. For the hydrolysis of fatty acid esters, concentrated aqueous solutions of sulfuric acid and sodium hydroxide (≥ 95 wt. % purity) were used.

2.2 Methods

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Method of Hydrolysis of Technical Vegetable Oil

Technical vegetable oil - a by-product of "Shedevr" sunflower oil production represents a viscous liquid with a dark brown color. 50 g of technical vegetable oil and 120 ml of a 15 wt. % NaOH solution were placed in a three-neck flask and, with continuous stirring, the mixture was heated in a water bath at a temperature of 60°C for 1 hour. Then the temperature was raised to 85°C, and an excess of 160 ml 15 wt. % H₂SO₄ solution was added. After that, the mixture was stirred for another hour. The formation of acids during hydrolysis was monitored by measuring the "acid number" of the mixture using the potentiometric titration method (Fig. 1).

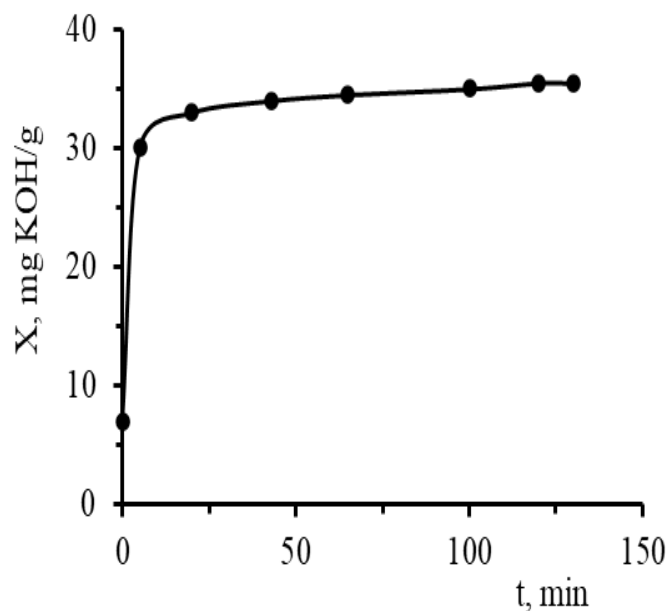


Fig. 1: Change in the acid number of the mixture during the hydrolysis process of technical vegetable oil over time.

The acid number of the oil (X , mg KOH/g) was calculated using Eq. (1)^[44]:

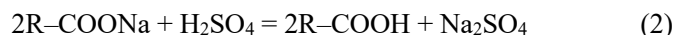
$$X = (5.611 \times V) / m \quad (1)$$

where 5.611 is the mass of KOH in 1 cm³ of a solution with a molar concentration of $c(\text{KOH}) = 0.1 \text{ mol/dm}^3$, mg, V is the volume of a KOH solution with a molar concentration of $c(\text{KOH}) = 0.1 \text{ mol/dm}^3$, spent on titration, cm³, m is the mass of the sample, g.

As a result of the hydrolysis reaction sodium salts of fatty carboxylic acids and glycerol are formed. The upper organic layer was separated using a separator funnel and washed several times with distilled water at a temperature of 50°C to remove glycerol and other impurities. Then the organic phase was dried in a vacuum drying oven for 5 hours. The yield of the fatty carboxylic acid mixture was 88 wt.%. Acid number is equal to 35 (Fig. 1). When hydrolysis was carried out at a temperature of 50°C, the yield of the organic phase was 85 wt.%. Therefore, further hydrolysis was performed at a temperature of 60°C.

Method of Extraction of Fatty Carboxylic Acids from the Hydrolysis Product.

To separate the fatty carboxylic acids formed during the hydrolysis of technical vegetable oil, the sodium salts of carboxylic acids must be converted into their acidic form. Therefore, a 15 wt. % excess solution of H₂SO₄ was added to the product formed during the hydrolysis process, the temperature was raised to 80–90°C, and the mixture was continuously stirred for 1 hour. During this reaction, the sodium salts of fatty carboxylic acids react with the acid and are converted into fatty carboxylic acids Eq. (2):



Due to the presence of long hydrocarbon radicals (C₁₂–C₁₇), the fatty carboxylic acids are poorly soluble in water. Therefore, they form a separate organic phase (they are extracted into the organic medium). The water-soluble components - glycerol and sodium sulfate formed during the hydrolysis process transition into the aqueous phase. As a result, two layers are formed: an organic (oil) layer and an aqueous layer. The oil layer was separated using a separator funnel and washed several times under continuous stirring with distilled water at a temperature of 50–60°C to remove residual glycerol and sodium sulfate. Then the mixture of isolated fatty carboxylic acids was dried in a vacuum drying oven for 5 hours. The product was a viscous liquid of dark brown color.

Thus, the optimal conditions for the extraction of fatty carboxylic acids from the hydrolysis product of technical vegetable oil by the extraction method are as follows: a temperature of 80–90°C, a process duration of 1 hour, and, at the final stage, the fatty acid mixture should be washed several times with bidistilled water at a temperature of 50–60°C. The entire process should be carried out under continuous stirring of the mixture.

The IR spectrum of the fatty carboxylic acid mixture was recorded using a Nicolet 5700 FTIR spectrometer (Thermo Corporation, USA) in the frequency range of 4000–500 cm^{−1}, while the IR spectra of the synthesized surfactants and other related compounds were obtained using a BRUKER ALPHA FTIR spectrometer.

¹H and ¹³C NMR spectra were obtained on a JNM-ECA Jeol 400 NMR spectrometer operating at 399.78 MHz and 100.53 MHz, respectively, using CDCl₃ as the solvent. Chemical shifts were referenced to the residual proton and carbon signals of deuterated chloroform.

Gas chromatography–mass spectrometry (GC–MS) analysis of the mixture was performed using an Agilent 7890B gas chromatograph equipped with an Agilent 5977B quadrupole mass-selective detector (ionization energy: 70 eV; ion source temperature: 230 °C; quadrupole temperature: 150 °C), following the procedure described in.^[45,46] Separation was carried out on a HP-5ms UI capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Agilent, USA). Helium was used as the carrier gas at a flow rate of 1 mL/min. Sample

introduction was performed in split mode (1:20). The oven temperature program was as follows: isothermal at 80 °C for 2 minutes, then ramped to 280 °C at a rate of 5 °C/min. The injector temperature was set at 280 °C; injection volume was 1 µL. The detector interface temperature was maintained at 280 °C. The mass scan range was 30–550 m/z.

The software used for processing the chromatographic–mass spectrometric data included MassHunter Qualitative Analysis (Version B.06.00, Agilent Technologies), NIST MS Search 2.0, and the NIST11 mass spectral library (release date: May 19, 2011).^[45]

The surface tension (σ) of aqueous surfactant solutions at the air/water interface was measured at room temperature using the Wilhelmy plate method with a SZFL-A1 tensiometer (model A1 series).^[47] The measurement accuracy was ± 0.1 mN/m. In this method, a platinum plate is gradually lowered into the surfactant solution until it makes contact with the surface. Upon contact, the force required to detach the plate from the surface is measured. Based on the measured detachment force, surface tension is calculated using Eq. (3):

$$\sigma = F / (L \cdot \cos \theta), \quad (3)$$

where: σ is the surface tension of the solution (mN/m), F is the detachment force (mN), L is the perimeter of the wetted portion of the plate ($L = 2 \cdot l$, where l is the width of the lower edge of the plate), in meters.

Due to the roughness of the platinum plate surface, complete wetting occurs ($\theta = 0$), and therefore $\cos \theta = 1$. Surface tension for each solution was measured five times, and the arithmetic mean value of σ was reported.

To evaluate the surface activity of the synthesized surfactants, the following parameters were determined:

1. Surface pressure at the critical micelle concentration (π_{CMC}) was calculated as the difference between the surface tension of pure water (σ_0) and that of the surfactant solution at the CMC (σ_{CMC}) Eq. (4):^[48,49]

$$\pi_{\text{CMC}} = \sigma_0 - \sigma_{\text{CMC}} \quad (4)$$

2. Maximum surface excess concentration (Γ_{max}) at the air/water interface was determined from the surface tension isotherm $\sigma = f(\ln C)$, using the Gibbs adsorption Eq. (5):^[50,51,52]

$$\Gamma_{\text{max}} = -a / R \times T \times n, \quad (5)$$

where a is the slope of the linear portion of the σ vs. $\ln C$ plot below the CMC (*i.e.*, $a = (d\sigma/d\ln C)$, R is the universal gas constant (8.314 J/(mol×K)), T is the absolute temperature (K) and n is the number of species adsorbed at the interface. For nonionic surfactants, $n = 1$.

3. Minimum area per molecule (A_{min}) in the saturated adsorption layer was calculated according to the following Eq. (6):^[51,52]

$$A_{\text{min}} = 10^{18} / N_A \times \Gamma_{\text{max}}, \quad (6)$$

where N_a is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$).

4. pC_{20} , an empirical parameter characterizing the efficiency of surface tension reduction, was calculated using Eq. (7):^[53]

$$pC_{20} = -\log(C_{20}), \quad (7)$$

where C_{20} is the surfactant concentration at which the surface tension of water is reduced by 20 mN/m.

The zeta potential (ζ) and hydrodynamic diameter (D) of colloidal particles in aqueous surfactant solutions at the CMC were determined using a Zetasizer Advance Series ZSU3200-Pro (Blue Label, Malvern Panalytical).

Foaming ability of surfactant solutions was evaluated according to the procedure described in.^[54] Aqueous solutions of surfactants at specified concentrations were prepared, and 20–50 mL of each solution was transferred into a graduated cylinder with a ground-glass stopper. The cylinder was shaken vigorously for 20 seconds. Immediately after shaking, the initial foam height was recorded. Foam height was then remeasured at specified time intervals (*e.g.*, 1, 2, 5, and 10 minutes) to assess foam stability. Foam stability (β) was calculated using Eq. (8):

$$\beta = (H_\tau / H_0) \times 100\%, \quad (8)$$

where H_0 is the initial foam height (cm) and H_τ is the foam height at time τ .

Foam was considered unstable (low stability) if more than 50% of the initial foam volume collapsed within 1–2 minutes. If more than 70% of the foam remained after 5 minutes, the foam was classified as stable.

The influence of surfactants on the stability of an emulsion of industrial oil (I-20A) in water was evaluated in accordance with the procedure outlined in.^[55] Equal volumes (25 mL each) of surfactant solution (at a given concentration) and industrial oil were mixed in a graduated cylinder. The mixture was then subjected to ultrasonic dispersion using a probe-type ultrasonic disintegrator (Scientz JY92-IIDN, Horn 2, program 1, power 50%, T-on 2.0 s, T-off 2.0 s.) for 3–5 minutes at room temperature.

After sonication, phase separation of the emulsion was monitored at 1, 24, 48, and 72 hours under ambient conditions. Emulsion stability (Z) was assessed by measuring the volume of oil separated from the emulsion according to Eq. (9):

$$Z = (V_0 - V_\tau) \times 100\% / V_0, \quad (9)$$

where V_0 is the total volume of oil (25 mL) added to the aqueous surfactant solution, and V_τ is the volume of oil separated from the emulsion at time τ . Ultrasonic dispersion was used to generate fine and more stable emulsions compared to conventional mechanical stirring.

3. Results and discussion

3.1 Analysis of the IR Spectrum of the Fatty Carboxylic Acid Mixture

Fig. 2 presents the IR spectrum of the mixture obtained during the extraction of fatty carboxylic acids from the—

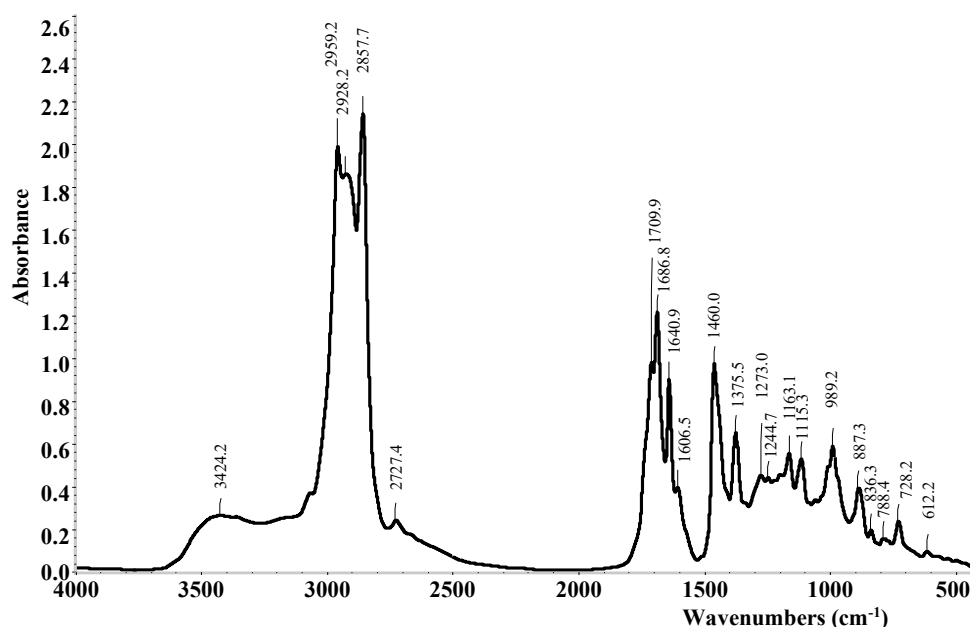


Fig. 2: IR spectrum of the extract obtained from the hydrolysis product of technical vegetable oil

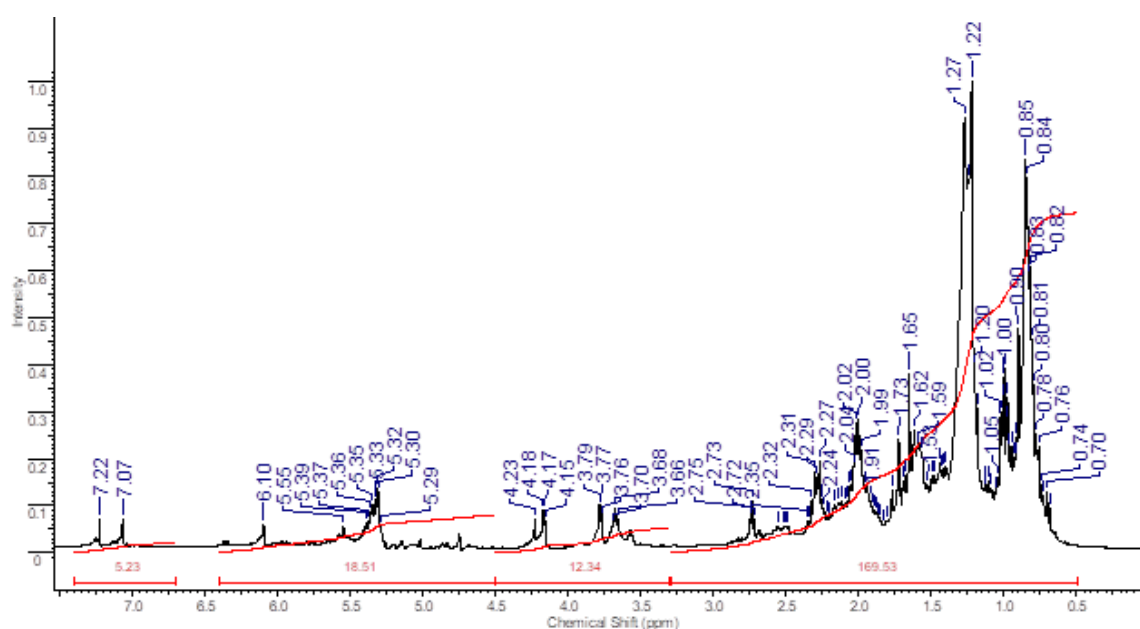


Fig. 3: ^1H NMR spectrum model of the mixture obtained during extraction from the hydrolysis product of technical vegetable oil.

hydrolysis product of technical vegetable oil.

The IR spectrum shows an absorption band at 1709 cm^{-1} , corresponding to the carboxyl group $-\text{CH}_2-\text{CH}_2-\text{COOH}$ of saturated carboxylic acids. An additional band appears at 1686 cm^{-1} , which corresponds to the carboxyl group $-\text{CH}=\text{CH}-\text{R}-\text{COOH}$ of unsaturated carboxylic acids. A band at 3424 cm^{-1} is characteristic of free hydroxyl groups, while bands in the range of $2857\text{--}2959\text{ cm}^{-1}$ are typical of bonded hydroxyl groups.^[56,57] Absorption bands in the range of $1244\text{--}1273\text{ cm}^{-1}$ correspond to the C-O group, and a band at 1686 cm^{-1} is associated with carboxylic acids linked by hydrogen bonds. Adsorption bands expected at $1200\text{--}1170$

cm^{-1} , which are characteristic of the $-\text{C}-\text{O}-\text{C}-$ bond in carboxylic acid esters, are either absent or exhibit very low intensity in the spectrum. Therefore, based on the IR spectrum, it can be concluded that the organic phase formed during the hydrolysis of technical vegetable oil consists predominantly of a mixture of saturated and unsaturated fatty carboxylic acids (FCA).

3.2 Analysis of the NMR Spectra of the Fatty Carboxylic Acid Mixture in CDCl_3 Solvent.

The ^1H NMR spectrum of the mixture obtained during the extraction from the hydrolysis products of technical vegetable oil is characterized by the presence of proton signals from

various structural fragments throughout the entire spectral range (Fig. 3). In the region of 0.50–3.30 ppm, signals range correspond to protons located adjacent to oxygen atoms or other electronegative functional groups. Their integral proton intensity is 12.36H. The proton signals of fatty acids observed in the range of 4.50–6.40 ppm are attributed to unsaturated fragments of carboxylic acids, with an integral proton intensity of 18.51H. The remaining signals in the range of 6.70–7.40 ppm indicate the presence of aromatic protons in the composition of the fatty acids, with an integral proton intensity of 5.23H. Based on the results presented above, it can be assumed that in the mixture obtained after extraction from the hydrolysis product of technical vegetable oil, the content of unsaturated hydrogen atoms is approximately 9.00%, while the content of aromatic protons does not exceed 2.54%.

In the ^{13}C NMR spectrum of the extract obtained from the hydrolysis product, the signals of carbon atoms from methyl and methylene groups appear in the region of 10.00–49.32 ppm (Fig. 4). Signals of carbon atoms adjacent to oxygen atoms and other electronegative atoms are located further downfield than the methyl and methylene groups, appearing in the range of 49.32–73.00 ppm. The integral carbon intensity of these nuclei is 291.34. A minor group of signals observed in the region of 110.00–160.00 ppm corresponds to the carbon atoms of unsaturated groups, with an integral intensity of 21.87. The presence of a carboxyl group in the mixture is confirmed by the appearance of a signal at 174.2 ppm in the carbon NMR spectrum, with an integral intensity of 0.59.

Based on the results obtained above, the average molecular mass of the fatty carboxylic acid mixture can be determined. It is approximately equivalent to 532 carbon atoms in the fatty acid fragment per one carboxyl group. This of fatty carboxylic acids are observed.^[57] This is the most abundant group of fragments in the mixture, with an integral indicates that the

corresponding to the protons of methyl and methylene groups proton intensity of 169.53H. Signals in the 3.30–4.50 ppm molecules of fatty carboxylic acids in the mixture exist in the form of dimers and trimers.

The structure of the fatty carboxylic acid mixture was also confirmed by two-dimensional NMR spectroscopy methods, including COSY (^1H – ^1H), HMQC (^1H – ^{13}C), and HMBC (^1H – ^{13}C), which allow for the identification of homo- and heteronuclear spin-spin couplings. The observed COSY (^1H – ^1H), HMQC (^1H – ^{13}C), and HMBC (^1H – ^{13}C) NMR correlations in the fatty carboxylic acid mixture are presented in Fig. 5–7 and support the aforementioned conclusions.

Analysis of the Chromatography –Mass Spectrometry Results of the Extract Obtained from the Hydrolysis Product of Technical Vegetable Oil

In order to determine the composition of the mixture obtained after the hydrolysis of technical vegetable oil and the extraction of fatty carboxylic acids, a chromatography–mass spectrometry analysis of the mixture was conducted. For this purpose, the fatty carboxylic acids in the mixture were preliminarily converted into methyl esters by means of an esterification reaction. The results of the chromatography–mass spectrometry analysis are presented in Fig. 8 and Table 1 and 2.

According to the fragmentation mechanism of fatty carboxylic acids resulting from electron ionization (EI) of the analyzed compounds, base peaks characteristic of the studied fatty acids were identified.^[45,46] The identification of components in the reaction mixture, represented as peaks on the chromatogram, was carried out based on the analysis of the mass spectra of each compound. Through detailed examination of the mass spectra and according to the fragmentation mechanism under electron ionization, the composition of the methyl esters of fatty carboxylic acids

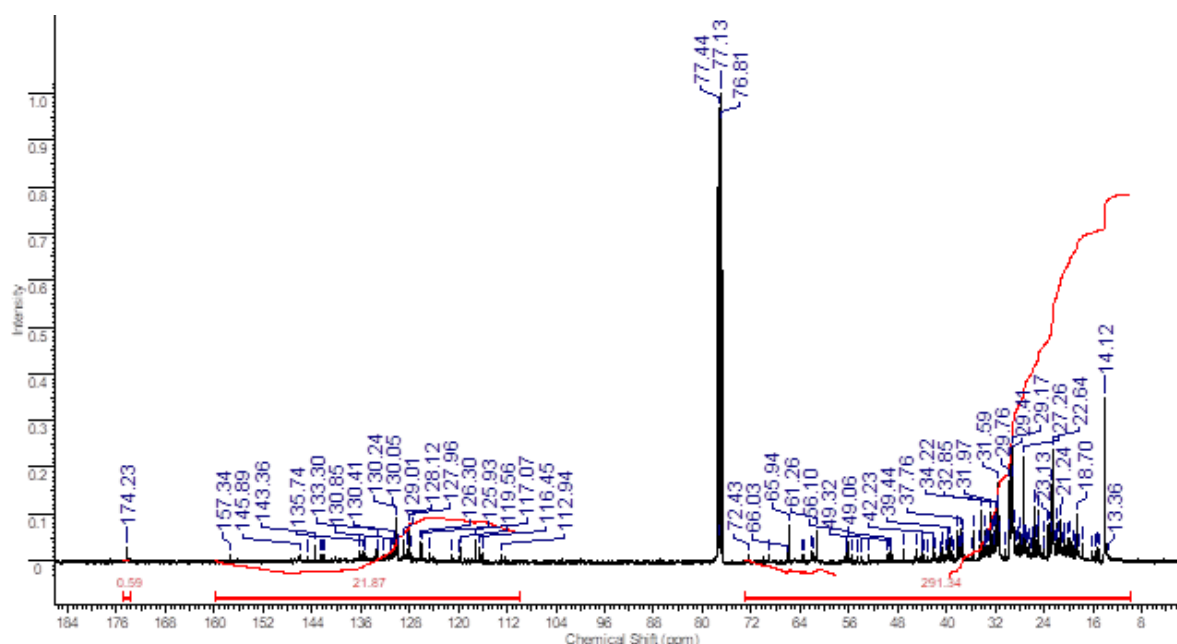


Fig. 4: ^{13}C NMR spectrum model of the mixture obtained during extraction from the hydrolysis product of technical vegetable oil.

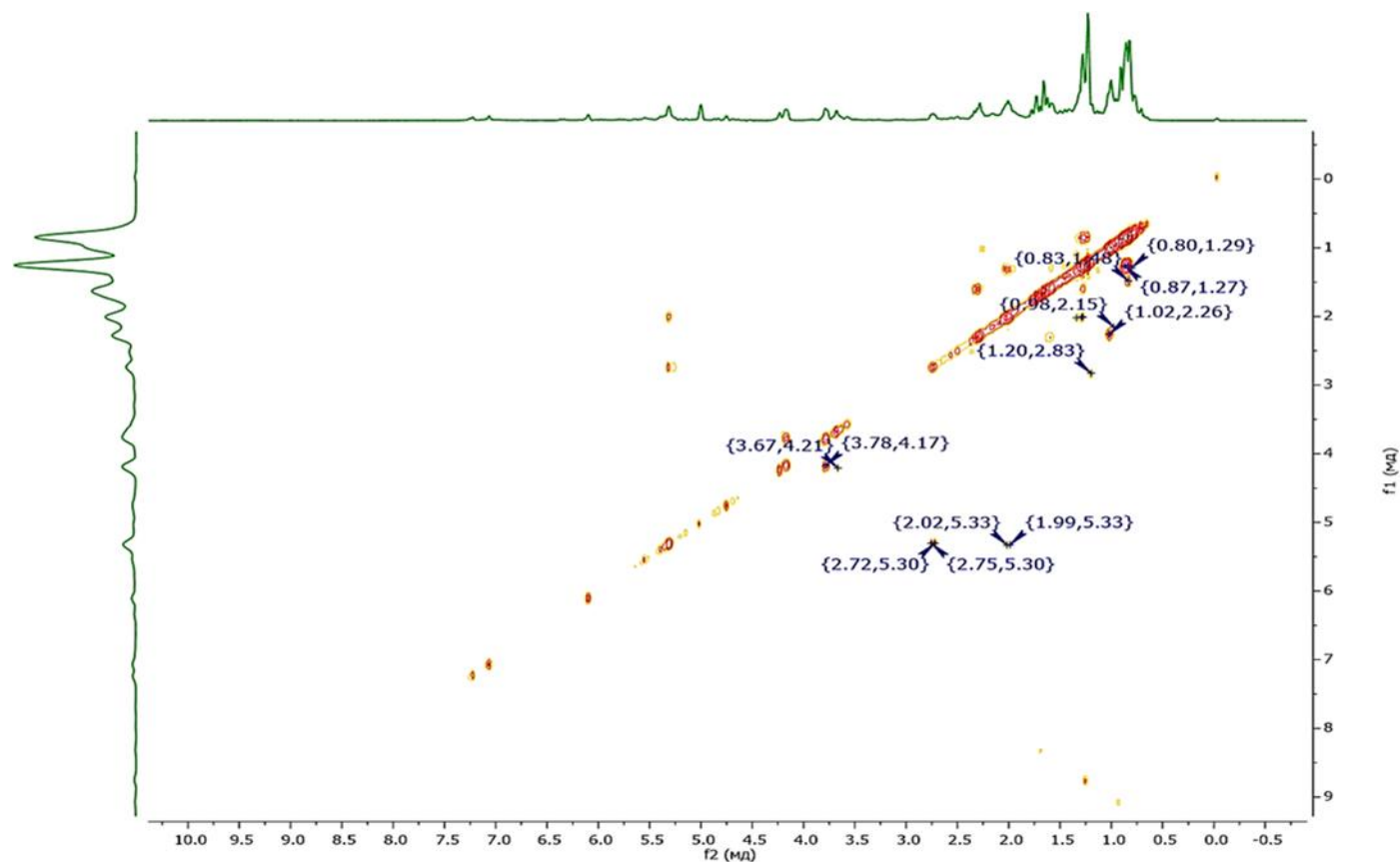


Fig. 5: COSY (^1H - ^1H) spectrum model of the mixture obtained during extraction from the hydrolysis product of technical vegetable oil.

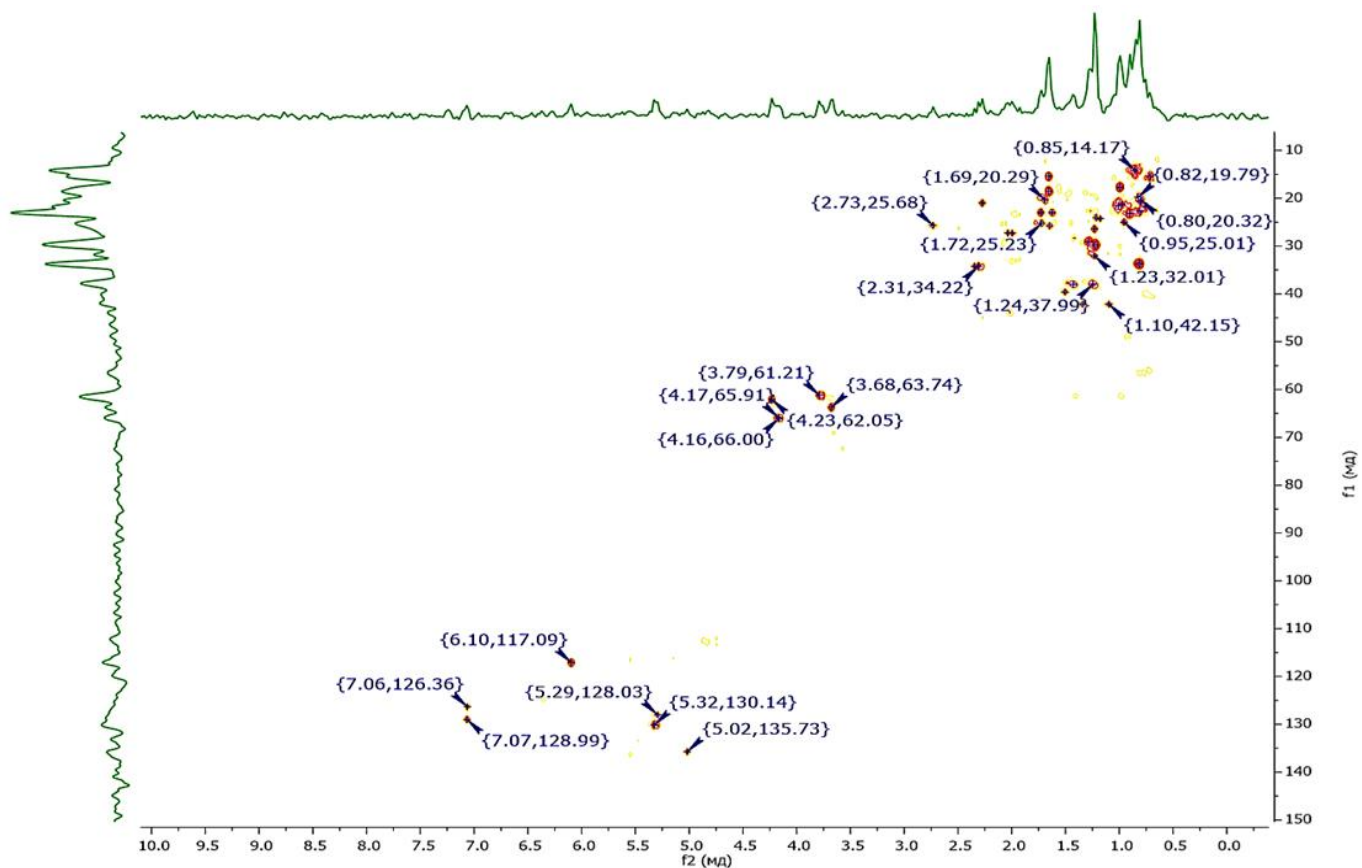


Fig. 6: HMQC (^1H - ^{13}C) spectrum model of the mixture obtained during extraction from the hydrolysis product of technical vegetable oil.

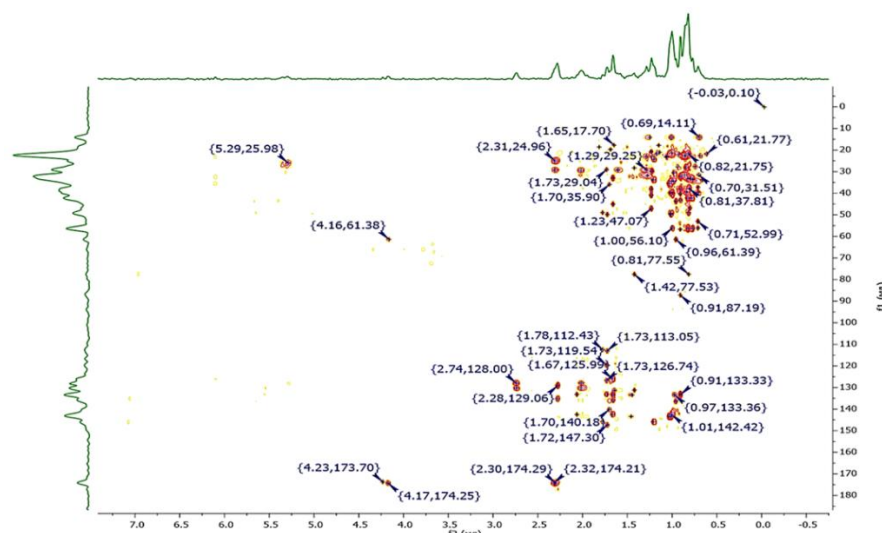


Fig. 7: HMBC (^1H – ^{13}C) spectrum model of the mixture obtained during extraction from the hydrolysis product of technical vegetable oil.

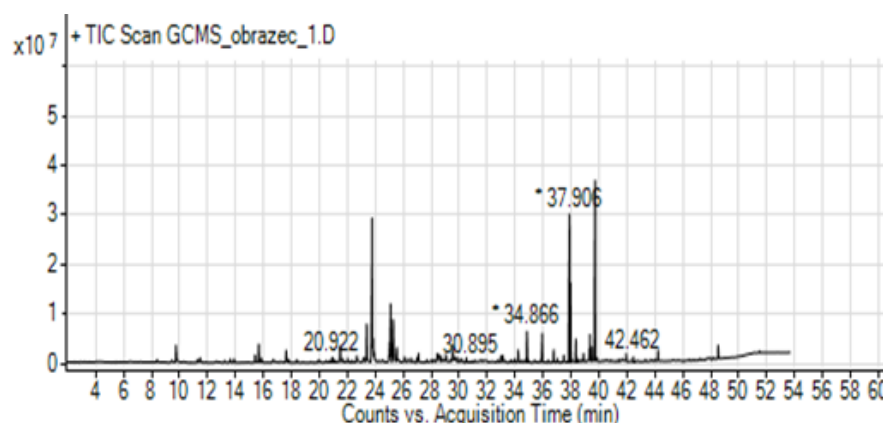


Fig. 8: Chromatogram of the extract (methyl esters of fatty carboxylic acids) obtained from the hydrolysis product of technical vegetable oil.

(FCA) was determined and presented in Table 2. The results of the chromatography–mass spectrometry analysis are expressed as the percentage content of individual methyl esters of fatty acids. The analysis was performed using a flame ionization detector (FID), which allows the peak areas to be interpreted as relative mass fractions.

As shown in Table 2, the mixture of fatty carboxylic acids consists of 9 types of saturated and unsaturated acids, with the highest mass fractions corresponding to 9,12-octadecadienoic acid (linoleic acid) and 9-octadecenoic acid (oleic acid). In addition to fatty carboxylic acids, other cycloaliphatic and unsaturated cyclic organic compounds were also detected, including: 2,6,6-trimethylbicyclo [3.1.1] hept-2-ene, bicyclo [3.1.0] hexane, 4-methylene-1-(1-methylethyl)-, and 2-(1R,4R)-4-hydroxy-4-methylcyclohex-2-enyl) propan-2-yl acetate.

3.3 Synthesis of Nonionic Surfactants

For the synthesis of nonionic surfactants (NIS) from the mixture obtained after extraction from the hydrolysis product of technical vegetable oil, monoethanolamine (MEA) and

diethanolamine (DEA) were selected as hydrophilic reagents. The primary reason for selecting these reagents is the ability to vary the molar ratio of hydrophilic fragments (ethylenoxy units and terminal hydroxyl groups) in the structure of the resulting fatty carboxylic acid (FCA) amides. By adjusting the number of ethylene oxide and hydroxyl groups, it is possible to modify the hydrophilic–lipophilic balance (HLB) of the resulting NIS molecules. As a general trend, increasing the number of hydrophilic fragments in NIS enhances the water solubility of the FCAs and increases the HLB value of the resulting surfactants. Therefore, by altering the HLB of the molecules, it is possible to synthesize surfactants with specific practical applications (e.g., detergents, emulsifiers, demulsifiers, flotation agents, wetting agents, foaming agents, etc.).

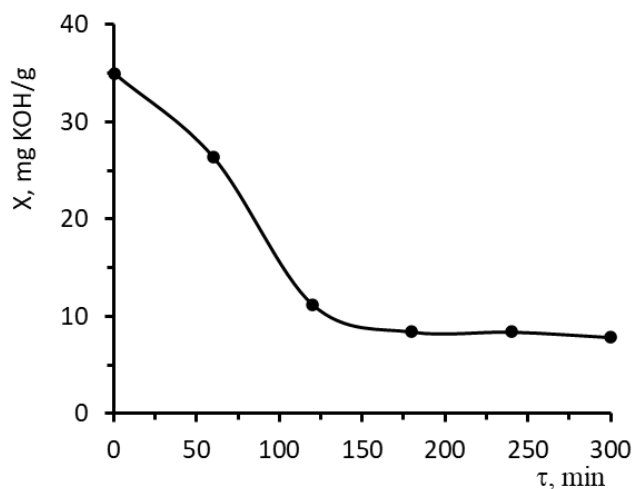
Synthesis of a Nonionic Surfactant from the Mixture Obtained After Extraction from the Hydrolysis Product of Technical Vegetable Oil (Fatty Carboxylic Acids, FCA) and Monoethanolamine (MEA) The reaction was carried out in a three-neck flask equipped with a magnetic stirrer, a thermometer, and a Dean–Stark trap, which was necessary for

Table 1: User Chromatogram Peak List.

RT	Height	Height %	Area	Area %	Area Sum %	Symmetry	Width
20.741	277218.32	0.93	2447951.6	2.49	1.34	1	0.25
20.922	1000995.5	3.35	3100876.84	3.16	1.7	0.63	0.095
21.12	348225.12	1.16	1918437.48	1.95	1.05	2.33	0.146
30.895	318313.78	1.06	2614859.57	2.66	1.43	0.6	0.258
34.866	6338783.5	21.18	20394066.08	20.75	11.18	1.4	0.129
37.906	29921448.68	100	98282399.33	100	53.88	0.46	0.129
37.992	16050644.47	53.64	37760134.75	38.42	20.7	0.77	0.103
38.363	4725054.69	15.79	13149403.69	13.38	7.21	3.02	0.155
42.462	978826.63	3.27	2741811.75	2.79	1.5	3.6	0.189

Table 2: Content of Methyl Esters of Fatty Carboxylic Acids.

Compound Label	RT	Name	Area Sum, %
Cpd 1: 2-Decenoic acid, methyl ester	20.741	2-Decenoic acid, methyl ester	1.34
Cpd 2: 4-Decenoic acid, methyl ester	20.922	4-Decenoic acid, methyl ester	1.7
Cpd 3: Decanoic acid, methyl ester	21.12	Decanoic acid, methyl ester	1.05
Cpd 4: Oxiraneundecanoic acid, 3-pentyl-, methyl ester, cis-	30.895	Oxiraneundecanoic acid, 3-pentyl-, methyl ester, cis-	1.43
Cpd 5: Hexadecanoic acid, methyl ester	34.866	Hexadecanoic acid, methyl ester	11.18
Cpd 6: 9,12-Octadecadienoic acid (Z,Z)-, methyl ester	37.906	9,12-Octa-decadienoic acid (Z,Z)-, methyl ester	53.88
Cpd 7: 9-Octadecenoic acid (Z)-, methyl ester	37.992	9-Octadecenoic acid (Z)-, methyl ester	20.7
Cpd 8: Methyl stearate	38.363	Methyl stearate	7.21
Cpd 9: Docosanoic acid, methyl ester	42.462	Docosanoic acid, methyl ester	1.5

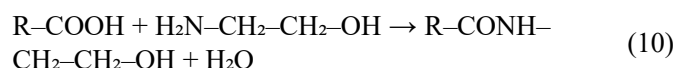


Molar ratio FCA:MEA = 1:1.2.

Fig. 9: Change in the acid number of the mixture during thereaction of fatty carboxylic acids (FCA) with monoethanolamine (MEA).

removing water from the reaction medium. Into the flask, 0.45 mol of monoethanolamine (MEA) and a catalyst - *p*-toluenesulfonic acid (1% of the total mass) were introduced. After mixing the catalyst with MEA, the required amount of fatty carboxylic acids was added. The molar ratio of FCA to MEA in the reaction medium was 1:1.2. The amidation reaction was conducted in an air-heated bath at a temperature of 150–160°C for 2 hours under continuous stirring. During the reaction, monoethanolamide of fatty carboxylic acids (FCA–MEA) was formed:

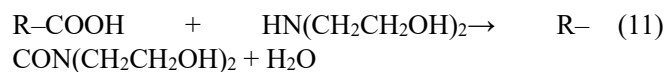
The reaction was continued until the acid number of the Eq. (10):



mixture reached a constant value. The amount of monoethanolamides formed during the reaction (reaction yield) was calculated based on the volume of water collected in the Dean–Stark trap and the acid number of the mixture (Fig. 9). At the end of the reaction, the reaction mass was dried in a vacuum oven at 50°C until constant weight was achieved. The reaction yield, based on the acid number, was 92%. The resulting product was a viscous liquid with a dark brown color.

Synthesis of a Nonionic Surfactant from the Mixture Obtained After Extraction from the Hydrolysis Product of Technical Vegetable Oil (Fatty Carboxylic Acids, FCA) and Diethanolamine (DEA)

The reaction was carried out in a three-neck flask equipped with a magnetic stirrer, a thermometer, and a Dean–Stark trap for the removal of water from the reaction medium. Into the flask, 0.45 mol of diethanolamine (DEA) and a catalyst - *p*-toluenesulfonic acid (1% of the total mass) were introduced. After mixing the catalyst with DEA, the required amount of fatty carboxylic acids was added. The molar ratio of FCA to DEA in the reaction medium was 1:1.2. The amidation reaction was conducted in an air-heated bath at a temperature of 150–170°C for 2 hours under continuous stirring. During the reaction, diethanolamides of fatty carboxylic acids were formed according to the following Eq. (11):



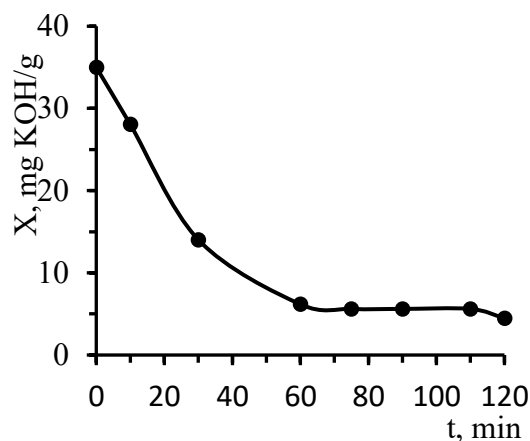
The reaction was carried out until the acid number of the mixture reached a constant value. The amount of diethanolamides formed during the reaction (reaction yield) was calculated based on the volume of water collected in the Dean–Stark trap and the acid number of the mixture (Fig. 10). At the end of the reaction, the reaction mass was dried in a vacuum oven at 50°C until constant weight was achieved. The reaction yield, based on the acid number, was 95%. The resulting product was a viscous liquid with a dark brown color.

3.4 Analysis of the FTIR spectra of the nonionic surfactants

FTIR Analysis of the Nonionic Surfactant Synthesized from the Mixture of Fatty Carboxylic Acids (FCA) and

Monoethanolamine (MEA).

In the FTIR spectrum of MEA (Fig. 11a), a broad absorption band is observed in the region of 3200–3400 cm⁻¹, corresponding to the stretching vibrations of –OH and –NH₂ groups. In the region of 1075–1036 cm⁻¹, bands are detected corresponding to the vibrations of C–O and C–N bonds. The absence of pronounced bands in the region of 2850–2950 cm⁻¹ indicates the absence of long aliphatic chains.^[56]



Molar ratio FCA:DEA = 1:1.2.

Fig. 10: Change in the acid number of the mixture during the reaction of fatty carboxylic acids (FCA) with diethanolamine (DEA).

In the FTIR spectrum of the surfactant (Fig. 11b) synthesized from the FCA–MEA mixture, intense bands are observed at 2922 and 2853 cm⁻¹, corresponding to the symmetric and asymmetric stretching vibrations of methylene groups (–CH₂–), indicating the presence of long-chain aliphatic fragments of fatty acids in the structure of the surfactant. The band at 1646 cm⁻¹ may indicate the presence of C=O groups typical of amides. The band at 1505 cm⁻¹ corresponds to the deformation vibrations of the N–H bond in secondary amides, confirming the formation of an amide bond between the amino group of MEA and the carboxyl group of the fatty acids. The reduced intensity of the broad band in the region of 3200–3400 cm⁻¹ compared to pure MEA is attributed to the partial consumption of amino groups in amide formation. The band in the region of 1067 cm⁻¹, corresponding to C–O and C–N bond vibrations, remains in the surfactant spectrum, indicating the presence of a hydroxyl group that did not participate in the reaction. The band at 723 cm⁻¹ is characteristic of the rocking vibrations of long alkyl chains –(CH₂)_n–.^[56]

Thus, the FTIR spectroscopy results unequivocally confirm the successful progress of the amidation reaction, resulting in the formation of an amphiphilic surfactant molecule containing both hydrophilic (–OH, –NH–) and hydrophobic (aliphatic) parts. The bands at 2934 and 2834 cm⁻¹ are attributed to the C–H stretching vibrations in –CH₂– groups. The band at 1451 cm⁻¹ is associated with C–H deformation vibrations. Intense bands are observed in the region of 1120–1040 cm⁻¹, corresponding to C–N and C–O (alcohol) vibrations. The band at 681 cm⁻¹ may indicate rocking motions of CH groups.^[57]

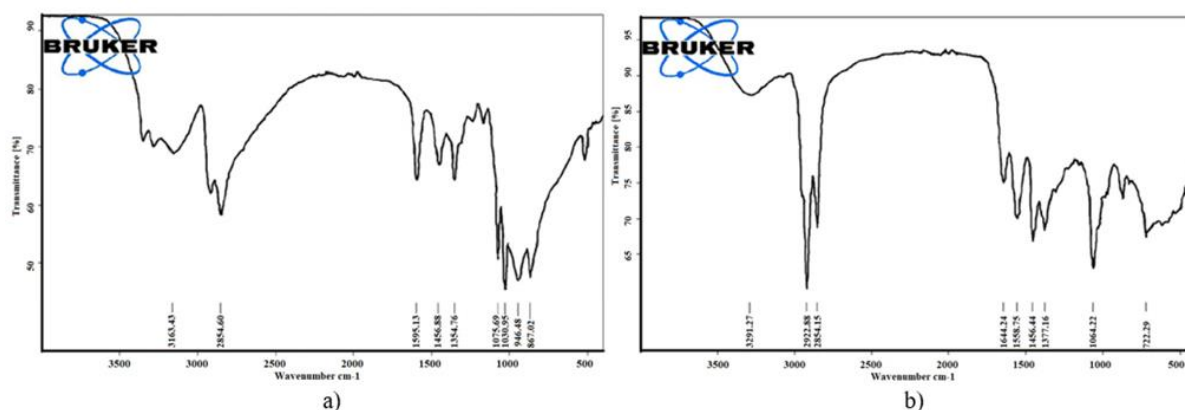


Fig. 11: FTIR spectra of MEA (a) and FCA-MEA surfactant (b).

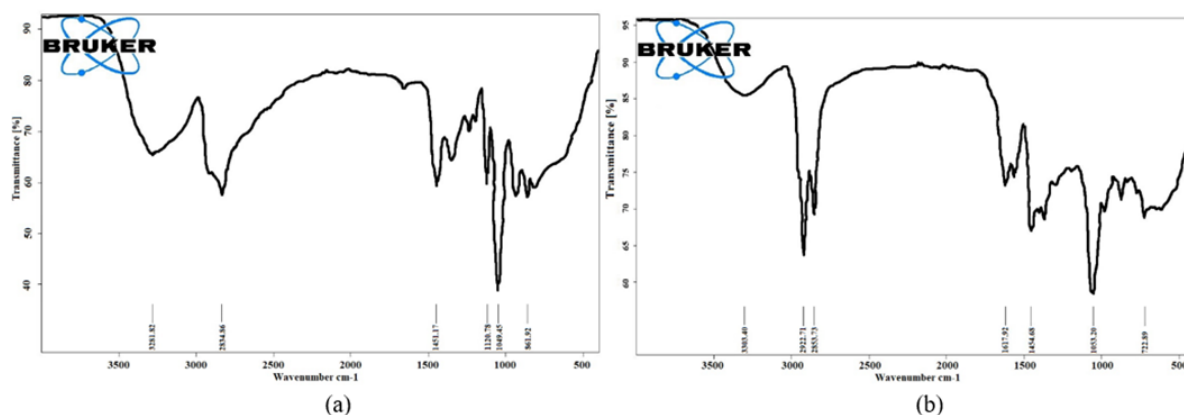


Fig. 12: FTIR spectra of DEA (a) and FCA-DEA surfactant (b).

In the spectrum of the FCA-DEA surfactant (Fig. 12b), the broad band at 3303 cm^{-1} is retained, indicating the presence of -OH groups, though changes in shape and intensity are observed, which are associated with the involvement of hydroxyl groups in amide formation.

The C-H stretching vibrations are shifted and appear at 2922 and 2853 cm^{-1} , which are typical of long-chain alkyl radicals of fatty acids. A new band at 1617 cm^{-1} may indicate the presence of C=O groups characteristic of amides. The band at 1454 cm^{-1} is retained but may be a combination of CH_2 deformation and C-N vibrations. Significant changes are observed in the region of 1053 cm^{-1} , possibly due to C-N vibrations. The band at 722 cm^{-1} is characteristic of the rocking vibrations of long alkyl chains – $(\text{CH}_2)_n$.^[57]

Therefore, the comparative analysis of the FTIR spectra indicates that the interaction between DEA and the components of the FCA mixture led to the formation of new chemical bonds, primarily amide bonds (C=O , C-N). This serves as confirmation of the successful synthesis of the FCA-DEA surfactant.

FTIR Analysis of the Nonionic Surfactant Synthesized from the Mixture of Fatty Carboxylic Acids (FCA) and Diethanolamine (DEA).

In the FTIR spectrum of DEA (Fig. 12a), a broad band is observed at 3297 cm^{-1} , corresponding to the stretching vibrations of -OH and -NH groups.

3.5 Surface activity of surfactants based on fca and ethanolamines at the water/air interface

To determine the surface activity, the surface tension of aqueous solutions of the synthesized nonionic surfactants was measured, and surface tension isotherms of the solutions were plotted (Fig. 13). From the surface tension isotherms, the critical micelle concentration (CMC) and the surface tension at the CMC (σ_{CMC}) were determined. The calculation results are presented in Table 3 and 4. According to these data, the surface activity (*i.e.*, the ability to reduce the surface tension of water) of the FCA-DEA surfactant is greater than that of the FCA-MEA surfactant.

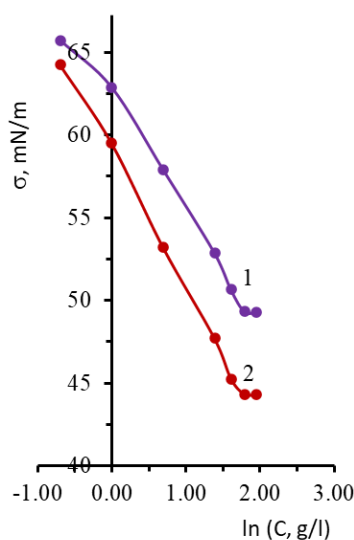
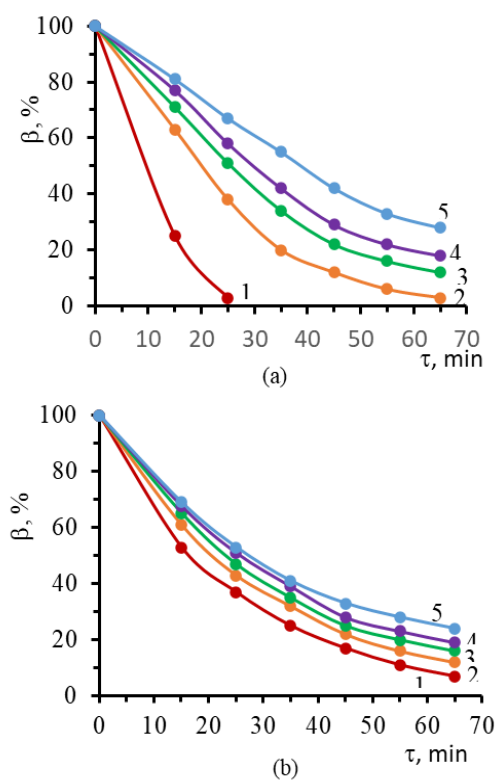
Table 3: Micelle formation parameters, particle size, and zeta potential of colloidal particles in aqueous surfactant solutions. $T = 301.15\text{ K}$. $\sigma(\text{H}_2\text{O}) = 71.5\text{ mN/m}$.

Surfactant	CMC, g/l	σ_{CMC} , mN/m	Π_{CMC} , mN/m	D_{CMC} , nm	ζ_{CMC} , mV
FCA-MEA	6.0	49.3	22.2	332.7	-40.3
FCA-DEA	5.5	44.3	27.2	327.8	-23.2

At the same time, the CMC, negative zeta potential, and colloidal particle diameter of FCA-DEA are lower than those

Table 4: Adsorption Parameters of the Surfactants.

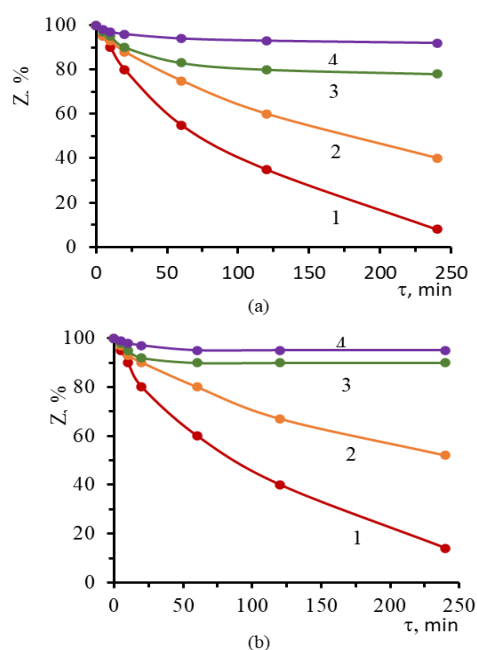
Surfactant	$\Gamma_{\max} \times 10^6$, mol/m ²	$A_{\min}$, nm ²	C_{20} , g/l	pC_{20}	CMC/ C_{20}
FCA-MEA	2.67	0.62	4.57	- 0.66	1.31
FCA-DEA	3.20	0.52	2.46	- 0.39	2.26

**Fig. 13:** Surface tension isotherms of aqueous surfactant solutions. $T = 301.15$ K. Surfactants based on FCA-MEA (1) and FCA-DEA (2).

Surfactant concentration (g/L): 5.0 (1); 10.0 (2); 15.0 (3); 20.0 (4); and 25.0 (5). $T = 298$ K.

Fig. 14: Effect of FCA-MEA (a) and FCA-DEA (b) surfactant concentrations on foam stability.

of the second surfactant. These data indicate that the hydrophobicity of FCA–DEA surfactant molecules is higher than that of FCA–MEA molecules. It should also be noted that the σ_{CMC} values for the synthesized nonionic surfactants are somewhat higher than those of alkyl glycosides, fatty alcohol ethoxylates, sodium soap salts,^[49] sodium oleate, and sodium laurate,^[47] C_{12} -Sulfate,^[34,58,59] $\text{C}_{12-14}(\text{EO})_2$ -Sulfate, $\text{C}_{12}(\text{PO})_{8-12}$ -Sulfate^[34,60] (where EO-ethylene oxide, PO-propylene oxide). But it is close to the σ_{CMC} of $\text{C}_{12}(\text{PO})_4$ -Sulfate^[34,60] and lower than that of sodium hexanoate (at pH 6–10).^[47] Among the synthesized surfactants, FCA–DEA exhibits the highest adsorption and, accordingly, the smallest surface area occupied by a single molecule in the saturated adsorption layer (A_{min}) (Table 4). All these data indicate that FCA–DEA surfactant molecules have a more compact conformation, stabilized by hydrophobic interactions between hydrocarbon radicals and hydrogen bonding between hydroxyl groups, compared to FCA–MEA. In terms of the A_{min} value, the obtained nonionic surfactants are close to the properties of octylphenyl ethers of octaethylene glycol^[61] and C_{12} -Sulfate ($0.53\text{--}0.58\text{ nm}^2$,^[34,58,59] but their A_{min} are smaller than those of $\text{C}_{12-14}(\text{EO})_2$ -Sulfate, $\text{C}_{12}(\text{PO})_{4-12}$ -Sulfate ($1.54\text{--}1.66\text{ nm}^2$).^[34,60]

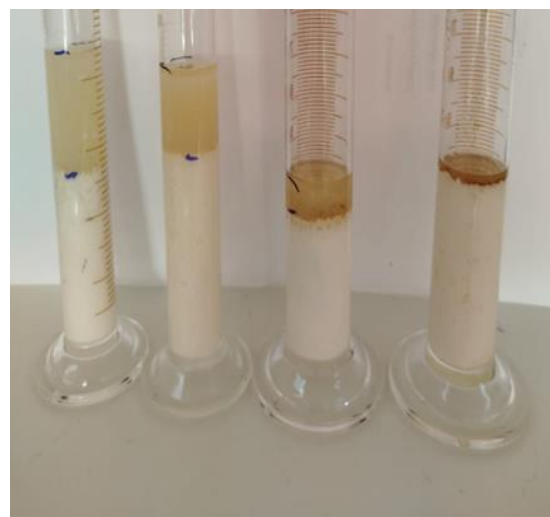


Surfactant concentration (g/L): 0.5 (1), 2.0 (2), 3.0 (3) and 4.0 (4). $T = 298\text{ K}$.

Fig. 15: Influence of surfactant concentration based on FCA–MEA (a) and FCA–DEA (b) on the stability of an industrial oil-in-water emulsion.

According to,^[49,62,63] the parameter Π_{CMC} demonstrates the ability of a surfactant to reduce the surface tension of water, and the CMC/C_{20} parameter is a measure of the tendency of a surfactant to adsorb relative to its tendency to form micelles. The parameters of Π_{CMC} and CMC/C_{20} for FCA–DEA are

higher than those for FCA–MEA. But the parameters of Π_{CMC} and CMC/C_{20} for FCA–DEA and FCA–MEA are much lower than that of alkylpolyglucoside (APG), sodium soap and alkylethoxylated fatty alcohol (AE) ($44.5\text{--}51.2\text{ mN/m}$) [49]. The CMC/C_{20} values of the synthesized nonionic surfactants are close to the value of C_{12} -Sulfate (2.6).^[34]



(a)



(b)

Surfactant concentration (g/L): (a) 0.5 (1), 2.0 (2), 3.0 (3) and 4.0 (4). (b) 0.5 (1), 1.0 (2), 2.0 (3), 3.0 (4) and 4.0 (5). $T = 298\text{ K}$.

Fig. 16: Emulsions in FCA–MEA (a) and FCA–DEA (b) surfactant solutions after 72 hours.

3.6 Foaming in aqueous solutions of surfactants based on fca and ethanolamines

Fig. 14 shows the effect of the concentration of synthesized nonionic surfactant solutions on foam stability. According to,^[54,64] foam is considered stable if more than 70% of it remains after 5 minutes. Based on this criterion, it can be stated that the synthesized nonionic surfactants produce stable foams. Foam stability depends on both the concentration of the solution and the functional composition of the nonionic surfactant. At relatively low concentrations, more stable foams

are formed in solutions of the FCA–DEA surfactant. For example, at a concentration of 5.0 g/L, the foam in FCA–MEA solutions almost completely collapses after 25 minutes (curve 1, Fig. 14a), whereas in FCA–DEA solutions at the same concentration, only 65% of the foam is destroyed over the same period (curve 1, Fig. 14b). Moreover, as the concentration of the surfactant increases, foam stability improves. At a concentration of 25.0 g/L, approximately 25–30% of the foam remains stable after 65 minutes. (Fig. 15b). Notably, these emulsions maintain their stability for up to 72 hours (Fig. 16).

The relatively stable emulsions are ensured by the formation of strong interfacial adsorption layers of the surfactants at the oil/water interface, which possess elastic and cohesive properties.^[66,67] These interfacial layers formed by the nonionic surfactants prevent the coalescence of oil droplets in the emulsion.

Therefore, it can be concluded that the results of the emulsion stability study are in good agreement with the adsorption data obtained for the FCA–Ethanolamine surfactants at the water/air interface. A more stable emulsion is formed in FCA–DEA surfactant solutions, whose molecules exhibit greater surface activity and more effectively reduce the surface tension of water. The obtained nonionic surfactants can be used as an emulsifier and stabilizer for industrial oil emulsions.

4. Conclusion

1. A mixture of fatty carboxylic acids was obtained from technical vegetable oil the waste from sunflower oil production through alkaline hydrolysis at 60°C, subsequent acid treatment at 85°C, and extraction. The optimal conditions for extracting fatty carboxylic acids from the hydrolysis product were determined.
2. The composition of the mixture of fatty carboxylic acids and other compounds was identified using NMR and FTIR spectroscopy and chromatographic-mass spectrometric analysis. It was established that the mixture contains nine types of saturated and unsaturated fatty carboxylic acids.
3. Through esterification of the fatty carboxylic acid mixture with monoethanolamine (MEA) and diethanolamine (DEA), nonionic surfactants were synthesized: monoethanolamide (FCA–MEA) and diethanolamide (FCA–DEA) of fatty carboxylic acids. The reaction yields were 92% and 95%, respectively. The formation of fatty acid amides was confirmed by FTIR and NMR spectroscopy.
4. From surface tension isotherms of aqueous solutions of the synthesized nonionic surfactants ethanolamides of fatty carboxylic acids the critical micelle concentration (CMC), Gibbs adsorption values at the water/air interface, area per molecule in the saturated adsorption layer, and other adsorption parameters were determined. It was found that FCA–DEA exhibits greater surface activity at the water/air interface than FCA–MEA.

5. It was also found that the maximum Gibbs adsorption for FCA–DEA surfactant is greater than that for FCA–MEA surfactant. This indicates a more compact conformation of the FCA–DEA surfactant's molecules, stabilized by intramolecular hydrophobic interactions and hydrogen bonds between hydroxyl groups.

6. Comparison of the zeta potentials of surfactant particles at the CMC showed that the negative charge of FCA–MEA colloidal particles is nearly twice as high as that of FCA–DMEA particles, although the opposite might be expected due to the presence of two hydroxyl groups at the chain end of the FCA–DEA surfactant. This "anomalous" change in zeta potential can be explained by the more compact conformation of FCA–DEA molecules, stabilized by intramolecular hydrophobic interactions and hydrogen bonds between hydroxyl groups, compared to FCA–MEA. Apparently, the compact conformation limits the interaction of FCA–DEA molecules with water, thereby reducing the polarization (dissociation) of terminal hydroxyl groups.

7. The study of foaming behavior in aqueous solutions showed that the synthesized nonionic surfactants form stable foams. Foam stability depends on both the concentration and the functional composition of the surfactants. At relatively low concentrations, more stable foams are formed in FCA–DEA solutions. These foams can be used for dust collection and dust suppression and also for flotation of minerals from raw materials.

8. The study of industrial oil-in-water emulsion stabilization in the presence of FCA–Ethanolamine surfactants showed that relatively stable (95%) emulsions are formed in FCA–DEA solutions at concentrations of 3.0–4.0 g/L. These emulsions maintain their stability for up to 72 hours. These surfactants can be used in industry as environmentally friendly (biodegradable) foaming agents and emulsifiers.

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Conflict of Interest

There are no conflicts to declare.

Supporting Information

Not applicable.

CRedit Statement

K. Zh. Abdiyev and **B. B. Sadykov**: Conceptualization, methodology. **M. B. Zhurumbayeva**: software. **G. K. Kussainova** and **Zhexenbek Toktarbay**: validation. **M. B. Zhurumbayeva**, **N. Zh. Seitkaliyeva** and **Z. N. Kambarova**: formal analysis. **Zhexenbek Toktarbay**: investigation. **G. K. Kussainova**, **M. B. Zhurumbayeva**, **N. Zh. Seitkaliyeva** and **Z. N. Kambarova**: resources. **Z. N. Kambarova**: data curation. **Zhexenbek Toktarbay** and **M. B. Zhurumbayeva**: writing-

original draft preparation. **K. Zh. Abdiyev** and **B. B. Sadykov**: writing-review and editing. **K. Zh. Abdiyev** and **Chien-Hsiang Chang**: visualization. **Zhexenbek Toktarbay** and **Chien-Hsiang Chang**: supervision. **K. Zh. Abdiyev** and **B. B. Sadykov**: project administration. **K. Zh. Abdiyev**: funding acquisition. **K. Zh. Abdiyev**. All authors have read and agreed to the published version of the manuscript.

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