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SYNTHESIS AND STUDY OF AMIDE SOLEIN BASED ON OLEIC ACID AND PIPERIDINE

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Abstract. *The article presents results for the preparation of salts of sulfated amides based on oleic acid and piperidine. The products were synthesized in several steps: the first step of the reaction of oleic acid with piperidine, second step of sulphonation with sulfuric acid of the obtained compounds, the third step of the reaction of NH_4OH and $(HOCH_2CH_2)$ 2NH. The structure of the synthesized salts is confirmed by the methods of IR-, NMR-spectral analyses, and the method of high-performance liquid chromatography. The synthesized salts at room temperature are brown crystals. Some of their physical and chemical indicators have been determined. It is recommended to use synthesized products as oil-purifying and oil-dispersing products.*

Key words: *piperidine, oleic acid amides, active surface, sulfation, high-performance liquid chromatography.*

In recent decades, world practice has shown a tendency to use plant-based raw materials for industrial purposes. This is dictated by the need for careful treatment of hydrocarbon resources, as well as environmental protection requirements [1].

Fatty acids isolated from vegetable oils or fats of animal origin are quite often used in the manufacture of surfactants and film-forming substances for industrial purposes. The structure of the lipid aggregates formed is highly dependent on the nature of the constituent components [2]. Amfifilny differently, define connections often are the superficially active agents (SAA) [3].

[4] provides information on the preparation and study of the properties of salts of sulfated amides based on oleic acid and ethanolamine Natural monocarboxylic acids included in vegetable oils are one of the suitable raw materials for the synthesis of surfactants. The authors investigated anionic surface-active soline based on oleic sulfonic acids [5].

Other authors of [6] have developed a convenient method of synthesis of quaternary salts by the interaction of individual acids (caprylic, pelargonic, palmitic, stearic, oleic) with various amine compounds (diethylamine, triethylamine, morpholine, ethylenediamine) and investigated their surface activity.

[7-8] provides information on the preparation and study of the properties of surfactants synthesized based on triglycerides of certain vegetable oils and amines. The thick oil layer spilled onto the water surface is removed mechanically [9-10]. For the removal of thin-film, distinct types of surfactants are used, which, together with high oil-cleaning and oil-dispersing capacity, must be ecologically and harmless [11-12]. Information on the preparation and study of surfactants on plant oil base triglycerides is found in the literature [13-14]. Reagents based on acid fractions isolated from vegetable oils and diethylenetriamine (DETA) have been synthesized to investigate the oil and dispersing efficacy of this type of environmentally friendly surfactants.

We have developed a convenient method of synthesis of quaternary azole [a] pyridinium salts, which enables us to obtain derivatives with alkyl, aryl, and dietary substituents in the pyridine moiety of the molecule. The scheme for preparing compounds of this type involves two steps: alkylation of 1-R-1,3-diazoles with unsaturated y-Bromo-ketones and further cyclization

of quaternary azolium salts by bases. High yield of azolium salt cyclization products is mainly determined by heterocyclic nature, and for 1-methyl-, 1-ethyl, and 1-benzyl-substituted salts are 60-80% [15-16].

The work developed surfactants based on amidoamine, amides, and esters of long-chain fatty acids [17].

Auto rams have developed and investigated cationic surfactants based on oleic and stearic acids containing a head group of imidazolium and functional groups with two esters, and their ability to self-aggregate and biodegradable has been investigated. These novel surfactants have lower CMC values than conventional cationic surfactants, and the surface properties of these surfactants vary depending on the nature of the hydrophobic tail of the fatty esters. The surfactant-containing the tail of oleyl ether showed a remarkable ability to reduce the surface tension of the aqueous solution [18].

We have also investigated new surfactants and investigated them for their self-aggregation properties and biodegradability in aqueous solution. These fatty acid surfactants were able to self-aggregate into micelles at a lower concentration than conventional surfactants and were found to be readily biodegradable. Superficial properties and speed of biodegradation of these newly renewed surfactant depend by nature hydrophobic tail. The oleic acid surfactant-containing the double bond in the hydrophobic oleyl tail showed a more remarkable ability to reduce the surface tension of the aqueous solution, along with a more excellent biodegradability than the saturated hydrophobic stearyl tail containing stearic acid [19].

As can be seen, the synthesis and study of oleic acid-based surfactant properties with nitrogen-containing compounds are of both scientific and practical interest. In this connection, we present the results of preparing salts of sulfated amides based on oleic acid and piperidine, as well as studying their structure and physical and chemical properties.

The subjects of research are monounsaturated oleic acid and piperidine. To identify optimal synthesis conditions, the influence of temperature, reaction duration, and the ratio of reactive reagents was investigated. The starting reagents were purified according to known procedures [20].

For the synthesis of amides and salts of sulfated amides, piperidine (PiP), oleic acid (OK), and ceric acid in the form of 20% dilute solution of reactive product (98%) "hh" were used. The synthesis reaction of pipe ricinoleic acid and its sulfation was carried out 1:1 by the following procedure: oleic acid and PiP were charged into a three-necked flask with a stirrer and thermometer. The reaction mixture was heated to 98-102 °C. After that, the reaction mixture was slowly heated to 45-50 °C and stirred at this temperature for 3 hours. The next day, 0.2 moles of 20% sulfuric acid was added to the reaction mixture, and stirring was continued at 50 °C for 8-12 hours of idobavilidiethanolamine. Brown crystals form. The obtained salts are recrystallized with an organic solvent. TLC checked purity. TLC analysis was performed on SilufolUV -254 plates in a methanol-benzene (3:1) volume system.

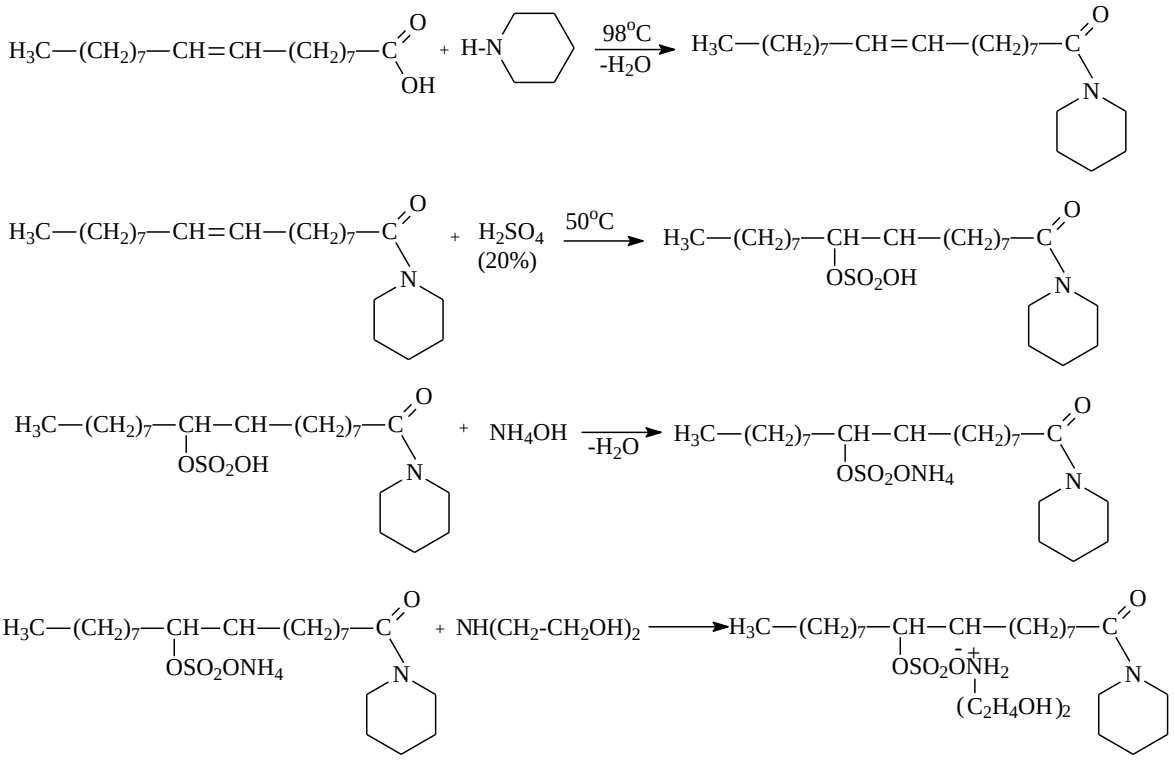
The IR spectra of the samples were recorded on the IR-Fourier spectrophotometer IRRAffinity (Japan). Samples were prepared by pressing of tablets with KBr (spectral range on a scale of wave numbers-4000÷400 of cm^{-1}; Resolution 4 cm^{-1}, sensitivity ratio noise signal - 60,000:1; Scan rate - 20 spectra per second).

Identification of the synthesized compounds was carried out by high-performance liquid chromatography (HPLC) under the exclusion gel permeation chromatography (GPC) mode with

a RI detector and a Multi Chromium GPC computer. Elyuentatsetonitril / water =50/50. The feed rate of 2.00 ml/min.

The 1H and 13C NMR were captured on a Bruker pulse Fourier spectrometer at 300 MHz as the solvent used a dimethyl sulfoxide (DMSO) and CCl_4.

This paper presents results on the synthesis and investigation of properties of sulfated amides of oleic acid and piperidine. The following scheme can represent the reaction between oleic acid and piperidine:



Scheme. Synthesis of (salts of sulfated oleic acid amides based on piperidine)

The synthesized products at room temperature are brown crystals.

It has been experimentally established that the synthesized sulfated oleic acid amides of piperidine are well soluble in water, chloroform, dimethyl ether, but are not soluble in toluene and benzene. Structure of synthesized salts of oleic acid amides and obtained surfactant is confirmed by data of IC-, NMR-spectroscopy, a composition by method of high-performance liquid chromatography.

The following absorption bands (p.p.) are observed in the IR spectrum of the salts of the sulfated oleic acid amides based on piperidine: at 621 cm^{-1}, responsible for pendular fluctuations of C-H of communication, CH_2 group (n≥6), at 1385-1386 cm^{-1} and 3007 cm^{-1} deformation and valent fluctuations of C-H and CH_3 of communications, absorption strips at 1419 cm^{-1} and 3300 cm^{-1} correspondings to deformation and valent fluctuations of C-H and CH_2 - groups, respectively. At 1081cm^{-1} deformation oscillations - OH of the group. Representative absorption

bands for S-O bonds at 1130 and 1124 cm^{-1} responsible for S = O bonds at 1555 cm^{-1}. C = O and N-H bonds in the CONH group at 1626 cm^{-1} corresponding to C = O bonds in the CON group. Absorption bands of NH_4 groups were observed in the 3052cm^{-1} region. These data confirm that the reaction sulfates oleic acid amides and sulfuric acid is attached to a C = C bond, which corresponds to the absorption band with a maximum at 1258 cm^{-1} characteristic of the C-H bond in amides (Figure 1).

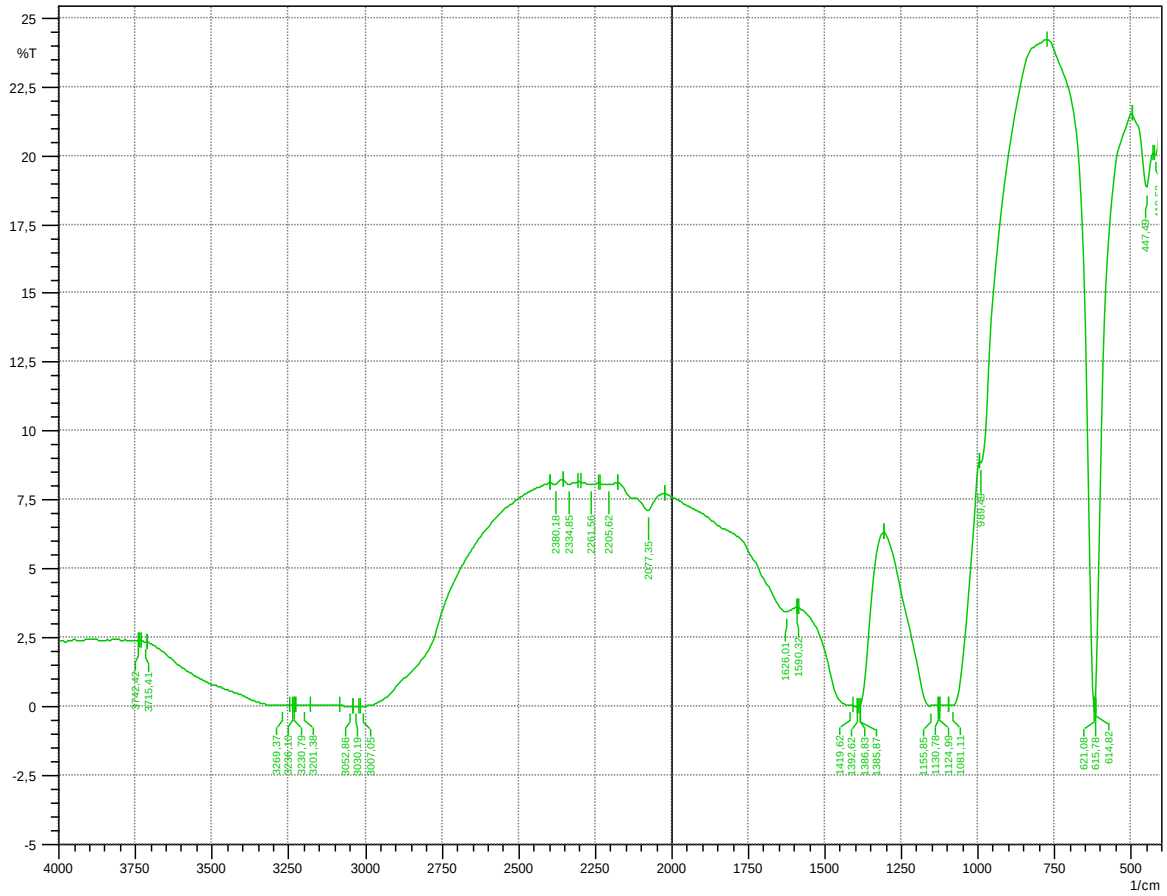


Figure 1. IR spectrum of salts of sulfated oleic acid amides based on piperidine.

Also, the structure of the salts was identified as 1H NMR spectral analysis (Fig.3).

Range 1H of nuclear magnetic resonance (300.13 MHz, DMSO and CCl_4) d, m: 0.73 (CH_3), 1.22 (chain CH_2), 2.07 (-CH_2CO-), 2.7 (NH_2 (CH_2) 6NH), 2.80 (NH3 - CH_2), 3.35 (NH_3 CH_2CH_2OH).

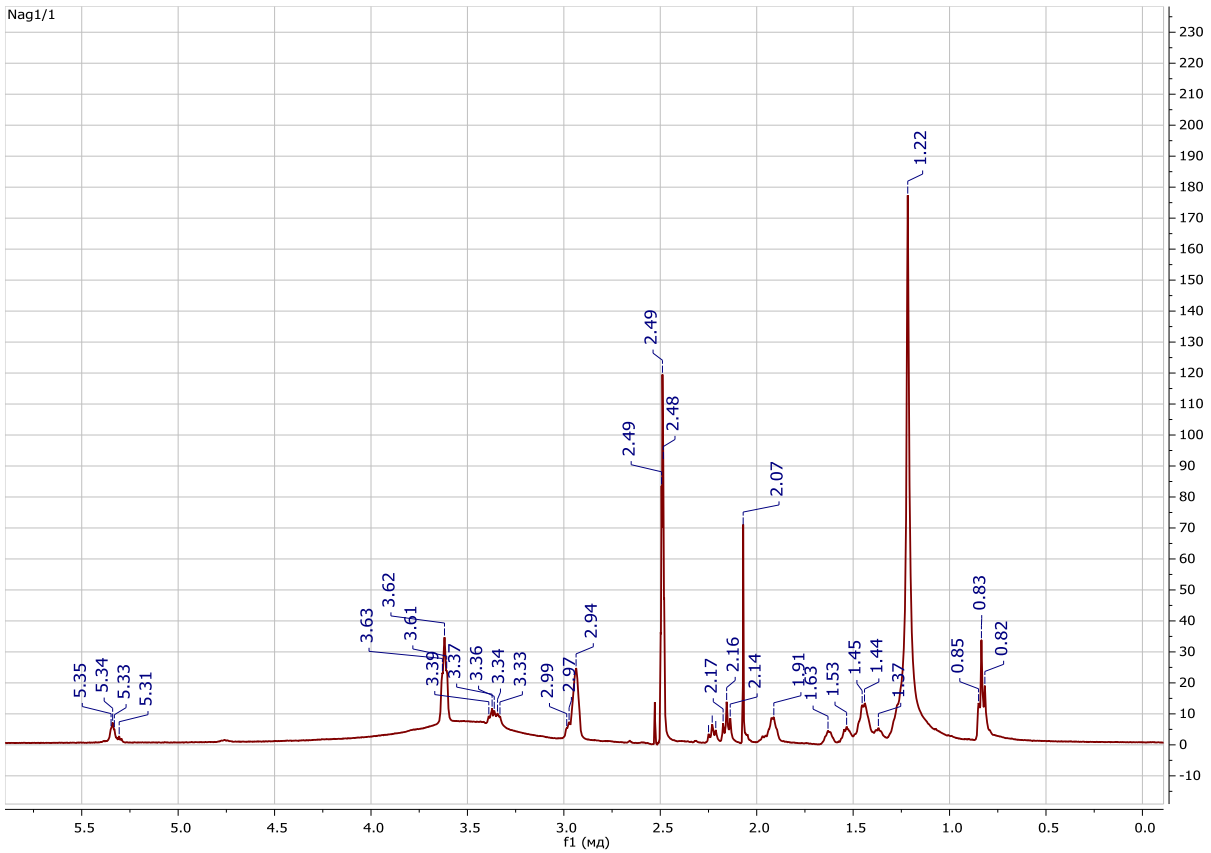


Figure 2. NMR,1H spectrum of salts of sulfated oleic acid amides based on piperidine.

Further, a chromatography analysis of PiP and OK was carried out by high-performance liquid chromatography (HPLC) Fig. 2.

At the same time as a mobile phase, we selected: acetonitrile with water, in a ratio of 1:1. The feed rate was 2.00 ml/min. The process of distributing sample components between the mobile and stationary phases takes place in a solution within a chromatographic column filled with porous particles of organic or inorganic sorbents (based on polymers or silica gel).

Table1.

Results of HPLC of salts of sulfated piperidine-based amino oleic acid.

# Peak	Name	Time, sec	Height, mV	Area, mV * sec	FO	Concentration, %
1	Pipiridine	1346	15.14	501.12	1.000	27.46
2	Sulfuric acid	1377	9.52	366.69	1.000	24.85
3	Oleic acid	1441	21.33	703.81	1.000	47.69
4	Ammonium hydroxide	1708	2.3	145.76	0.050	12.59

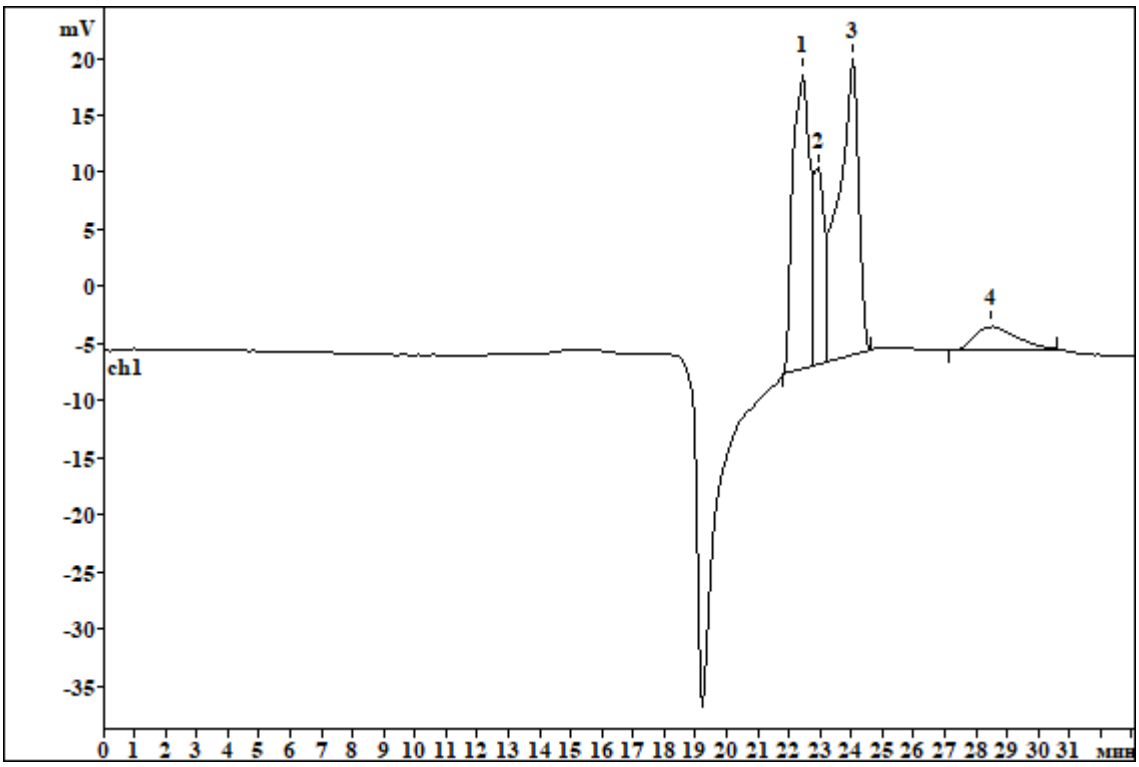


Figure 3. High-performance liquid chromatography (HPLC) of salts of sulfated oleic acid amides based on piperidine: 1-piperidine, 2-sulfuric acid, 3-oleic acid, 4-ammonium hydroxide

As can be seen from the chromatogram, the most abundant molecules (greater molecular weight) that can penetrate the minimum number of pores of the stationary phase are the first to exit the column. The latter comes out substances with small sizes of molecules, which can freely penetrate pores. It can be seen from the present chromatogram that all four components under the selected conditions are entirely separated.

The research thus succeeded in synthesizing sulfated oleic acid and piperidine amides. The process of preparing salts consists of the following steps: the limiting step of the reaction of oleic acid with piperidine does not occur on the double bond, but on the carboxyl group of the acid; A second step of sulphurizing the resulting compounds with sulfuric acid, a third step and a final step of reacting NH_4OH and $(HOCH_2CH_2)$ 2NH, as proved by IR and NMR spectroscopies.

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