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SYNTHESIS AND PROPERTIES OF ETHANOLAMIDES ACIDS OF HIGLYERUCIC RAPESEED OIL

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Abstract. *First are synthesized a series of surface-active substances (surfactants) by transamidation of high erucic rapeseed oil with mono- and diethanolamines. Due to the specific composition of initial oils and products on their basis, the synthesized surfactants are characterized by multifunctional properties and can be used for creation of effective emulsion-suspension systems for petroleum refineries and lubricants with improved antioxidant, anticorrosion, anti-wear and extreme pressure characteristics.*

Keywords: ethanolamides; phosphatides; surface-active substances; synthesis; rapeseed oil.

1. Introduction

The world market of surface-active substances (surfactants) has a large variety of marketable products of different function, cost and principles of operation. Generally, for their preparation producers use petrochemical raw materials. The production of such surfactants is gradually growing in Ukraine, but their prices are still high (more than 1000 c.u. per ton) and inaccessible for many consumers. The demand for these products will steadily increase that may cause using of ecologically harmful materials with lower consumer values, and further, to deepening dependence of Ukraine from import of vital goods [Burlaka, Pop 2003].

Globalization of environment pollution by slow and incomplete (10–30%) biodegradation of petrochemical surfactants is an obvious concern. Their using is led to the formation of xenobiotics – the substances with high toxicity which don't participate in biodegradation processes. Xenobiotics are foreign to the biosphere and therefore they collect on the Earth and cause emergence of unpredictable diseases.

The other factors that cause to the search of alternative sources of surfactants, fuels and lubricants are: increasing prices on energy resources, high power intensity of GDP (3–5 times higher than developed countries) and low rates of its decreasing: in Ukraine – 0,1%, EU countries – 2,2%, USA – 3,0%, Poland – 5,6% [Bilodid 2003].

The listed factors present a real threat to the resource and energy security in Ukraine. Therefore one of the most actual problems of the present is the search of recoverable vegetable raw materials, synthesis of ecologically safe surfactants and creation of effective technological systems for various technical applications on this basis.

So, the objective of our work is the synthesis of alternative ecosafe surfactants based on high erucic oil and creation on their basis surface-active, lubricant and conservation materials with improved qualities

For achievement of this goal, this stage of work had demanded:

1. To analyze and select oils with the designed fatty-acid composition.
2. To synthesize surfactants of high thermal-oxidative stability and activity on the interface boundary of phases.
3. To determine a structure of the synthesized surfactants and their structure in solutions and at the phase boundary.
4. To investigate the properties of surfactants and estimate possibilities of their practical use.

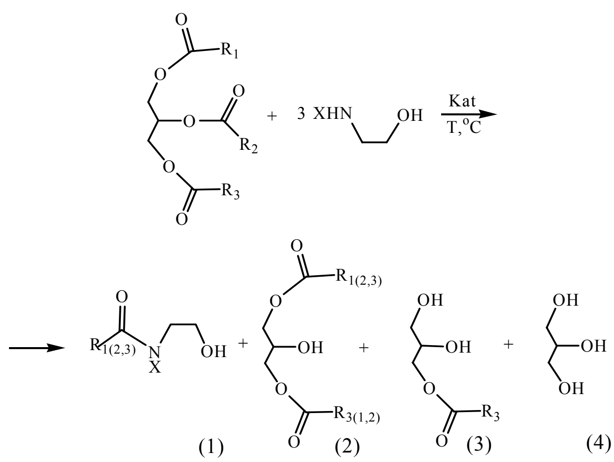
The analysis of scientific, technical and patent literature is shown that for synthesis of surfactants are mainly used refined oils of food quality, with fatty-acid composition which limits its use in lubricant composites due to the poor structuring and low consumer qualities [Yevdokimov et al. 2012].

For removing of these defects, we have chosen high erucic rapeseed oil, which is unusable for food purposes due to the toxicity of erucic acid. However, due to the high concentration of long acyl chains of this acid ($C_{22}H_{41}$) it is supposed that transamidation of triglycerides by aliphatic aminoalcohols will transform chemical structures of triglycerides. This adds to the strengthening of thermal-oxidative, protective properties and surface activity of new products.

2. Materials and Methods

We used high erucic rapeseed oil, extracted from new crop, selectively grown, oil high-yielding winter oilseed rape, which was produced at the experimental farm at the State Agricultural Experimental Station of Ivano-Frankivsk, with the following characteristics: yellowy viscous liquid with acid number – 1,2 mg KOH/g, moisture content – 0,20%, density – 920 kg/m^3, interfacial tension with the air – 33 mH/m and cinematic viscosity at 20 °C – 98 mm^2/s, flash point – 340 °C and freezing-point – minus 6 °C. Fatty-acid composition of this oil was measured according to the GOST 30418-96 "Vegetable oils. Method for determination of fatty acid composition". As for the original and purified (from phospholipids) oils we have obtained next parameters, wt%: palmitic $C_{16:0}$ – 1,9 and 2,1, stearic $C_{18:0}$ – 1,8 and 2,0, oleic $C_{18:1}$ – 15,3 and 17,7, linoleic $C_{18:2}$ – 21,5 and 25,3, linolenic $C_{18:3}$ – 7,0 and 8,0, eicosenic $C_{20:1}$ – 2,1 and 2,3, erucic $C_{22:1}$ – 35,9 and 41,3, phospholipides – 14,5 and 0,3.

Interaction between oils and mono – (MEA) and diethanol- (DEA) amines was performed at presence of alkaline catalysts (KOH, NaOH, $Ca(OH)_2$, CaO), due to the next scheme:



where R_1, R_2, R_3 – the chains of the acids: palmitic ($-C_{15}H_{31}$), stearic ($-C_{17}H_{35}$), oleic ($-C_{17}H_{33}$), linoleic ($-C_{17}H_{31}$), linolenic ($-C_{17}H_{29}$), eicosenic ($-C_{19}H_{35}$), erucic ($-C_{21}H_{41}$); X = N, C_2H_4OH.

The reaction of transamidation was performed at interaction of calculated quantities of oil, amines and reagent-catalyst in atmosphere of nitrogen at temperature 120–125 °C at permanent stirring, during 1,5–2,0 hours. In case of solvent using, after the reaction mixture homogenization, the solvent such as toluene, was distilled off. The course of the reaction was monitored by changes in the concentration of amines, which were measured by potentiometric titration and interfacial tension (σ) on the border of 1% solution of the product in diesel fuel and water. It was found that simbatic reduction of amine number and σ of emulsifier with the simultaneous linear growth of electrical stability of the stabilized emulsions indicates on the progress of the main reaction with the formation of surface-active mono – $RCONHCH_2CH_2OH$ and diethanolamides $RCON(CH_2CH_2OH)_2$. The ratio of initial reagents, yields, acid numbers and some physical properties of the synthesized surfactants are shown in Table 1.

Establishment of composition and structure of the synthesized products was performed by means of element microanalysis, IR – (Fourier spectrometer Vertex 70) (IBPC NASU), mass spectrometry (IOC NASU), and also by properties of standard techniques of organic chemistry.

3. Results and Discussion

According to the Table 1 it's obvious that all obtained products are uniform, solid, waxy or oily substances with color from light yellow to dark brown, with specific amine smell. Most of the products are soluble in organochlorine solvents, individual aliphatic and aromatic hydrocarbons and their technical mixtures, as well as in industrial oils. Separated compounds are well dissolved in water at heating and cooling in presence of water leads to a gel formation.

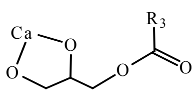
We determined that reaction proceeds already at temperature 80–90 °C, but the yield of the main ethanolamides of acids is then only 36 % (Table 1, sample 1). Temperature increasing to 160 °C greatly intensifies the reaction, but at the same time stimulates the proceeding of by-processes. The most reasonable experimentally found temperature of glycerides transamidation, which was accepted as a model for all next subsequent syntheses was 120–125 °C.

Table 1. The synthesis conditions, yield and properties of surfactants based on high erucic oil

Samples number	Initial reagents – moles			The synthesis condition and the yield of major product			Physical properties of surfactants			
	Rape oil	Amine	Catalysts	Tempera-ture, °C	Duration, hour	Yield, % mas.	Consistence	Colour	Acid numbers, mgKOH/g	Fluidity temperature, °C
1	1	MEA – 3	KOH – 0,4	80-90	4,0	36,3	Oily	Brown	-	80
2	1	MEA – 3	NaOH – 0,4	80-120	2,0 2,0	98,0	Waxy	Hazelly	8,96	82
3	1 (toluene)	MEA – 3	NaOH – 0,4	80-125	2,0 2,0	97,2	Waxy	Canary	6,32	89
4	1	MEA – 3	NaOH – 0,4	80-120	2,0 2,0	88,6	Waxy	Canary	9,23	88
5	1 (toluene)	MEA – 3	NaOH – 0,4	80-125	2,0 2,0	86,9	Waxy	Canary	8,71	87
6	1	MEA – 3	$Ca(OH)_2$–0,4	80-120	0,4 1,5	100	Solid	Hazelly	2,36	76
7	1	MEA – 3	CaO – 0,4	80-110	0,4 1,5	100	Solid	Hazelly	2,12	78
8	1	DEA – 3	NaOH – 0,4	140-160	2,0 2,0	98,7	Oily	Canary	8,86	54
9	1	DEA – 3	CaO – 0,4	140-160	0,4 1,5	100	Oily	Canary	3,86	62

Following to the optimum conditions of the reaction it was shown that refined vegetable oil in presence of hydroxides of alkali metals, as well as the use of acid catalysts, interacts almost quantitatively with the formation of acids ethanolamides (samples 2 and 3), while unrefined oil (samples 4 and 5) at these conditions forms a solid, brown, plastic product which is separated into two parts due to its densities proportionally to the presence of phosphatides in the initial product. The top layer is easily dissolved in hydrocarbons (hexane, condensate, diesel fuel, toluene, etc.), but lower layer that makes 12–14% forms insoluble sediment. These residues, as it was predicted, are the mix of hydrophilic phosphatidyl glycerols, which are dispersed in the water with formation of milk white dispersion. It should be noted that authors [Corma et al. 2007; Kovalev et al. 2007] obtained the similar products when didn't use erucic rapeseed oil. Those products then were yellowy-gray pastes with a melting point within 42–46 °C.

The presence of calcium hydroxide or calcium oxide as a catalyst (samples 6 and 7) and more soft conditions of the reaction (100–110 °C) helped to eliminate the "ballast" sediments by transferring phosphatidyl glycerols to calcium phosphatidyl glycerols (5), phosphatidyl serines, phosphatidic acids, diphosphatidyl inositols and triphosphatidyl inositols, which characterized by acidic properties, to calcium complex compounds (6) [Hendrickson, Fullington 1965; Korneva, Litvinova 1978]. Hydrophobic phosphatidic compounds with ethanolamides form homogeneous solution at temperature of 60 °C, which is then fully soluble in hydrocarbons:



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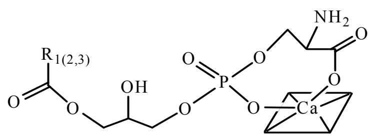

(6)

The product, which was isolated from hexane solution was, as it was expected according above-mentioned reaction scheme, a mixture of acid N-alkylolamides (1), mono - (2) and diacylglycerols (3), and it was confirmed by liquid chromatography, NMR, IR and mass spectroscopy.

The interpretation of IR spectra was focused on the detection of valence vibrations frequencies of OH, C=O, CH_2, CH_3 groups in the molecule of the original triglycerides and appearance of the characteristic frequencies of C–N, N–H-groups which are characterized organic compounds with amide groups. Regardless of the purity and composition of oils (samples 2-7), due to transamidation of triglycerides by monoethanolamines, the intense absorption band at 1740 cm^{-1}, that corresponds to glycerides disappears.

Instead appears new band of valence vibration of C=O groups (amide I) at 1650 cm^{-1} and deformation vibrations group NH (amide II) at 1548 cm^{-1}, which indicates the formation of mostly secondary amides.

The analysis of PMR and mass distribution of the fragments (M/z) are correlated well with each other, confirm the results of IR spectroscopy and also indicate the formation of amide compounds with characteristic signals of –NH groups at δ = 7,82 ppm [Sergeev 1981]. Next to the amide component in the spectrum of H^1NMR is detected wide multiplet in the range of δ = 3,32–3,67 ppm, which indicates the presence of free glycerol in the product [Lu-Yun, Gordon 2011].

By tensiometric and ultramicroscopic analysis it was shown that the obtained surfactants have high surface activity, which provide an easy and rapid preparation of inverted emulsions and suspensions. According to the Table 2, the obtained systems are highly dispersed and aggregately stable, also a number of perimeters such as electric stability, daily settling are better in comparison with a similar product based on the oil with less erucic acid (LERO) content and with widely used in industry esters of long chain fatty acids with triethanolamine – Emultal.

Given the large amount of variance in the use of these dispersions in oil and gas industry, we developed a series of emulsion-suspension systems with adjustable density, resistant, protective, rheological, structural and mechanical properties according to the terms of use. General characteristics are given in Table 3.

All synthesized ethanolamides of the acids are mixable with almost all conventional mineral and synthetic oils. Tribological tests are shown below indicate that HERO is characterized by improved surface activity and rheological characteristics, and also by the number of other functional properties, in particular, can serve as a high-quality anti-friction, anti-wear and extreme pressure additive.

Analysis of experimental data is summarized in Table 4. The HERO is shown greater oxidative stability and better tribotechnical characteristics compared with oil MS-20, initial oil and analogous LERO, which based on unrefined oil.

It is obvious positive effect of erucic acid on thermal-oxidative stability of the obtained biosynthetic products, but the presence of lipases, phospholipides and other biological impurities, promotes the formation of organic free radicals and hydroperoxides at the high temperature, which then are decomposed to form ketones, aldehydes and low molecular weight carboxylic acids under the action of enzymes [Lu-Yun, Gordon 2011]. These acids are significantly stronger than the original fatty acids, and are therefore responsible for the corrosion.

Thus, the synthesized HERO products are characterized by the following advantages.

1. Availability, reproducibility, toxicological and environmental safety of the raw material.

Table 2. Properties and composition of the stabilized by Emultal and ethanolamides of LERO and high erucic rapeseed oil (HERO) emulsion systems

Emulsifier	Concentration, % vol	Aqueous solution, % vol	Diesel fuel, % vol	Consistence	Density, kg/m^3	Viscosity, Pa·s	Electrical stability, V	Separation of hydrocarbon layer, % vol/day
HERO	0,5	59,7	39,8	Tarry	983	0,17	260	0,2
	2,0	58,8	39,2	Paste	985	0,25	440	0,0
HERO (unrefined)	0,5	59,7	39,8	Tarry	986	0,21	230	0,0
	2,0	58,8	39,2	Paste	988	0,35	420	0,0
LERO	1,5	59,7	38,8	Easy fluid	982	0,18	140	6,0
	3,0	58,8	38,2	Tarry	984	0,40	355	1,9
Emultal	1,0	59,7	39,3	Fluidity	983	0,15	140	5,6
	3,0	58,8	38,2	Fluidless	985	0,23	330	2,3

Table 3. Properties of Inverted Dispersions

Indicators	Values of Indicators
Appearance	White-yellow system
Consistence	From easy movable liquid to fluidless paste
Viscosity, Pa·s	0,04 - 4,2
Density, kg/m^3	460 - 2800
Daily settling, %	0 - 10
Electric stability, V	100 - >1200
Filtering, cm^3/30 min	0 - 3
Corrosion rate of Steel-3, $g/(m^2 \cdot g)$	$(2{,}09 \div 1{,}5) \cdot 10^{-3}$

3. Were determined the composition and chemical structure of the synthesized products as well as their structure in dispersed systems by the complex of physicochemical methods. It is shown that a great advantage over existing synthesized substances is the mixed composition of ethanolamides, mono- and diacylglycerols of the acids and phosphatidyl glycerols. The first of them have high surface activity and thus dispersing capacity, and the second provide stability to the oleodispersed systems as a result of spatial structure formation, and generation of mixed adsorption-solvated layer.

Table 4. Accordance of antioxidant (by DIN 51352) and tribological (by GOST 9490) properties of lubricating products and compositions on their basis

Oil, lubricants and composition on their basis	Load, N		Spot wear, D_w, mm	IW	Bio-splitting, %	Acid number, mg KOH/g	
	Critical, P_{cr}	Weld, P_w				Before test	After 12 hour
Oil MS-20	617/490	1568/1410	0,90/0,96	–	36	0,06	13,0
Rapeoil	823/647	1568/1460	0,83/0,95	43,5	95	1,2	14,6
MS-20 + LERO	960/942	1890/1790	0,79/0,84	–	83	1,8	9,4
MS-20 + EVROн	890/740	1830/1780	0,83/0,91	–	80	3,4	12,1
MS-20 + EVRO	980/965	1960/1840	0,68/0,72	–	86	0,6	2,9

2. Increased thermal stability, emulsifying and stabilizing properties that allow using them at temperatures up to 140 °C in fuels, lubricants and lubricant-coolant, or in combination with other systems in long production processes of energy sector.

3. Film formation and protective ability for metallic pipes and equipment against corrosion.

4. Antioxidant and protective properties with improved anti-friction and anti-wear characteristics in mineral oils.

4. Conclusions

1. By transamidation reaction of high erucic rapeseed oil with mono- and diethanolamine was first synthesized a mixture of ethanolamides and mono- and diacylglycerols of the fatty acids, and in case of unrefined oil also phosphatidyl glycerols,

2. First was shown that interaction of unrefined high erucic oil with monoethaolamine at introduction of fine calcium hydroxide or calcium oxide into the reaction mixture can accelerate the reaction transamidation and allows transferring insoluble "ballast" sediment of phosphatidyl glycerols into soluble form of calcium.

4. It was proved, that due to the specific structure of initial oils and products based on them, the synthesized surfactants have multifunctional properties and can be used for a creation of effective emulsion-suspension systems in the oil and gas industry and lubricants with improved antioxidant, anti-corrosion, anti-wear and extreme pressure characteristics.

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Ю.С. Бодачівський[1], Ю.В. Білокопитов[2], Г.С. Поп[3]. Синтез і властивості етаноламідів кислот високоерукової ріпакової олії

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Трансамідуванням високоерукової ріпакової олії моно- та діетаноламінами вперше синтезовано низку поверхнево-активних речовин. Доведено, що завдяки специфічному складу вихідних олій синтезовані поверхнево-активні речовини і продукти на їх основі володіють поліфункціональними властивостями і можуть використовуватися для створення ефективних емульсійно-суспензійних систем у нафтогазовидобувній галузі та мастильних матеріалів із покращеними антиокиснювальними, антикорозійними, протизадирними і протизношувальними характеристиками.

Ключові слова: етаноламіди; поверхнево-активні речовини; ріпакова олія; синтез; фосфатиди.

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Трансамидированием высокоэрукового рапсового масла моно- и диэтаноламинами впервые синтезирован ряд поверхностно-активных веществ. Доказано, что благодаря специфическому составу как исходных масел, так и продуктов на их основе синтезированные поверхностно-активные вещества обладают полифункциональными свойствами и могут использоваться для создания эффективных эмульсионно-суспензионных систем в нефтегазодобывающей отрасли и смазочных материалов с улучшенными антиокислительными, антикоррозионными, противозадирными и противоизносными характеристиками.

Ключевые слова: поверхностно-активные вещества; рапсовое масло; синтез; фосфатиды; этаноламиды.

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