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SYNTHESIS AND PROPERTIES OF NEW SURFACTANTS BASED ON COTTON-SEED OIL TRIGLYCERIDES, ETHANOLAMINES AND ORTOPHOSPHORIC ACID**I.A.Zarbaliyeva***Y.Mamedaliyev Institute of Petrochemical Processes, NAS of Azerbaijan**ilhamachem447@mail.ru*

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By interaction of cotton-seed oil triglycerides with monoethanolamine monoethylolamide of cotton-seed oil acid fraction is obtained which is further phosphated by orthophosphoric acid. The obtained phosphate-derivative is reacted with mono-, di- and triethanolamine synthesizing respective ethanolamine complexes. The structure and composition of these complexes were identified by NMR (^1H and ^{13}C) and IR-spectroscopy methods. Some of the physico-chemical indices of the ethanolamine complexes have been determined. By stalagmometric measurements their high surface activity at the water–kerosene border has been shown. Laboratory tests revealed strong petroleum collecting and dispersing properties of these complexes that enable to remove thin petroleum films from the water surface.

Keywords: cotton-seed oil triglycerides, ethanolamines, monoethylolamide, monoethylolamide phosphate, etanolaminophosphate complexes, surfactants, petroleum collecting, dispersing.

Contamination of the World Ocean with petroleum is one of the most serious ecological problems standing before the mankind. Petroleum spills occurring due to various reasons lead to formation of thick slicks. Such petroleum slicks may be liquated using special mechanical devices. After such operations thin petroleum films inevitably remain on the water surface. These films may be removed only applying colloidal-chemical means which include usage of petroleum-collecting and petroleum-dispersing reagents [1–4]. Among such reagents which are surfactants, of a particular interests are reagents based on renewable and alternative raw materials. Here, first of all, vegetable oils should be mentioned which are harmless to environment and cheap [5–8]. In the present article considered new surfactants possessing petroleum-collecting and dispersing effectiveness were synthesized on the basis of cotton-seed oil which is an available raw material in our country also having a relatively low cost.

Experimental

Cotton-seed oil is a local commodity product. Among residues of saturated fatty acids in this oil triglycerides, miristic acid (C_{14}) constitutes 0.3–0.5%, palmitic acid (C_{16}) – 20.0–22.0%, stearic acid (C_{18}) – 2.0%, arachinic acid (C_{20}) – 0.1–0.6%. From unsaturated fatty acids,

residues of oleic acid (C_{18}) make up 30.5–35.2% and those of linoleic acid (C_{18}) – 41.7–44.0%.

Monoethanolamine (MEA) was a reagent of "pure" grade produced by Olaynen Chemical Reagents Factory (Latvia).

Diethanolamine (DEA) was a product of "pure" analytical grade of "Merck" (Germany).

Triethanolamine (TEA) was from "Kazan-orgsintez" Joint Stock Company (Russian Federation).

The above-mentioned triethanolamines were used without any purification procedures.

Orthophosphoric acid was used as 86% wt. aqueous solution produced by "Component-Reactant" Joint Stock Company (Russian Federation).

Water used as a bidistillate.

Surface activity of the synthesized surfactants was estimated at the water–kerosene border by stalagmometric method.

Specific electroconductivity (κ) of the surfactants aqueous solutions was measured by "Anion 4120" conductometer (Russian Federation).

NMR ^1H and NMR ^{13}C spectra were registered by Bruker Advance II 300.13 (75.468 for ^{13}C) spectrometer under room conditions.

IR spectra were recorded by Vertex 70 (Bruker) spectrometer in the range 4000–400 cm^{-1} using KBr pellets.

Petroleum collecting and dispersing properties of the synthesized surfactants were studied by the following procedure both for pure-state reagents and their 5 wt % aqueous solutions. In the laboratory tests, Ramana petroleum (density at 20°C – 0.862 g/ml, kinematic viscosity at 20°C – 16.80 cSt) was used. Into Petri dish, 40 ml of petroleum is added. After formation of thin petroleum layer [thickness is ~ (0.16–0.17) mm] 0.02 g of surfactant (or its 5.0 wt % aqueous solution) is given onto the petroleum layer from the peripheral side. Petroleum-collecting coefficient is calculated according to the relationship $K=S_0/S$, where S_0 is the area of the petroleum layer surface prior to addition of a reagent whereas S is a current area of the surface of petroleum spot formed under the

action of the reagent. Time intervals – τ of measurements were also registered. The values of petroleum-collecting coefficient at different times enable to judge about dynamics of change of reagents impact.

Results and discussion

The reactions of obtaining monoethylolamide of cotton-seed oil acid fraction are conducted in an autoclave made of stainless steel and equipped with temperature-regulating system at 140–160°C. This reaction is carried out without a solvent and a special catalyst at molar ratio of cotton-seed oil triglycerides and MEA equaling 1:3 monoethylolamide is formed according to this reaction scheme (R is hydrocarbon radical of fatty acid) [5, 6]:

Phosphation of the obtained monoethylolamide with the purpose to increase its hydrophilicity is performed with participation of equimolar amount of orthophosphoric acid. This

reaction is carried out in a thermostat at 50–60°C during 20–23 hours. The scheme of obtaining phosphate-derivative of monoethylolamide may be described as follows:

This reaction is accompanied with an increase of viscosity and colour darkening.

Then, to the obtained phosphate-derivative, ethanolamine (separately MEA, DEA and TEA) is added at equimolar ratio. Com-

plexation reaction is conducted at 50–60°C in a thermostat during 20 hours. Further increase of viscosity and colour darkening are observed. The scheme of complexation reactions may be written in such a form:

where x may be 0, 1 or 2.

Table 1. Conditions of the complexation reaction and some physico-chemical indices of ethanolamine complexes of monoethylolamido-phosphate of cotton-seed oil acid fraction

Ethanol-amine complex	Temperature of synthesis, °C	Duration at of synthesis, hour	External appearance	Solubility	Amine number, mg HCl/g	Specific electroconductance, Ohm ⁻¹ m ⁻¹
MEA	50–60	20	dark-brown flowing liquid	soluble in water, acetone, CCl ₄ , benzene, practically soluble in isooctane and kerosene, practically insoluble in isopropanol	0.23	0.007875
DEA	"_"	"_"	brown-red, moderately flowing liquid	"_"	0.16	0.005250
TEA	"_"	"_"	brown-viscous liquid	"_"	0.38	0.005325

Identification of the synthesized complexes was made using NMR (¹H and ¹³C) and IR spectroscopy methods. In Figure 1a, spectrum ¹H NMR and in Figure 1b, spectrum ¹³C NMR of TEA complex are depicted.

In spectrum ¹H NMR, there are proton resonance signals of CH₃-group at 0.80 ppm, CH₂-group at 1.20 ppm, CH₂C(O) group at 1.50 ppm, OCH₂-group at 1.85–2.30 ppm, NCH₂-

group at 2.60–2.80 ppm, double bond at 3.10–3.60 ppm, C–OH group at 5.25 ppm and P–OH group at 7.60 ppm.

At spectrum NMR ¹³C (Figure 1b), carbon-atom resonance signals are recorded at 13.5–41.4 ppm for carboxylic acids backbone carbons, 60.0 ppm for OCH₂ carbon, 127.0–129.0 ppm for CH₂–NH and CH₂N groups carbons, 174.0 ppm for C(O)N group carbon atom.

Fig.1a. Spectrum ¹H NMR of TEA complex of monoethylolamidophosphate of cotton-seed oil acid fraction. **Fig.1b.** Spectrum NMR ¹³C of TEA complex of monoethylolamidophosphate of cotton-seed oil acid fraction.

In IR spectrum of TEA complex (Figure 2), the following absorption bands are observed: OH-valent and N-H valent vibration at 3299 cm^{-1} , C-H of double bond 3011 cm^{-1} , C-H saturated valent 2918 and 2850 cm^{-1} , NC=O valent vibration 1644 cm^{-1} , N-H deformational 1556 cm^{-1} , C-H deformational 1465 and 1377 cm^{-1} , C-N valent 1215 cm^{-1} , C-O valent in C-OH fragment 1057 cm^{-1} , P-O valent 1039 cm^{-1} and $(\text{CH}_2)_x$ "pendulum" vibrations 719 cm^{-1} .

Surface activity of the synthesized complexes has been studied at the water-kerosene border by stalagmometric method. The results of stalagmometric measurements have been included into Table 2.

As is seen from the obtained results, all three complexes exhibit surface activity at the indicated border. The most active one is MEA complex which decreases the interfacial tension from 46.0 down to 2.1 mN/m (at 5% concentra-

tion). The least active is TEA complex (9.2 mN/m at the same concentration).

The results of laboratory tests of the synthesized complexes on petroleum-collecting and petroleum-dispersing capacities have been presented in Table 3.

These results show that the synthesized complexes manifest high petroleum-collecting and petroleum-dispersing capacities. Thus, for 5% aqueous solution of MEA complex, the duration of the reagent action in fresh water is longer than 13 days, the value of K being 42.6. In the sea water, this solution is a strong dispersant ($\tau > 13$ days). 5% aqueous solution of DEA complex demonstrates good dispersing properties both in fresh and sea waters ($\tau > 13$ days). 5% aqueous solution of TEA complex shows a mixed (petroleum-dispersing-collecting) capability in fresh water ($K_{\max} = 28.6$, $\tau > 13$ days) and purely dispersing properties in the sea water ($\tau \sim 10$ days).

Fig.2. IR spectrum of TEA complex of monoethylamidophosphate of cotton-seed oil acid fraction.

Table 2. Results of stalagmometric studies of surface activity of ethanolamine complexes of monoethylamidophosphate of cotton-seed oil acid fraction at the water-kerosene border (21°C)

Reagent	Solvent of reagent	Concentration of reagent, wt %				
		0.025	0.050	1.000	3.000	5.000
		Surface tension at the water–kerosene border, mN/m				
MEA complex	Water	4.8	7.1	2.5	4.2	2.1
DEA complex	"—"	2.8	7.3	11.4	8.5	3.5
TEA complex	"—"	7.8	8.5	21.8	12.1	9.2

Table 3. Results of studies of petroleum-collecting and petroleum-dispersing properties of ethanolamine complexes of monoethylamidophosphate of cotton-seed oil acid fraction; Ramana petroleum

Distilled water		Fresh water		Caspian sea water	
τ , hours	K	τ , hours	K	τ , hours	K
5 wt. % aqueous solution of MEA complex					
0 3.33–198.00	39.00 Disp.	0–24.5 123.5–320.00	42.6 Disp.	0–320.00	Disp
Pure-state MEA complex					
0–3.33 24.5–123.50 199.5–320.0	36.12 37.20 32.60	0–118.00 123.5	Disp. Dag	0–204.00 320.00	Disp Disp
5 wt. % aqueous solution of DEA complex					
0–3.33 24.5–320.50	36.20 Disp.	0–118.00 320.00	Disp. Spilled	0–392.00	Disp.
Pure-state DEA complex					
0–123.00 128.5–320.50	26.80 Disp.	0–248.00	Disp.	0–123.00 148.00	Disp. Spilled
5 wt. % aqueous solution of TEA complex					
0–320.00	Disp.	0–3.33 24.50–48.50 62.45–392.00	28.60 Disp. 8.70	0–392.00	Disp.
Pure-state TEA complex					
0–3.33 23.50–264.00	32.60 36.60	0 3.33–320.00	Disp. 22.78	0–234.00 248.00	Disp. Spilled

Thus, it has been established that phosphorylation of monoethylamide of cotton-seed oil acid fraction and further complexation of the phosphate with MEA, DEA and TEA enable to obtain ethanolamine complexes which have a high surface activity at the water-kerosene border and possess strong petrocollecting and petrodispersing properties that make possible to use them for removing thin oil films from the water surface.

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**PAMBIQ YAĞI TRIQLİSERİDLƏRİ, ETANOLAMİNLƏR VƏ ORTOFOSFAT TURŞUSU ƏSASINDA
YENİ SƏTHİ-AKTİV MADDƏLƏRİN SİNTEZİ VƏ XASSƏLƏRİ****İ.A.Zərbəliyeva**

Pambiq yağı triqliseridlərinin monoetanolaamnlə qarşılıqlı təsirdən pambiq yağı turşu fraksiyasının monoetilolamidini alınmış və ortofosfat turşusu ilə fosfatlaşdırılmışdır. Bu fosfat törəməsinin sonradan mono-, di- və trietanolaamnlə reaksiyalarından müvafiq etanolamin kompleksləri sintez edilmişdir. Alınmış komplekslərin quruluşu və tərkibi NMR (^1H və ^{13}C) və İQ spektroskopiya üsulları ilə təsdiqlənmişdir. Etanolamin komplekslərinin bəzi fiziki-kimyəvi göstəriciləri təyin edilmiş, stalaqmetrik üsulla onların su-kerosin sərhədində yüksək səthi aktivliyə malik olduğu göstərilmişdir. Laboratoriya sınaqları nəticəsində müəyyən edilmişdir ki, bu komplekslər qüvvətli neftiyyəçilik və neft-dispersləmə xassələrinə malikdir. Bu onların tətbiqi ilə su səthindən nazik neft təbəqələrini kənar etməyə imkan verir.

Açar sözlər: pambiq yağı triqliseridləri, etanolaminlər, monoetilolamid, monoetilolamidofosfat, etanolaminofosfat kompleksləri, səthi aktivlik, neftiyyəmə, neftdispersləmə

**СИНТЕЗ И СВОЙСТВА НОВЫХ ПОВЕРХНОСТНО-AКТИВНЫХ ВЕЩЕСТВ НА ОСНОВЕ
ТРИГЛИЦЕРИДОВ ХЛОПКОВОГО МАСЛА, ЭТАНОЛАМИНОВ И ОРТОФОСФОРНОЙ КИСЛОТЫ****И.А.Зарбалнева**

Взаимодействием триглицеридов хлопкового масла с моноэтаноламином получен моноэтилоламид кислотной фракции хлопкового масла, который далее фосфатирован ортофосфорной кислотой. Реакцией конечного фосфата с моно-, ди- и триэтанолоамином синтезированы соответствующие этаноламинные комплексы. Строение и состав полученных комплексов подтверждены методами ЯМР (^1H и ^{13}C) и ИК-спектроскопии. Определены некоторые физико-химические показатели этих комплексов, сталагмометрическим методом показана их высокая поверхностная активность на границе вода–керосин. В результате лабораторных испытаний установлено, что синтезированные комплексы обладают сильными нефтесобирающими и нефтедиспергирующими свойствами. Это позволяет с их помощью удалять тонкие пленки с водной поверхности.

Ключевые слова: триглицериды хлопкового масла, этаноламины, моноэтилоламид, моноэтилоламидофосфат, этаноламинофосфатные комплексы, поверхностная активность, нефтесобирание, нефтедиспергирование