

UDC 66.092.46:665.12

Study of the Biodegradability of Anion-Active Surfactants on the Ground of Polyunsaturated Fatty Acids

V. M. ABBASOV¹, L. I. ALIEVA¹, Z. G. ASADOV¹, E. V. RACHMANOV² and I. G. NAZAROV³

¹Mamedaliev Institute of Petrochemical Processes, Azerbaijan NAS,
Pr. Khojali 30, Baku AZ1025 (Azerbaijan)

E-mail: leylufer-ipcp@rambler.ru

²Lomonosov Moscow State University,
Leninskiye Gory, GSP-1, Moscow 119991 (Russia)

³Lomonosov Moscow State University, Baku Branch,
Ul. B. Vahabzade, 14, Baku AZ 1143 (Azerbaijan)

(Received November 6, 2013; revised January 27, 2014)

Abstract

Anion-active surfactants on the ground of sulpho derivatives of a mixture of fatty acids isolated from corn oil and individual linolenic acid were obtained. Physicochemical properties of surfactants and calcium salts synthesized on their ground have been defined. Research with thin (0.16–0.17 mm) films of petroleum on the surface of various waters (fresh, distilled, sea) has shown that these salts as 5 and 10 % solutions of ethanol possess good petroleum collecting and petroleum dispersing properties. It has been established that 0.025 and 0.05 % solutions of calcium salts are biodegradable.

Key words: biodegradability, surfactants, fatty acids, linolenic acid, salts of sulpho acids, petroleum collecting

INTRODUCTION

Surfactants are heterogeneous group of compounds that facilitate the decrease of the surface tension at the concentration on the phase boundary. At the present time, surfactants are widely used in industrial and technological processes, since they allow intensifying, simplifying and making favourable and ecologically safe various processes of petroleum collecting, petroleum refining, water purification *etc.*

Among surfactants, there are compounds that decompose fast in the environment and compounds that do not decompose and get accumulated in organisms in unacceptable concentrations. One of the basic negative effects of surfactants in the environment is the reduction of the surface tension. For example,

the change of the surface tension in the ocean leads to the decrease in the index of retention of CO₂ and oxygen in the mass of water [1–3]. Only a few surfactants are considered to be safe, for instance, alkyl polyglucosides, degradation products of which are carbohydrates [4].

On the biodegradability one can distinguish several types of surfactants: 1) non-biodegradable or biodegradable by less than 30 % (tetrapropylenebenzene sulphonate and all oxyethylated alkylphenols); 2) biodegradable by more than 80 % but not to the simplest inorganic compounds (linear alkylbenzene sulphates); 3) fully biodegradable compounds (alkyl sulphates, alkane sulphonates, and olefin sulphonates).

Besides, surfactants are divided into ionogenic that is dissociating into ions in the aqueous medium and non-ionogenic. Ionogenic sur-

factants include: 1) anion-active (A-surfactants) that at dissociation form a macroanion showing a surface activity; 2) cationic surfactants (C-surfactants) forming a surface-active macrocation; 3) amphoteric or ampholytic dissociating as A-surfactants or as C-surfactants depending on the reaction medium.

The rate of the biodegradability of A-surfactants depends primarily on the structure of an alkyl chain. Compounds with an unbranched (linear) chain are destroyed relatively easily by microorganisms. On the contrary, branching in a chain slows down the decomposition of surfactants. The biodegradability is quicker with a longer alkyl chain, while in case of sulphonates with a greater distance between the chain and the hydrophilic group. However, with the increase of the length of an alkyl chain over C14–C18 the destruction activity falls due to a lower solubility. It has been established for alkylbenzene sulphonates that a single side group on the near or distant end of the chain only slightly slows down the process of the biodegradability. The presence of a terminal quaternary group is insignificant, if there is an open chain end. The process of the biodegradation slows down considerably in the opposite case. The destruction occurs following not the usual metabolite way and eases at the increase of the chain length [5–7]. However, the presence of a methyl group in the hydrophobic part of the molecule does not influence the degradability but enhances the process in some cases [8]. The increase of the number of oxyethylene groups slows down the biodegradation process in not ionogenic surfactants. The introduction of oxypropylene and oxybutylene links into a molecule of surfactants also slows down considerably the decomposition. In nitrogen containing C-surfactants compounds with one linear alkyl chain attached to the nitrogen atom decompose faster than compounds with two or three alkyl chains. The replacement of the methyl group by phenyl influences insignificantly on the rate of the decomposition of surfactants [9].

Over a half surfactants produced are accounted for A-surfactants. The hydrophilic polar group of A-surfactants is capable of the intense molecular interaction, hydrocarbon part, practically insoluble in water, is an elongated

chain that consists of 10–18 carbon atoms. The presence of these groups in the structure of A-surfactants gives diphilic properties. At the study of biodegradability it is necessary to consider numerous factors: the structure of A-surfactants, compositions of waters, presence of microorganisms in the medium, concentration, temperature *etc.*

In countries with developed petroleum industry and oil refining both at the production, transportation and refining it is practically impossible to avoid accidents and other unforeseen situations that leads to the contamination of the hydrosphere. Oil spilled on the water surface is mainly removed by mechanical means, except for thin oil films. In this case one has to apply special sorts of surfactants that should possess petroleum collecting and dispersing properties [10–12], in addition, they should be ecologically safe.

In this connection, that was interesting to study the biodegradability of A-surfactants with oil-collecting and dispersing properties obtained on the ground of individual fatty acids or a mixture of fatty acids isolated from vegetable oils.

EXPERIMENTAL

Linolenic acid (LA), *viz.*, monobasic carbonic acid with three isolated double bonds, as well as acids isolated from the vegetable oil were used as polyunsaturated fatty acids. A mixture of unsaturated fatty acids was isolated from the corn oil (CO) using the saponification followed by treatment with hydrochloric acid. Triglycerides available in the composition of CO convert into sodium soaps, while glycerin is formed as a by-product.

The mixture of acids obtained was used further without the separation. Acids isolated from CO and individual LA were sulphated with a solution of sulphuric acid. The structure of products obtained has been confirmed by the FTIR spectroscopy. Some properties of sulphated fatty acids (SLA, SFA) have been defined analytically.

For the preparation of calcium salts the 10 % salt of calcium chloride was mixed with sulpho acids with the ratio of 2 : 1 at room temperature. Calcium salt of sulpho acids is not soluble in water and it is isolated by filtration. The elemental and chemical composition of A-surfactant on the ground of LA were identi-

fied by the XRF microscopy. The elemental analysis of samples was carried out using a XGT-7000 X-Ray Analytical Microscope (Horiba, Japan) at an accelerating voltage of 50 kV; the diameter of the incident X-ray beam is 100 μm , measurement time is 60 s.

The elemental and chemical composition of A-surfactant on the ground of LA were identified by the XRF microscopy. The elemental analysis of samples was carried out using the Horiba XGT-7000 microscope (Japan) at an accelerating voltage of 50 kV; the diameter of the incident X-ray beam is 100 μm , measurement time is 60 s.

^1H NMR spectra of the reaction products were characterized using a Bruker Avance 400 MHz spectrometer; the solvent is $\text{DMSO}-d_6$, standard is HMDS (hexamethyldisiloxane). The chemical structure of fatty acids isolated from CO and sulphated acids has been characterized by physicochemical and spectral methods. IR spectra were recorded on a Bruker FTIR spectrometer by use of KBr pellets in the frequency range of 4000–500 cm^{-1} , as well as the PerkinElmer Spectrum BX II spectrometer, in the range of 4200–400 cm^{-1} .

Petroleum collecting properties of A-surfactant (calcium salts of sulpho acids) have been investigated on the example of oil of the Romany deposit (Apsheron Peninsula, Azerbaijan). The characteristics of petroleum: the density 0.86 g/cm^3 , kinetic viscosity at 20 $^\circ\text{C}$ is 16 mm^2/s . A surface active compound or its solution (5–10 % solution in ethanol) was added to a thin film of oil (the thickness is 0.16–0.17 mm) in a Petri (cell-culture) dish to the surface of various waters (distilled, fresh, sea). The coefficient

of petroleum collecting (K) was counted according to the formula $K = S_0/S$, where S_0 is the area of the surface of the initial film; S is the area of the surface of the collected film. Measurements of the area of the spot were carried out in the fixated interval of time (τ). The coefficient of petroleum collecting expresses the relation of the initial area of oil film to the area of a petroleum spot formed. In the dispersing of the oil slick was determined by the degree of purification of the water surface or coefficient of petroleum collecting (K_d), calculated as the ratio of the area of the oil film on the peripheral portion to the original area of the film.

Tests on the identification of biodegradation A-surfactant were performed as follows. Samples filtered (solutions in the river water) were prepared daily or through certain time intervals and the interfacial tension was determined at the phase boundary water/kerosene according to the methodology described in [13]. The microflora of river water (Goychay River, Azerbaijan) on species on the species composition is mainly represented by bacteria adapted to the permanent dwelling: *Chromobacterium Violaceum*, *Bacterium Aquatilius*, *Mikrococcus Candicans*, *Pseudomonas Fluorescens* and *Micrococcus Roseus*. The number of bacteria in the clean river water does not exceed 100–120 cells in 1 mL.

Biodegradation (D) for each sample was calculated according to the equation

$$D = [(\gamma_t - \gamma_0)/(\gamma_{b/\tau} - \gamma_0)] \cdot 100 \%$$

where γ_t is the interfacial tension at time τ ; γ_0 is the interfacial tension at the initial time; $\gamma_{b/\tau}$ is the interfacial tension at the blank run.

TABLE 1

Physicochemical properties of fatty acids (FA) and sulpho acid (SA) on the ground of corn oil (CO)

Acids	n_d^{20}	ρ , g/cm^3	η , mm^2/s , at T , $^\circ\text{C}$		Iodine number, $\text{mg I}/100\text{g}$	Acidic number, $\text{mg KOH}/\text{g}$	Temperature, $^\circ\text{C}$		Zonality	Colour, units of CNT
			40	100			boiling	freezing		
Extracted from CO	1.4660	0.9180	32.85	7.53	103	147.5	313	–20	0.04	3.0
LA	1.4800	0.906	36.45	9.14	2735	224	232	–11	0.02	Colourless
SA	1.4580	0.915	40.31	9.78	–	284	241	–12	–	The same

Note. n_d^{20} is coefficient of refraction; ρ is density; η is kinematic viscosity.

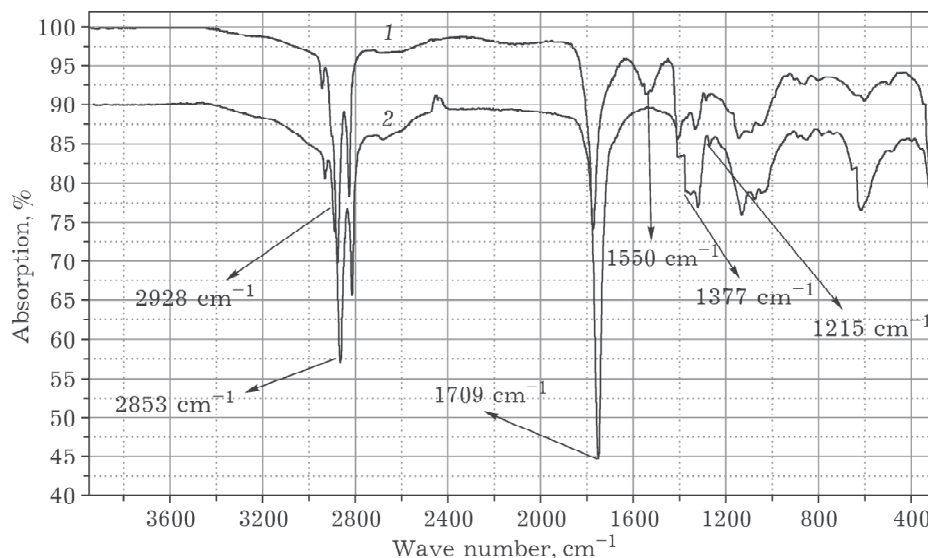


Fig. 1. IR spectrum of fatty acids: 1 – isolated from corn oil, 2 – after sulphatization.

RESULTS AND DISCUSSION

Physicochemical properties of the starting polyunsaturated fat acids and sulpho acid prepared on the ground of CO have been defined (Table 1).

The acidic number of sulphated FA is seen to increase from 147.5 to 284 mg of KOH/100 g of the product due to the formation of sulpho groups. The absence of the reaction of iodine indicates that the process of sulphatization has ended and there are no unsaturated bonds in the composition of the fatty acid.

It can be seen from the data of Fig. 1 that the absorption bands of fatty acids of 721 cm^{-1} correspond pendulum vibrations of CH_2 groups, 913 and 967 cm^{-1} due to the vibrations of the $\text{C}=\text{C}$, 1098 cm^{-1} (deformation vibrations of the bond $\text{O}-\text{H}$, 1237 cm^{-1} do stretching vibrations of the bond $\text{C}-\text{O}$, 2853 and 2922 cm^{-1} correspond to stretching vibrations of the $\text{C}-\text{H}$ bond of groups CH_3 CH_2 , 3008 cm^{-1} to unsaturated bonds, 1743 cm^{-1} is to the bond $\text{C}=\text{O}$. IR spec-

tra of sulphated fatty acids isolated from corn oil and sulphated LA are presented in Figs. 1 (curve 2) and 2. Here, absorption band at 1244 , 1283 and 1412 cm^{-1} are observed corresponding to vibrations of groups $\text{R}-\text{O}-\text{SO}_2-\text{OR}$, SO_3H . The peak at 1377 cm^{-1} is connected with the group SO ; the peak at 1550 cm^{-1} corresponds to the band $\text{C}=\text{C}$ that disappears after the process of sulphatization (see Fig. 1) of fatty acids isolated from corn oil (in Fig. 2 this peak is absent).

Physicochemical properties of Ca salts of sulpho acids on the ground of LA and fatty acids (FA) isolated from corn oil (Table 2) have also been identified.

The elemental and chemical composition of A-surfactants on the ground of LA (mass %): Ca 11.7, SO_3 36.5, C 51.7 (defined by the sample balance) by the XRFM method. It is noteworthy that there is no nitrogen and calcium in the composition in the Ca salts on the ground of LA.

The XRF spectrum and optical image of Ca salt of sulpho acids on the ground of LA is presented in Fig. 3.

TABLE 2

Physicochemical properties of Ca salts of sulpho acids on the ground of linoleic acid (LA) and fatty acids (FA) isolated from corn oil (CO)

Salts	Density, g/cm^3	Molecular mass	Freezing point, $^{\circ}\text{C}$	Solubility in ethanol
On the ground of LA	0.971	460	-21	+
On the ground of FA	0.952	462	-20	+

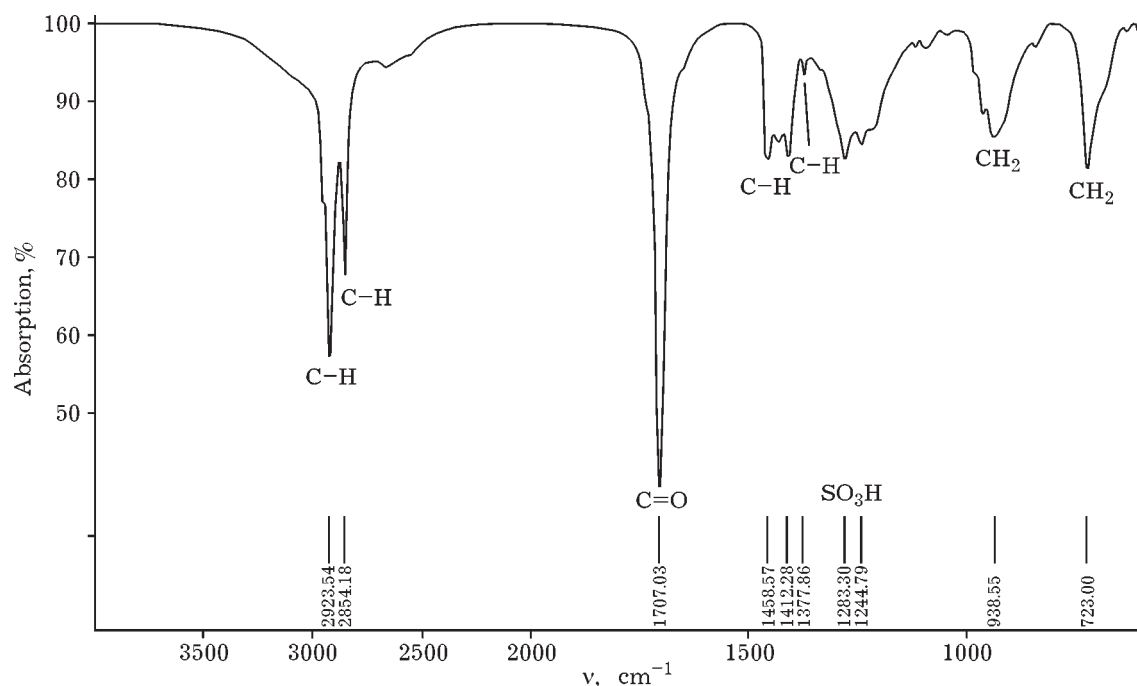


Fig. 2. IR spectrum of sulphated linolenic acid.

As a result of investigations carried out, it has been established that calcium salts synthesized on the ground of LA and acids isolated from CO display good petroleum collecting and dispersing properties in all environments tested (drinking, distilled, sea water) in the diluted form and they can hold thin oil films over 70–166 h (Table 3). However in the undiluted, they have a weak petroleum gathering capability in distilled and fresh water. The maximal coefficient of petroleum gathering is observed in case of sea water and it is 88.5 for a mixture of

acids and 90.2 for calcium sulphate of LA. In this case sea water (the density is 1.0098 g/cm^3 , pH 7.7) has the following chemical composition: Na^+ 2.99, Ca^{2+} 0.34, K^+ 0.09, Mg^{2+} 0.70, Cl^- 5.18, SO_4^{2-} 2.98. At the concentration of salts in ethyl alcohol of 5 and 10 % petroleum collecting properties of salts improve. At the concentration of 10 % the coefficient of petroleum collecting of calcium sulphate the fresh water reaches 93.3, the reagent is active during 6–7 days. Therefore, A-surfactant, calcium sulphate on the ground of a mixture of LA isolated from

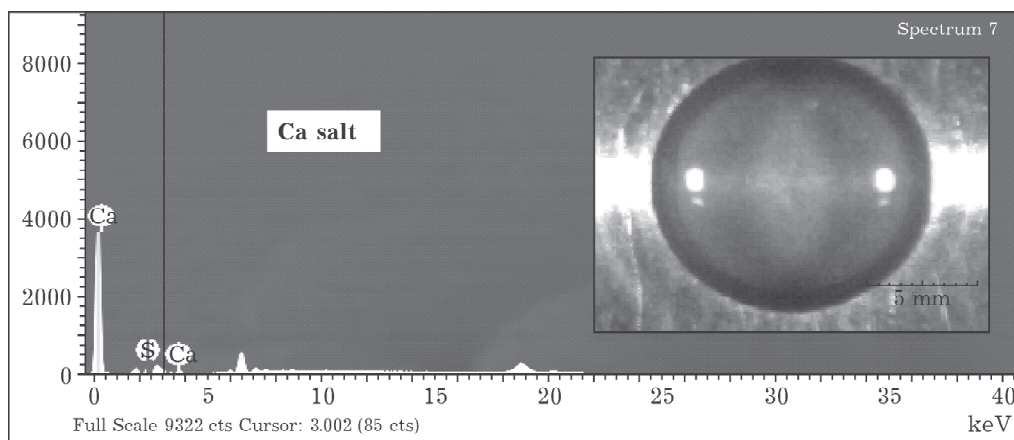


Fig. 3. XRF spectrum and optical image of Ca salt of sulpho acids on the ground of linoleic acid.

TABLE 3

Petroleum collecting and dispersing properties of calcium surfactants on the ground of SFA/SLA

Surfactants	Water					
	Distilled		Fresh		Sea	
	τ , h	$K(K_d, \%)$	τ , h	$K(K_d, \%)$	τ , h	$K(K_d, \%)$
Undiluted product	0/0	15.8/5.6	0/0	10.2/8.9	0-166/0-166	(88.5)/(90.2)
	30/70	32.5/13.5	5-166/70	26.6/22.7		
	166/96-166	35.8/34.9	/166	/28.7		
5 % solution in ethanol	0/0	12.2/12.2	0/0	15.2/(84.7)	0/0-166	10.1/(91.5)
	45-166/4-166	35.9/36.8	45/4-166	(82.6)/(91.7)	4-28/-	(82.6)/
			166/	(91.7)/	52/-	(84.7)/
					166/-	(88.9)/
10 % solution in ethanol	0/0-4	10.1/15.2	0/0	13.5/15.2	0/0	13.0/15.2
	52/76	23.5/36.3	40/45	(86.8)/(88.9)	40/45	(86.8)/(84.7)
	166/	35.4/	166/28.5	(91.7)/(91.7)	166/22	(91.7)/(86.8)
			/166	/(93.3)	/166	/(91.7)

Note. The first value is for surfactants on the ground of SFA, the second one is on the ground of SLA.

corn oil and calcium sulphate on the ground of LA possess high petroleum gathering and dispersed activity in relation to thin film of petroleum on the surface of ponds.

Forms of oil films on the surface of sea water before and after the addition of Ca salt on the ground of fatty acids isolated from corn oil are shown in Fig. 4.

The ability of Ca salts towards the biodegradation is studied at concentrations of 0.025 and 0.05 mass % in river water under stationary conditions (Table 4). It is seen that the salt on the ground of SLA at the concentration of 0.05 % mass possess a larger degree of the biodegradation, in comparison with the salt on the ground of SFA. With the decrease of the concentration twice the degree of biodegradation increase by three times. In the period of

5-15 days the level of biodegradation of salts SFA ranges in the range of 30.97-62.04 %, salts SLA in the diapason of 44.43-74.4 %. Starting for 25 days before testing this indicator for SLA reaches 81.4 %, while for SFA 72.4 %. Differences in the biodegradability of salts may be related to the composition of fatty acids, in particular, the structure and structure of the hydrophobic hydrocarbon part of molecules. It is known that the composition of CO include various acids including palmitic and stearic. After 25 days the product decomposes fully and it is not dangerous in the ecological aspect. Based on results of investigations Ca salts of SFA and SLA, according to the classification of surfactants, on biodegradation can be related to the 4th class (State Standard GOST 50595-93).

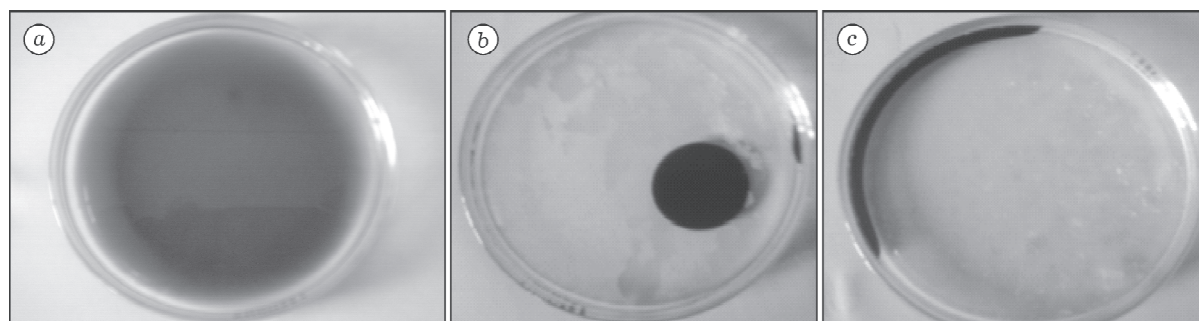


Fig.4. Forms petroleum films on the surface of water: a – before the addition of the reagent, b – the aggregation after the addition of reagents (petroleum collecting), c – the dispersion after the addition of reagents (petroleum dispersing).

TABLE 4

Results of the study of biodegradability of A-surfactants in river water at concentrations of 0.05 and 0.025 mass %

Ca salts	Time, day						
	2	4	6	10	16	25	30
C = 0.05 mass %							
SFA	9.95	13.07	15.30	19.14	22.20	24.20	–
SLA	12.25	16.08	19.14	22.94	25.27	26.79	–
C = 0.025 mass %							
SFA	6.88	20.93	30.97	48.26	62.04	72.40	–
SLA	11.12	29.64	44.43	62.81	74.40	81.40	–

CONCLUSION

Therefore, as a result of the study carried out, it has been established that petroleum collecting and dispersing reagents capable of decomposing in the environment to ecologically safe compounds can be obtained on the ground of Ca salts of sulphated fatty acids (a mixture of acids isolated from corn oil and linolenic acid). It has been established that most hydrophobic molecules of A-surfactant decompose primarily.

REFERENCES

- 1 Lange K. R., Poverkhnostno-Aktivnye Veshchestva. Sintez, Svoystva, Analiz, Primeneniye, Professiya, St. Petersburg, 2005.
- 2 Humbatov G. A., Dashdiev R. A., Primeneniye PAV dlya Likvidatsii Avariynykh Razlivov Nefti na Vodnoy Poverkhnosti, Elm, Baku, 1998.
- 3 Gornitskiy A. B., Gurvich L. M., Mironov O. G., Mochalova O. S., Nemirovskaya I. A., Nesterova M. P., in: Metody i Sredstva Bor'by s Neftyanyim Zagryazneniem Vod Mirovogo Okeana, in M. P. Nesterova (Ed.), Gidrometeoizdat, Leningrad, 1989.
- 4 Bocharov V. V., Peregudin Yu. F., Markina L. S., in P. A. Petrov (Ed.), Belgorod, 1991, p. 133.
- 5 Yoshizako F., Chubachi M., Ueno T., *Jpn. J. Limnol.*, 45, 3 (1984) 204.
- 6 Kuznetsov A. E., Gradova N. B., Nauchnye Osnovy Ekobiotehnologii, Mir, Moscow, 2006.
- 7 Rosen M. J., Surfactants and Interfacial Phenomena, 3rd ed., J. Wiley, NY, 2004.
- 8 Shuichi M., Kazayasu I., Sadao Y., Kazuo K., Tsuyohi U., *J. Am. Oil Chem. Soc.*, 67 (1990) 996.
- 9 Swisher R. D., Surfactantbiodegradation, 2nd ed., M. Dekker, NY, 1987.
- 10 Asadov Z. H., Ahmadova G. A., Rachimov R. A., *J. Kor. Chem. Soc.*, 55, 6 (2011) 1012.
- 11 Asadov Z. H., Salamova N. V., Eyubova S. K., *Proc. Petrochem. Oil Refining*, 11, 1(41) (2010) 28.
- 12 Lateef H., Abd El, Abbasov V. M., Aliyeva L. I., *Caspian J. Appl. Sci. Res.*, 1 (9) (2012) 57.
- 13 Fable J., Surfactants for Consumer, Springer Verlag, Heidelberg, 1986, ch. 4, p. 286.