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Research Article

REAGENT PREPARATION FOR OIL TREATMENT AND ITS USE IN THE PROCESS OF DEHYDRATION

KAZIM S. NADIROV [1*], GULNAZ ZH. MOLDABAYEVA [2], SALTANAT E. BAIBOTAYEVA [2], YURY V. ZEYGMAN [3] AND AYNUR S. SADYRBAYEVA [1]

[1]Department of Oil and Gas Business, M. O. Auezov South Kazakhstan State University 160012, Tauke Khan Ave. 5, Shymkent, Republic of Kazakhstan

[2]Department of Development and Operation of Oil and Gas Fields, K.I. Satbayev Kazakh National Technical University 050013, 22 Satpayev Street 22, Almaty, Republic of Kazakhstan

[3]Department of Development and Operation of Oil and Gas Fields, Ufa State Petroleum Technological University (USPTU) 450000, 1 Kosmonavtov Street, Ufa, Russian Federation

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ABSTRACT

Due to high stability of water-oil emulsions stabilized by natural surfactants and resins, their destruction can only be achieved with the help of demulsifiers. The consumption of the demulsifier is determined by the need to obtain commercial oil with a water content of less than 0.2%, at a higher water content, the cost of oil on the market is reduced, and at 1% oil is considered substandard. Since the cost of demulsifiers is quite high (1.5-2.8 thousand dollars per ton), the problem of reducing their consumption due to the increase in the efficiency of reagents and reducing the cost is very relevant. The aim of the work is to obtain a reagent-demulsifier based on fatty acids of cottonseed oil and to study the possibility of its use for dehydration of crude oil. It was determined the most favorable regimen of neutralization and separation of fatty acids of gossypol resin which subsequently provides the greatest yield of demulsifier. Oxyethylated derivatives of fatty acids and gossypol contained in the product isolated from the saponified gossypol resin were obtained by the action of ethylene oxide on it. To obtain reagent-surfactant on the basis of isolated fatty acids with high demulsibility, it is required to obtain an optimal ratio of the number of hydrophilic and hydrophobic groups (hydrophilic-lipophilic balance). Surface-active properties of reagents prepared by hydroxyethylation of AF and containing a different number of ethylene oxide groups were investigated. Analysis of the values of surface activity showed that the investigated demulsifier variants have similar surface activity values, but the maximum value was obtained with 70% ethylene oxide content. It has been established that the purity of the initial AFs also affects the demulsifying activity of oxyethylated derivatives, a pronounced deviation in the properties of the product obtained on the basis of purified AFs with an impurity content of about 1.2-1.3% is observed. The maximum value of the amount of water released from water-oil emulsions under these conditions is 94% with a content of 60% ethylene oxide in the reagent. The remaining versions of the raw material provide a water separation of 91% with an ethylene oxide content of 70%. The possibility of using a new raw material – purified

***Corresponding authors email: nadirovkazim@mail.ru**

fatty acids of gossypol resin – for the synthesis of nonionic demulsifiers of the "Gossilvan" series by the method of oxyethylation is shown. When the reagent "Gossilvan" is used in the amount of 30-60 g/m^3 the residual water content in oil is reduced to 0.08-0.5%, salts – to 60-210 mg/l, oil in water – to 50-170 mg/l, that is, the obtained "Gossilvan" reagent is a demulsifier which provides a good degree of desalting and dehydration at a flow rate of 30-60 g/m^3 of crude oil.

INTRODUCTION

At present, the exploitation of the oil fields in Kazakhstan, aimed primarily at achieving maximum oil production, has led to a clear increase in the share of hard-to-recover oil and a decrease in the share of active oil reserves (The economy of Kazakhstan, 2016; Ishekenova, 2017; Valisheva, 2013; Kapitonov, *et al*., 2016). For example, in some Kazakhstan deposits, the water-cut of the produced oil reaches 85-90%. Stable water-oil emulsions stabilized by natural surfactants and resins contained in the borehole products are very difficult to break down and create certain difficulties both in the supply to the main oil pipeline and during the processing of oil (Usheva, *et al*., 2013; Persiyantsev, 2000; KAZREFINEX, 2012). Because of the high stability of such emulsions, their destruction can only be achieved with the help of demulsifiers. The consumption of the demulsifier is determined by the need to obtain commercial oil with a water content of less than 0.2%, with a higher water content, the cost of oil on the market is reduced, and at 1%, oil is considered substandard. Since the cost of demulsifiers is quite high (1.5-2.8 thousand dollars per ton), the problem of reducing their consumption due to the increase in the efficiency of reagents and reducing their cost is very relevant (Mastobaev, *et al*., 2002; Manovyan, 2001; Mastobaev, *et al*., 2000). Solutions to the problem of destruction of persistent water-oil emulsions can be achieved in various ways. The chemical-technological method is the development of methods for the application and synthesis of new reagents with demulsifying ability. Deeper dehydration of oil at a lower consumption of reagents can be achieved by using composite demulsifiers from several chemical compounds, provided that a synergistic effect appears between these compounds: compounding of surfactants of different structures allows, in the presence of a certain set of initial components, to obtain compositions with different properties and efficiency (Mastobaev, *et al*., 2000; Semikhin, 2004; New technologies of extraction, 2014; Nurabaev, 2010; Nadirov, *et al*., 2015). It is also promising to increase the efficiency of demulsifiers by obtaining their nanomodifikatsii, in which they in their solutions are in a state of critical emulsion with particle sizes of the order of 30-100 nm (Semikhina, *et al*., 2009; Popova, *et al*., 2012; Nadirov, *et al*., 2016). These methods make it possible to improve the basic properties of demulsifiers and expand their functional action in the extraction, transportation and preparation of various classes of oils.

When selecting a surfactant for demulsifying action, it is economically justified to use the available raw materials in order to obtain a reagent with a low-cost price. In this aspect, the prospective raw materials are the by-products obtained during the processing of cottonseed oil, the so-called sapphonic refining and tar oils for vacuum distillation of fatty acids (gossypol resin). Since in sapustokah and tar, the content of fatty acids (AF) averages from 40 to 60%, thenõ taking into account the potential of fat-and-oil enterprises of Southern Kazakhstan, they can be considered a promising starting material for obtaining reagents of demulsifying action for oil dehydration (Nadirov *et al*., 2013; Nadirov, 2012). The aim of the work is to obtain a reagent-demulsifier based on fatty acids of cottonseed oil and to study the possibility of its use for dehydration of crude oil.

MATERIALS AND METHODS

1. Gossypol resin (GR)

In the course of the work, the following GR was used: 98.29% organic matter; 1.71% of inorganic substances; 100% of ether-soluble substances; The acid value is 68.5 mg KOH; Iodine number is 97; The saponification number is 200 mg KOH/g; The etheric number is 135 mg KOH; The hydroxyl number is 91%; AF, released by saponification is 62%; Low-fat substances, including gossypol is 38%.

2. Ethylene oxide C_2H_4O

Has a high reactivity, Due to the ease of opening the stressful three-membered epoxy cycle, ethylene oxide can attach substances containing a mobile hydrogen atom to form β-hydroxyethyl derivatives, and also polymerize. At ordinary temperature and pressure, ethylene oxide is in a gaseous state, at low temperatures it is an easily volatile colorless liquid.

3. Water-in-oil emulsions

In this paper, the effectiveness of the demulsifiers was investigated on artificial water-oil emulsions with a water content of 40-90% which were obtained by means of a mechanical stirrer with a rotation speed of about 3000 rpm for 10 min. As the aqueous phase of the emulsion, either mineral water taken from the well or its model was used which was a 1% NaCl solution in distilled water. As the oil phase of the emulsion, the oil from the Kumkol and Aschysai fields was used. In all cases, the mixing time of the emulsion was chosen such that, without the introduction of a demulsifier, within 1-1.5 hours, the amount of water emitted from the emulsion was close to zero.

4. Investigated demulsifiers

1) The product obtained on the basis of GR, which has a demulsifying ability and is called "Gossilvan"; 2) commercial demulsifier Dissolvan 4411.

5. Isolation and analysis of free fatty acids

GR contains from 52 to 64% of crude FA and their derivatives, the rest is the condensation and polymerization products of gossypol and its transformations, which are formed when the oil is extracted, mainly during the distillation of the FA from sapstock. Saponification of the GR with a solution of alkali resulted in a saponifiable fraction of the salt of FA and gossypol, which were then liberated in the treatment with sulfuric acid (Nadirov, *et al*., 2014).

To carry out the saponification process, 100 grams of resin was weighed on a technical scale, heated on a sand bath with stirring to a temperature of 90-100°C. Then, with the mixing, the amount of sodium hydroxide, calculated with respect to the acid number, was excessively introduced. The temperature of the mixture was increased by 10°C, the speed of the mixer was decreased and stirred for 10 minutes until a clearly visible layer of saponified fatty acids was formed. The stirring was then stopped and the mixture was centrifuged at a rotor speed of $50s^{-1}$ for 5 minutes. After separation and weighing, the separated saponified and unsaponifiable portions of the GR were subjected to assays (Nadirov, *et al*., 2014b). As a result of decomposition of the obtained saponified fraction with mineral acids, a mixture of FA and gossypol was obtained.

6. Carrying out the process of oxyethylation of FA

The oxyethylated derivatives of FA and gossypol contained in the product isolated from saponified GR were obtained by the action of ethylene oxide on it. The total reaction of the condensation of ethylene oxide with FA proceeds through the formation of an intermediate complex (Abramzon, *et al*., 1988; Shenfeld, 1982; Beskov and Safronov, 1999). The hydrophilic constituent of all non-ionic surfactants is polyethylene glycol chains obtained by sequentially attaching ethylene oxide to the hydrophobic component at the site of the mobile hydrogen atom. The yield of the product depends on a set of factors: the nature of the starting substance, the chemical nature of the catalyst, the process temperature, the molar ratio of the reactants (Shenfeld, 1982). Synthesis of hydroxyethylated derivatives based on FA was carried out on a plant, the scheme of which is shown in (Fig. 1).

In a pre-weighed reactor equipped with a stirrer, thermometer, condenser and bubbler for introducing ethylene oxide, a sample (50-80 g) of the feedstock was placed and 1% by weight was added. Catalyst (by weight of the sample). The entire plant was sealed to prevent loss of ethylene oxide. After the assembly of the plant, the electric motor was started and stirring was started, then heating was switched on. At a temperature of more than 1000 ° C, the water introduced into the flask with reagents began to evaporate. After evaporation of the moisture, the temperature was raised to 180-190°C and ethylene oxide gas was fed. The amount of ethylene oxide added was determined from the weight gain of the reaction mass (in % by weight). Usually, when oxyethylated, products containing 30%, 40%, 50%, 60% and 70% by weight can be obtained. Polyethylene glycol residues. Having obtained one preset sample of the ethoxylated product, a sample was taken from the reaction zone for analysis and the oxyethylation process was continued until the next sample of the target substance was obtained. Tertiary amines were used as a catalyst to reduce the rate of formation of by-products. The number of ethylene oxide groups was determined by the increase in the mass of the sample of the FA used for the synthesis and checked by the Sigia method (Levchenko, *et al*., 1967; Serebryakov, *et al*., 1989) and also for the express evaluation by a calibration graph constructed from experimental data and having the form of a linear dependence of the density of the oxidized product on the number of groups Ethylene oxide. Both methods yield well reproducible results. Subsequently, the reagent was run without weighing under optimal conditions. Quantitative analysis of the obtained product was carried out by gas-liquid chromatography.

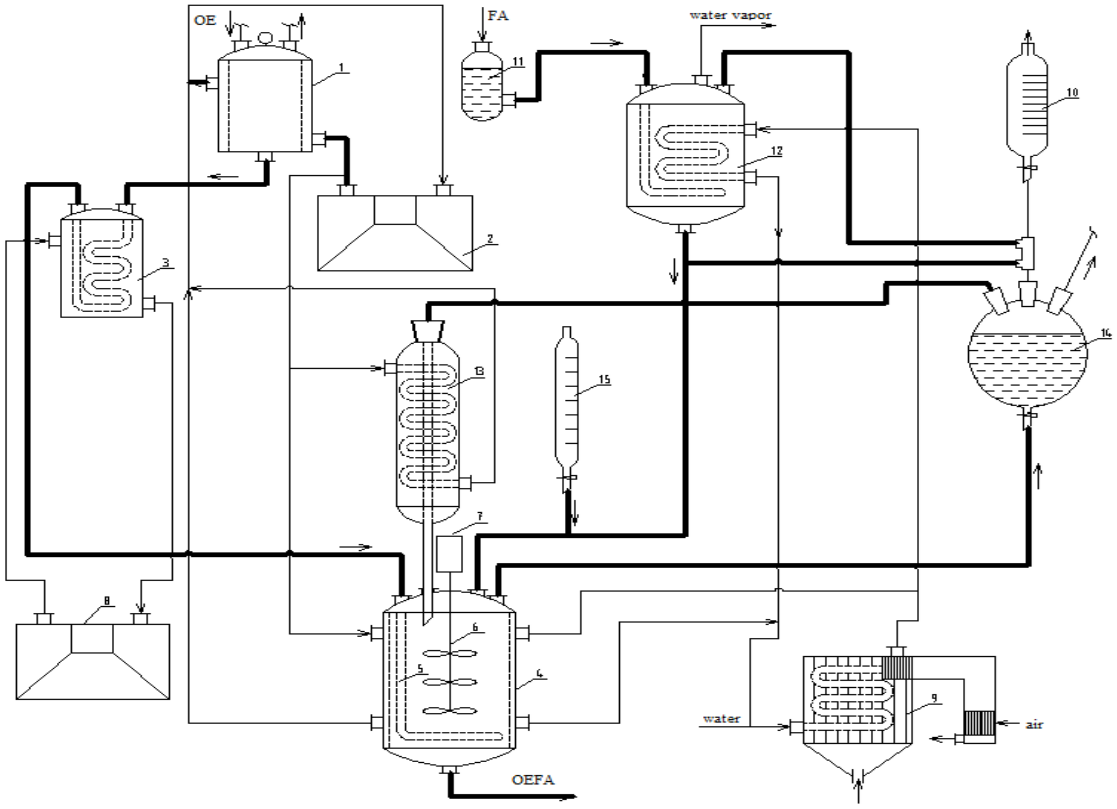


Fig. 1 Scheme of a laboratory unit for the oxyethylation of FA.
1 – measure of liquid ethylene oxide; 2 – thermostat-cooler; 3 – heater; 4 – reactor; 5 – bubbler; 6 – mechanical stirrer; 7 – the electric motor; 8 – thermostat; 9 – laboratory steam generator PGL-7M; 10 – alkali measure; 11 – capacity for FA; 12 – apparatus for drying FA; 13 – the return refrigerator; 14 – trap for ethylene oxide; 15 – a catalyst measuring device.
——— – material flows; ——— – energy flows.

7. Analysis of FA

To study the fractional and fatty acid composition, the FA was extracted from the studied objects by the Blay and Dyer method using the chloroform-ethanol-water solvent system. The fractional composition of the FA is determined by thin-layer chromatography on "Silufol" plates in the solvent system "hexane-diethyl ether-acetic acid" (70: 30: 2) followed by chromatograms in iodine vapor. The determination of the mass fraction of the trans-isomers of FA was carried out in accordance with GOST R 51483-99 "Vegetable oils and animal fats". Mass fraction of methyl esters of individual FAs to their sum was carried out by the method of gas chromatography according to GOST 30418-96 "Vegetative oils. Method for determination of fatty acid composition". The mass fraction of the FAs themselves in the GR was determined by the method of high-performance liquid chromatography by the method of "Certificate No. 36-08 dated 04.03.2008 FR.1.31.2008.04633" (Method for performing measurements of the mass fraction, 2008). The method is based on the destruction of the ester linkages of triglycerides of the sample by alkaline hydrolysis with the release of FA in free form and, after chromatographic separation in the isocratic mode, subsequent detection by a low-temperature light scattering detector. Preparation of samples for measurements included the following steps: alkaline hydrolysis of the ester linkages of triglycerides of the analyzed product with the release of FA; Selection of aliquots of hydrolyzate; Preparation of a sample for entering a chromatograph. Two parallel samples were prepared for the analysis. For chromatographic separation of LC isocratic high performance liquid chromatography (HPLC) – system with light scattering detection – was used. A liquid chromatograph "Stayer" was used with the characteristics: a light scattering detector, a low-temperature evaporator of 75; Personal computer with the installed software "MultiChrome for Windows XP" version 2x. Conditions: isocratic regime; Column: "Synergi Fusion-RP" 250 × 4.6 mm 4 microns (Phenomenex, USA); Protective column: "Synergi Fusion-RP" 4 × 3.0 mm (Phenomenex, USA); Mobile phase: acetonitrile-water-CH_3COOH solution (110: 12: 3 v/v); Flow rate: 0.9 ml/min; Temperature:

25°C; Volume of the loop dispenser: 10 µl; Detection: by light scattering; Evaporating tube temperature: +40°C; Gas pressure at the detector inlet: 3.0 bar; Gain factor of the output signal: 1.0.

Analyzes of oil and the efficiency of demulsification were carried out according to the methods (Sakhabutdinov, *et al*., 2009; ST-07.1-00-00-02, 2013). The incoming emulsion was taken from a sampler installed on a common collector to the point of supply of a demulsifier (booster pump stations). In test samples of the emulsion, the test demulsifiers with different unit costs were dosed, and then the samples were shaken for 2 minutes and stood for 90 minutes at 40°C. At certain intervals, the amount of water released and the quality of the oil-water phase were recorded. After the sludge, the separated water was removed with a special syringe, the remaining oil, together with the intermediate layer, was centrifuged for 5 minutes at a rotor speed of n=2000 rpm^{-1}. Centrifugation determined the residual water content in the oil and intermediate layer, with the remaining water after centrifugation being released as a free phase and a residual unbroken emulsion. The more residual water in the oil remains in the form of an undamaged emulsion, the lower the effectiveness of the demulsifier, the greater the risk of formation and accumulation of intermediate layers in slop equipment. In the control sample (without reagent) before and after settling, the aggregative stability of the emulsion was also determined by centrifugation, which characterizes the degree of stability of the emulsion, its ability to self-destruct in the settling process.

8. Complete synthesis of demulsifying reagent

Fig. 2 shows the principal technological scheme for the preparation of the demulsifying reagent developed by us (Nadirov, *et al*., 2013). In accordance with the technology in the mixer 2, an alkali solution was prepared, for this purpose water is supplied to the mixer from the tank 1, where alkali is simultaneously charged. The solution prepared in the mixer 2 enters the reactor 4. Then, the GR is pumped through the rotator 11 from the vessel 3. The jacket of the reactor

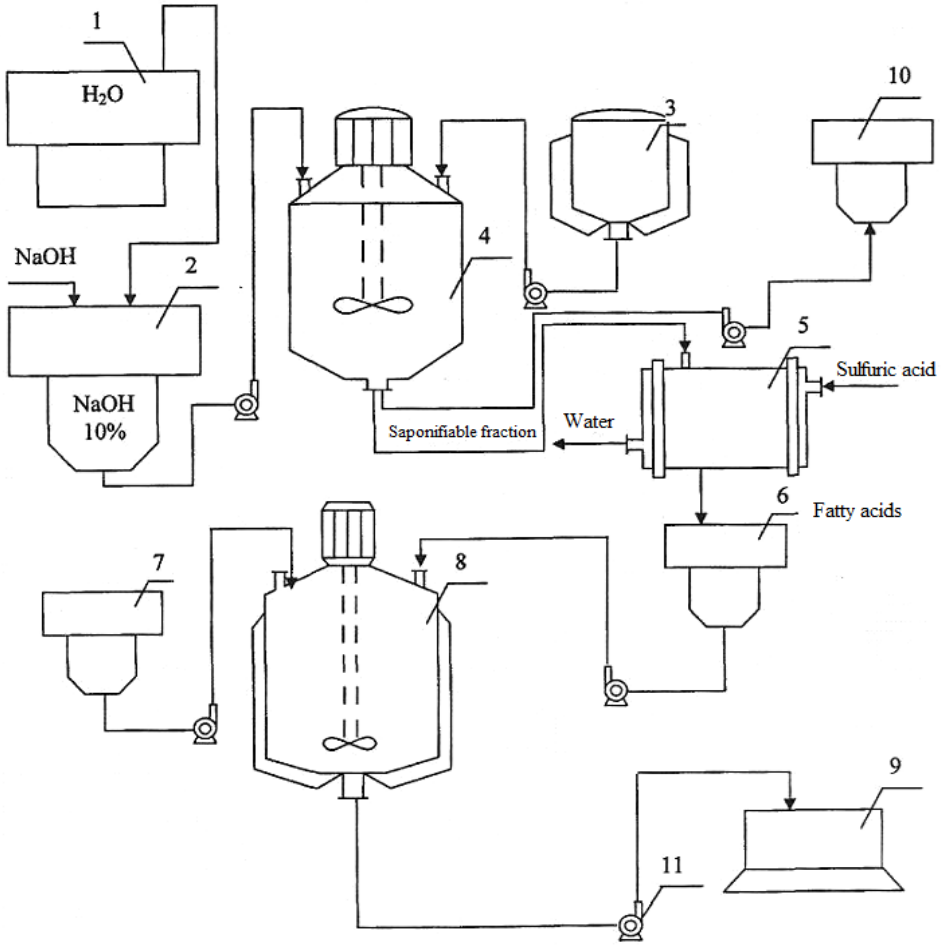


Fig 2 Principal technological scheme of reagent-demulsifier obtaining.
1, 2, 6, 7, 10 – capacity, 2 – mixer, 3,8 – reactors, 5 – centrifuge, 9 – reservoir of finished products, 11 – rotator.

is fed with steam, the temperature is gradually raised to 110° C and the saponification process is carried out for 2 hours. The result is a product of a dark brown color in the form of a gel, readily soluble in water. The saponifying part of the GR enters the centrifuge 5, and the unsaponifiable part enters the reservoir 10. In the centrifuge 5, the saponifying part of the GR is treated with 11% sulfuric acid solution to a pH of 4-5. Then, the obtained FA is separated into a container 6. Fatty acids are supplied from the vessel 6 through the rotator to the reactor 8, and ethylene oxide from the tank 7. The synthesis is carried out at a temperature of 120-130 ° C and 0.2-0.7 MPa for 2.5 hours. The resulting reagent-demulsifier solution is pumped to the finished product tank.

RESULTS AND DISCUSSION

Earlier, we determined the most favorable regime of neutralization of the FA GR, which subsequently provides the greatest yield of a demulsifier: the effective concentration of the alkali solution corresponds to 10-15%, the excess of alkali is 20%, the amount of the saponified GR additive is 9-12%, the temperature is 105-110°C, and the duration of the process is 120 minutes. For the developed method of isolating FAs, the optimal process parameters are: temperature – 90°C, concentration of saponifiable fraction before decomposition – 20%, concentration of sulfuric acid – 11%. Excess sulfuric acid is not required, because It lowers the output of FA. Such process conditions ensure the yield of FA in the amount of 85-87% of their content in the initial GR. Gossypol, both in free and in a bound form, allowing to determine its content, is extracted at the same time by 65-68% (Nadirov, *et al*., 2014). The oxyethylated derivatives of FA and gossypol contained in the product isolated from saponified GR were obtained by the action of ethylene oxide on it.

To obtain reagent-surfactant on the basis of isolated FA with high demulsibility, it is required to obtain an optimum ratio of the number of hydrophilic and hydrophobic groups (hydrophilic-lipophilic balance). In the process of oxyethylation, the length of oxyethylene chains attached to individual molecules of the starting material is not the same, so a mixture of molecules with oxyethylene chains of different lengths is always obtained. The resulting non-ionic compound is characterized by the average value of its oxyethylene chains. It is generally believed that in order to achieve the required quality and consumer properties of the product obtained, it is necessary that the distribution of oxyethyl polymer homologs in the reaction mixture be as narrow as possible (Abramzon, *et al*., 1988; Shenfeld, 1982; Nadirov, *et al*., 2015). However, in our case, taking into account the complex and unstable composition of the fatty part of the GR, as well as the subsequent task of obtaining composite demulsifiers from several chemical compounds, the oxyethylation process was carried out by us on the basis of the criterion chosen – the maximum yield of the target oxyethylated product.

Fig. 3 shows the dependence of the concentration of a mixture of polymer homologues on the degree of oxyethylation. The efficiency of the synthesis process is also affected by the amount of water in the feedstock and in ethylene oxide. When oxyethylated in the presence of water, polyoxyethylene glycols are formed, the content of which, depending on the water content, reaches 15-25% in the demulsifier. Therefore, all the initial reagents for the synthesis were subjected to dehydration.

The obtained batch of reagent with the degree of hydroxyethylation 5 is called "Gossilvan", in Table 1 its main characteristics are presented.

To study the possibility of using the obtained reagent

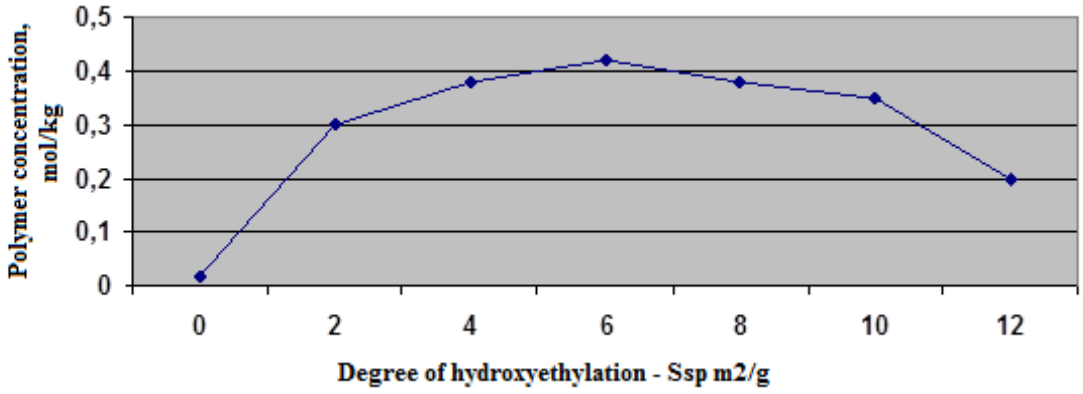


Fig. 3 Dependence of the mixture concentration of polymer homologues on the degree of hydroxyethylation.

as a demulsifier, its surface-active properties and demulsibility were investigated. Determination of the interfacial tension of the reagents under study was carried out in the "aqueous surfactant-toluene solution" system. Based on the results of studies of the interfacial tension isotherms, the surface activity values for the six tested variants of the demulsifying reagent were calculated. Surface-active properties of reagents prepared by hydroxyethylation of FA and containing a different number of ethylene oxide groups were investigated. It was found that the content of ethylene oxide in the product obtained influences its demulsifying activity (Fig. 4) and surface activity (Fig. 5).

Table 1. The main characteristics of the reagent "Gossilvan"

Indicators	Value
Appearance at room temperature	Light brown liquid
Density, g/cm^3 at 20°C	0.95 ± 0.02
Freezing point, °C	36
Viscosity, mPa*s at -20°C, at -20°C	25 400
pH value (1% in distilled water at 20°C)	9.0
Flash point, °C	11
Hydroxyl value, mg KOH/g, not higher	160
Content, %	
hydroxyethyl groups	40
cinder	0.25
polyethylene glycols, not higher	3
Biodegradation,%	не менее 80

Analysis of the values of surface activity showed that the demulsifier variants under study had similar surface activity values, but the maximum value was obtained at 70% ethylene oxide content, which agrees well with the data of Fig. 4 characterizing the demulsifying activity of oxyethylated products. These results indicate that the obtained reagents can be used as demulsifiers for dewatering crude oil.

It has been established that the purity of the initial FAs also influences the demulsifying activity of oxyethylated derivatives (Nadirov, *et al.*, 2015), with an abnormal deviation in the properties of the product obtained on the basis of purified FA with an impurity content of about 1.2-1.3% (Fig. 6). The maximum value of the amount of water released from water-oil emulsions under these conditions is 94% with a content of 60% ethylene oxide in the reagent. The remaining versions of the raw material provide a water separation of 91% with an ethylene oxide content of 70%.

Tables 2 and 3 show the results of using the "Gossilvan" demulsifier for dehydration and desalting of the crude oil in the Aschysai field.

CONCLUSION

Thus, the possibility of using a new raw material – purified FA GR – for the synthesis of nonionic demulsifiers of the "Gossilvan" series by the method of oxyethylation is shown. It has been established that when the "Gossilvan" reagent is used in the amount

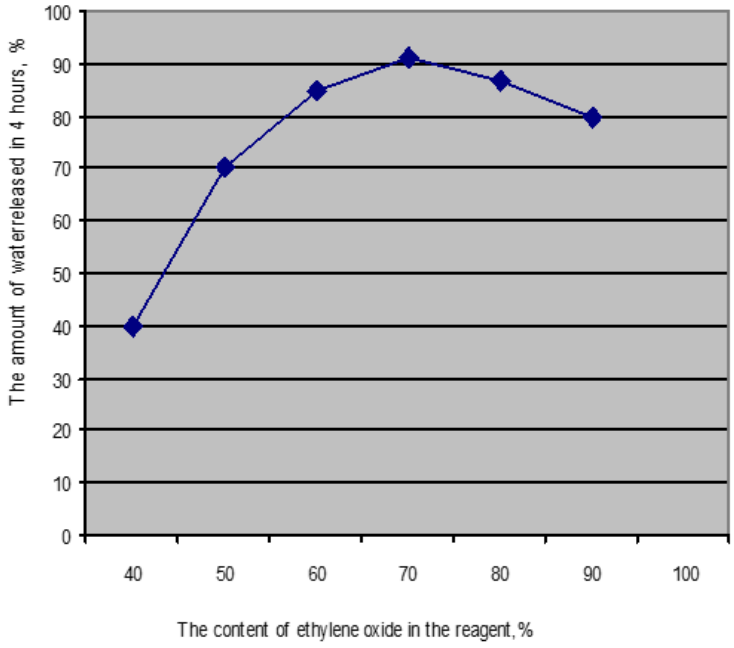


Fig. 4 Demulsifying activity of ethoxylated product depending on the content of ethylene oxide in it.

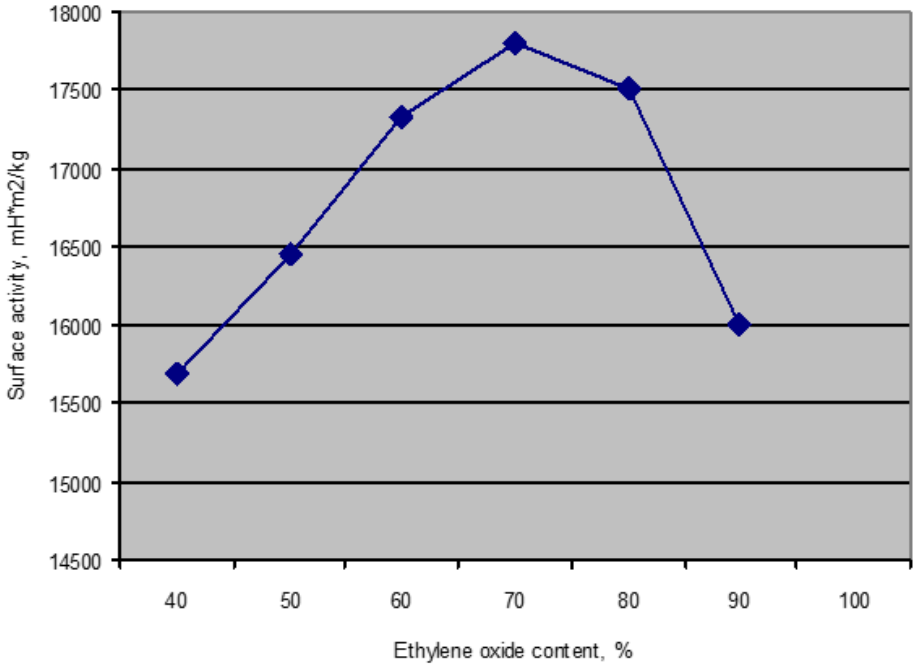
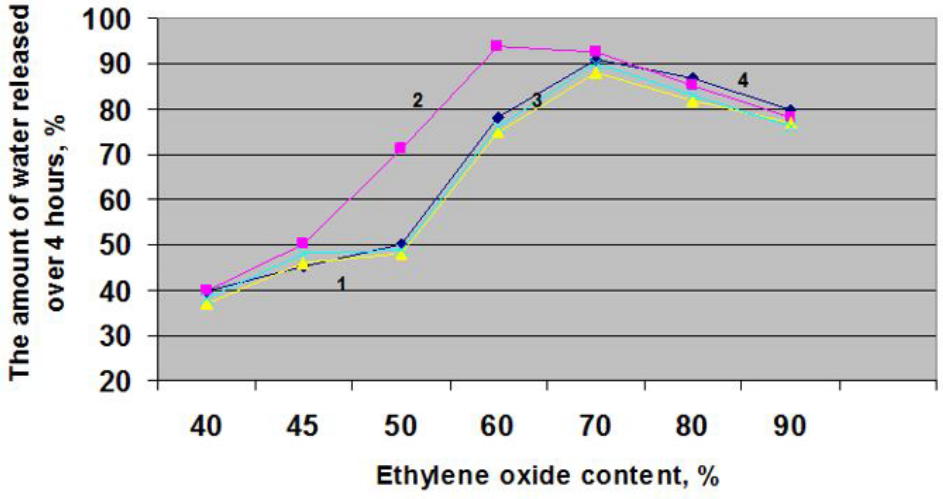


Fig. 5 Influence of the content of ethylene oxide in the ethoxylated product on the surface activity for various versions of the demulsifier reagent.



Characteristics of the options: 1. Unrefined FA. 2. FA after purification with impurity content of about 1.2-1.3%. 3. Distilled FA with an impurity content of about 0.2-0.3%. 4. Purified FA with an impurity content of about 0.02-0.04%.

Fig. 6 Demulsifying activity of oxyethylated products.

Table 2. Results of the use of the demulsifier "Gossilvan" for dehydration and desalting of raw Ashiysai oil (laboratory tests)

Consumption rate of the demulsifier "Gossilvan", g/m^3	Water content in oil, %	Salt content in oil, mg/l	Content of petroleum products in water, mg/l
0	20	3240	1670
5	10	2180	1230
10	6	1340	670
20	2,5	560	360
30	0,5	210	170
40	0,1	150	60
60	0,08	60	50

Table 3. Results of dehydration of oil field "Aschysai" in field trials*

Indicators	**Options**		**Dissolvene 4411**		**"Gossilvan"**		**Without a demulsifier**
Specific consumption, g/m ^{3}	Time, min		8	15	10	20	-
The amount of water released in time, in % of the total volume	3		2	4	1	3	-
	10		22	30	20	28	-
	60		64	70	61	70	-
	120		70	80	68	78	10
	Object		**Indicators**				
Observations of quality after sludge	Water		Good	Good	Good	Good	Bad
	Section "oil-water" phase		Good	Good	Good	Good	Bad
	Oil		Good	Excellent	Good	Excellent	Bad
	Type of research		**Indicators**				
Результаты центрифугирования	Residual water content in commercial oil, %	Water released during centrifugation into the free phase	0.3	0.3	0.4	0.3	Undefined
		Intermediate layer	0.5	0.4	0.6	0.4	Undefined
		Water	0.7	0.7	0.7	0.7	Undefined
	Residual water content in full oil, %	Water released during centrifugation into the free phase	1.9	1.5	1.8	1.5	30
		Intermediate layer	1.0	0.8	1.1	0.9	60

*The method "Bottle Test" was used. Conditions: initial centrifugation: 10% water in free form, 60% pr layer, 70% water total; Temperature – 40°C, duration of the test – 2 hours.

of 30-60 g/m^3, the residual water content in oil is reduced to 0.08-0.5%, salts – up to 60-210 mg/l. The resulting "Gossilvan" reagent is a demulsifier, which provides a good degree of desalting and dehydration at a flow rate of 30-60 g/m^3 of crude oil.

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