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DEMULSIFICATION EFFECT OF NON-IONIC SURFACTANTS TWEEN-20, TWEEN-80 ON MODEL WATER-IN-OIL EMULSIONS

Abstract. Breaking of water-in-oil emulsions is a necessary part of crude oil preparation for processingandthe development of new demulsifying compositions has importance for the Republic of Kazakhstan.In this research, the demulsificationeffectof non-ionic surfactants Tween-20, Tween-80 with a high value of hydrophilic−lipophilic balance (HLB)was considered. For thermal treatment of water-in-oil emulsion the model emulsions based on crude oil of North-West Konys with 30%, 40%, 50%, 60 % (vol.) of water phase concentrationwerestudied. *The degree of oil emulsion dewatering in the presence of* Tween-20 do not exceed 63% at temperature 60°C. The optimal term of thermal chemical breaking down by means of mixtures of non-ionic surfactants Tween-20, Tween-80 and anionic surfactant sulfanol at a ratio of 1:1 (vol.) was determined. The maximum demulsification equaled to 97.01% after 100 min for 30-50% water-in-oilemulsionwas found out for Tween-20 – sulfanol mixture at a ratio of 1:1 at 60°C. The results confirm the opportunity of using of mixtures of Tweens with anionic surfactant sulfanol as demulsifying reagents.

Keywords: thermal chemical demulsification, non-ionic surfactants, Tween-20, Tween-80, sulphanol, water-in-oil emulsions, breaking of water-in-oil emulsions.

Introduction

Water-in-oil emulsions (microheterogeneous and ultradispersed water droplets suspended in crude oil) are formed as a result of oil production. The stability of water-in-oilemulsions varies from few minutes to several years and depends on the oil field and the physicochemical characteristics of the crude oil [1, 2]. Breaking of oil emulsions is an important part of oil preparation for processing, therefore the development of new demulsifying compositions has importance for the Republic of Kazakhstan.

Crude oil emulsions must be broken down because they makecorrosion of pipelines and equipment used for oil refining due to the presence of water droplets with dissolved chloride salts. Itfavors an increase in the cost of transportation and refining of oil. In addition, the emulsified water causes changes the properties of crude oil, such as viscosity, density, etc. [3].

The high molecular weight nonionic surfactants are widely used for breaking of oil emulsions. They show a good demulsifying effect and do not leave any counter ions in crude oil and petroleum products [4].

In the research, polysorbates or so-called Tweensrelated to polymer surfactants were used to select highly effective destabilizers of water-in-oil-emulsions with the optimal composition and nature of components.Tweens are viscous, oily liquids and they are derivatives of polyethylene glycols – sorbitan esterified with fatty acids. Groups of ethylene oxide -(CH_2CH_2O)- and polyester of carboxylicacidprovidethe hydrophilic properties to Tweens andpolysorbitan favor the lipophilic properties. Tweensare widely used to stabilize the oil-in-water emulsions in practice [1]. Therefore, it was expectedthatthis type of nonionic surfactantscan be effective for breakingofthe water-in-oil emulsion, i.e. they can be used for the breaking downthecrude emulsions (reverse emulsions)[1, 5]The polymeric demulsifiers with rather high value of hydrophilic-lipophilic balance (HLB)adsorb at the water/oil interfaceand destroy the adsorptionlayer of emulsifiers [1]. The presence of a developed hydrophilic part contributes to a greaterseparation of water from oil. Tweens have a suitableHLBdue to the large number of ethylene oxides. Oxyethylatedgroupsinteract with the aqueousphase due to hydrogen bonds and provide a strong hydrophilic partto the surfactant molecule.

It was shown in [6, 7] that a high molecular weight, an increase of the number of hydroxyl agents, and a percentage of nonionic polymers in demulsifier compositions improves the demulsifying effect of the surfactant. Studies have shown that an increase in the number of HLB is effective for demulsification [8]. Since Tweens have a high value of HLB, they can contribute to the breaking of in crude oil emulsion.

At present, there isno detailresearch on the demulsifying effect of Tweens and their compositions for the destruction of oil emulsions of local oil fields lacking effective demulsifiers.

Experimental

For demulsificationinvestigation the non-ionic polymer surfactants Tween-20, Tween-80 and anionic surfactant Sodium dodecylbenzenesulfonates(sulfanol)were used.

Tween-20– polyethylene (20) sorbitanmonolaurate, $C_{58}H_{114}O_{26}$.Tween-80 –polyethylene (20) sorbitanmonooleate, $C_{64}H_{124}O_{26}$.

Sulfanolis produced as a mixture of related sulfonates.Itconforms to the formula $R\text{-}C_6H_4SO_3Na$, where R is a radical corresponding to C_nH_{2n+1}, n=14-18.

For preparation of a model emulsion the oil of North-West Konys oil field was used. Some physical-chemical properties were determined: density (833 kg/m^3), content of chloride salt (1,5mg/L), mechanical impurities (0,067 %), sulphur (0,163 %)[9].

Water-in-oil emulsions of 30%, 40%, 50%, 60 % (vol.) concentration were prepared by mixing of oil with 20 %solution of sodium chloride in water. Emulsification was carriedoutusing an IKA T 10 basic ULTRA-TURAX homogenizer (Germany) at 10000 rpm for 30 min. The prepared emulsion was left for a week to stabilize by adsorption of surface active components of the crude oil. The increase of the mixing time and the number of rotations did not have a significant effect on the oil emulsion stability.

The kinematic viscosity of the oil emulsions was measured by means of glass viscometer for oil and oil products bythe time of the outflow of the oil emulsion.

The dispersion of water droplets was measured using an optical microscope. A drop of crude oil was placed on the glass slide and spread on it. The images were processed using a «Leica DM6000M» microscope of the National nanotechnology laboratory of al-FarabiKazakh National University.

To determine the destabilizating ability of demulsifyer 50 ml of crude oil in graduated glass test tubes and placed into a thermostat. The aqueous phase separation was visually monitored at regular time intervals. The water separation in percent (W, %) was calculated as relation of volume of separated water to the original volume of water in the emulsion.

To determine the demulsifying ability of the demulsifyer, 50 ml of oil was placed in a graduated test tube, the required amount of demulsifier was added with a microdoser and mixed with a homogenizer for 5 minutes at 10000 rpm. Then the tube was placed into a thermostat at 40-60 °C and the volume of water separated was determined every 10 minutes. At the same time, the state of water layer and the interface were observed and assessed visually.

Results and discussion

Concentrations of model emulsions vary from 30% to 60% (vol.). The watering of crude oil emulsions corresponds to these concentrations for oil fields of Kazakhstan in average as a result of exploitation. Increasing of water content helps to model oil emulsion with different viscosity.

Emulsions with 10% and 20% of water are close to initial oil without water by their viscosity. Increasing of water content in oil till50 % - 60 % effects on oil emulsion viscosity significantly (Fig. 1). The viscosity of 60 % (vol.) model emulsion increases by 50 times in comparison with dewatered oil.

It is known that naphtenic acids, fatty carbon acids and their salts, asphaltenes, resins and high molecular weight paraffins are the base natural stabilizers of oil emulsion [10, 11]. According to quantitative analysis of oil components (asphaltenes, resins andparaffins) the stabile emulsions can formon the basis of the probe of North-West Konysoil[9]. Analysis of the dispersion degree of the model emulsion samples by means of the optical microscopy allows to relate them to highly dispersed system. Hence, it confirms that the water droplets cannot sedimentunder the gravity. Theinvestigatedwater-in-oil emulsions are characterized by droplets of spherical shape and polydispersity. The sizes of water droplets range from 0.91 μm to 19.1 μm (Fig. 2).

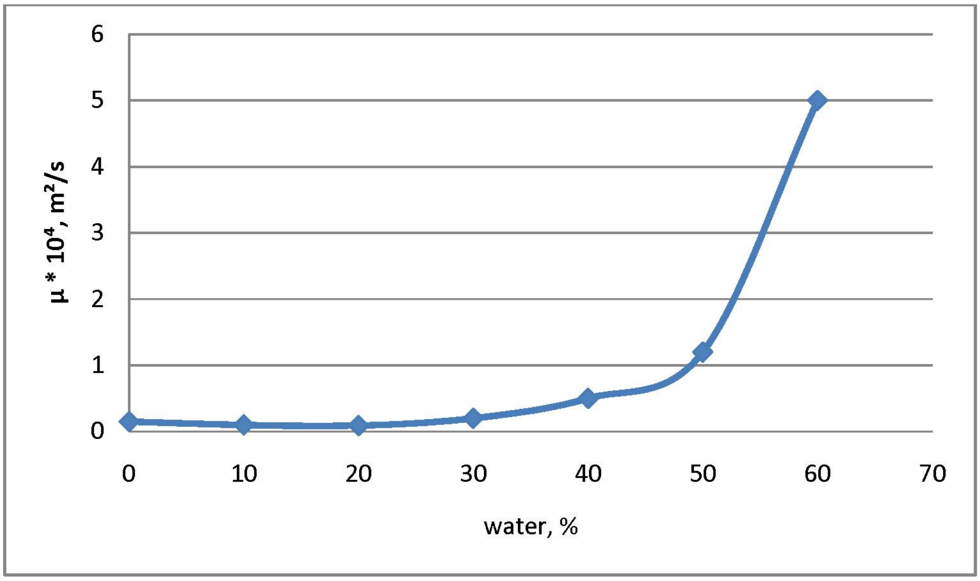
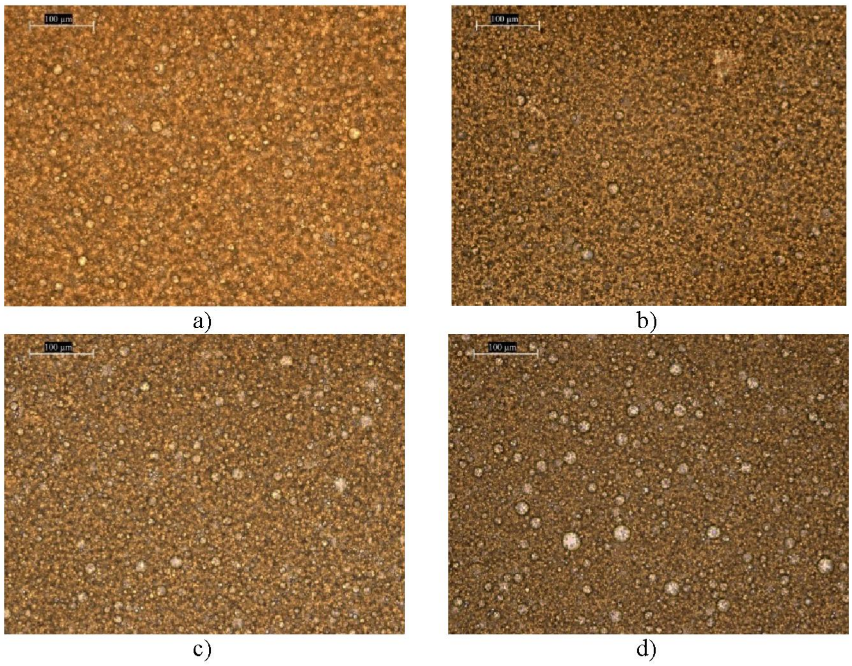


Figure 1– Influence of water concentration on kinematic viscosity of oil emulsion. T=20^{0}C

According to the optical microscopy images,theincreasing of water concentration in the emulsions is accompanied by growth of the average diameter of the droplets(Fig. 2).It is obvious that the increasing the water dropletsize in an emulsions results inan increaseof watering degreeanddecreasing the emulsionstability. However, so-called "cold settling" of model emulsions, i.e. sedimentation without heating, and the thermal treatment of them from 40-60° C did not lead to the separation of water.



a) –30% a – 30%; b) – 40%; c) – 50%; d) – 60%

Figure2– Optical microscopy images of oil emulsions with different water concentration (resolution 100 μm)

To study the demulsification 1 ml of 1% aqueous solution of Tweens was introduced into model emulsionsof different concentrations and then emulsionswere mixed with Tween surfactant for 5 min usingthe homogenizer.

The addition of Tween-20 and Tween-80 solutions showed that there is no separation of water at 40° C and 50° C. The risein the temperature to 60° C led to the separation of water within 10 minutes and reached a constant value after 120 minutes of observation.

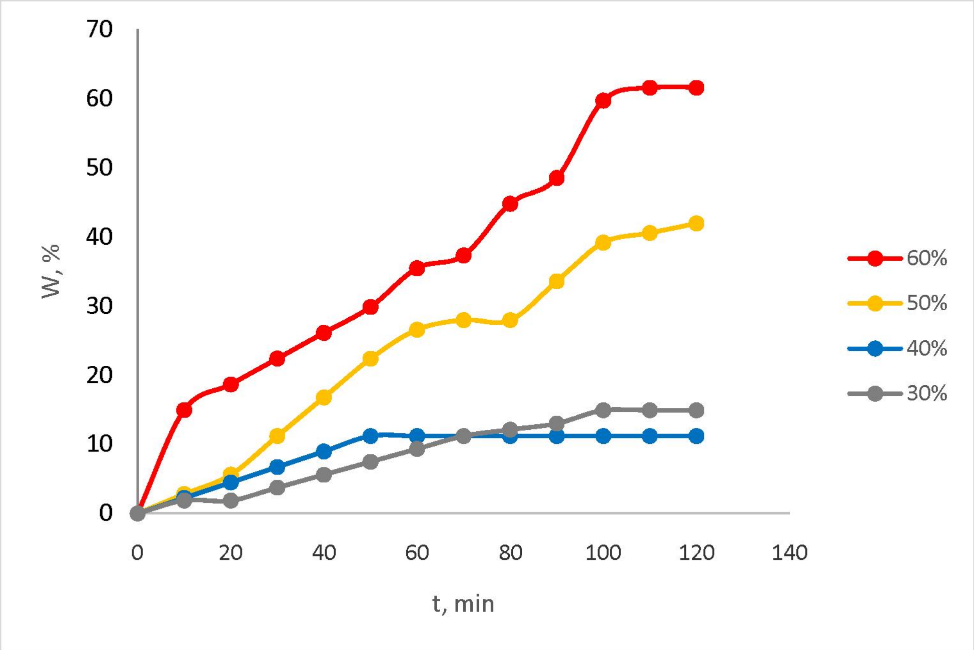


Figure3– The amount of water separated from oil emulsions of different concentrations at the addition of Tween-20. T = 60°C

Fig.3 shows that water separation percentage increases with the growth of dispersed phase concentration of water-in-oil emulsions. For 60% emulsion, the water separation was 63 %.

The maximum degree of dewatering for Tween-80 was insufficient, about 12% for emulsions studied after the same observation time.

The greater demulsifying effect of Tween-20 can be explained by the difference of interfacial activity at the water/oil interface and different hydrophilic-lipophilic balance of their molecules (HLB for Tween-20 is 16.7, and for Tween-80 is 15.0) [1]. The higher the number of polysorbate, the higher the value of its HLB, the lower its value; the ability to create stable emulsions of o/w decreases. The use of Tweens for demulsification was interesting, since they are of natural origin, based on sorbitol and fatty acids from base oils: coconut oil for Tween-20, olive oil for Tween-80. Tweens have the property of easily decomposing in natural environments[12]. Therefore, they will not cause a deterioration of the quality of oil processed, in comparison withotherchemical reagents.

In addition, the great amount of ethylene oxides, their number in Tweens equals to 20, favors the study of demulsifying action of them. They have developed hydrophilic part able to penetrate to an interfacial layer around the water droplet.

Heating to 60 °C reduces the viscosity of the oil medium and increases the difference between the density of the dispersed phase and the dispersion medium, facilitating the coalescence of water globules in accordance with the Stokes law when they collide. However, a further increase of temperature to increase the water separation is not advisable, since this can lead to volatilization of light oil fractions.

The demulsifying effect of compositions of Tweens with anionic surface-active substance sulfanolwas studied. Sulfanol is a more hydrophilic surfactant than non-ionic Tween. Therefore, for increasing the hydrophilic-lipophilic balance the demulsifying effect of the Tween-sulfanolmixedcomposition was investigated. Composition Tween 20 – sulfonolwas used in a ratio of 1: 1 (vol.).In addition, sulfanol refers to a sufficiently accessible technical anionic surfactantbecause it is produced as a mixture of related sulfonates and can be obtained from an wastes of petroleum industry.

At room temperature and with a temperature rise up to 40 °C in the presence of the surfactantcomposition, the water separation, as in the case of individual Tween-20 and Tween-80, was not observed. Starting from 50 °C, after 10 minutes of settling, the degree of dehydration was 60 % and reached 95.24% for 30-50 % of water-in-oil emulsions after 100 minutes of treatment. At 60 C for 30-50 % emulsions the maximum degree of dehydration is 97.01%, and for 60% of emulsion - 83.96% (Fig. 4).

For Tween-sulfanol mixture in the difference with individual non-ionics it is seen that 60% emulsion has lower water separation in comparison with emulsions with small water concentration.

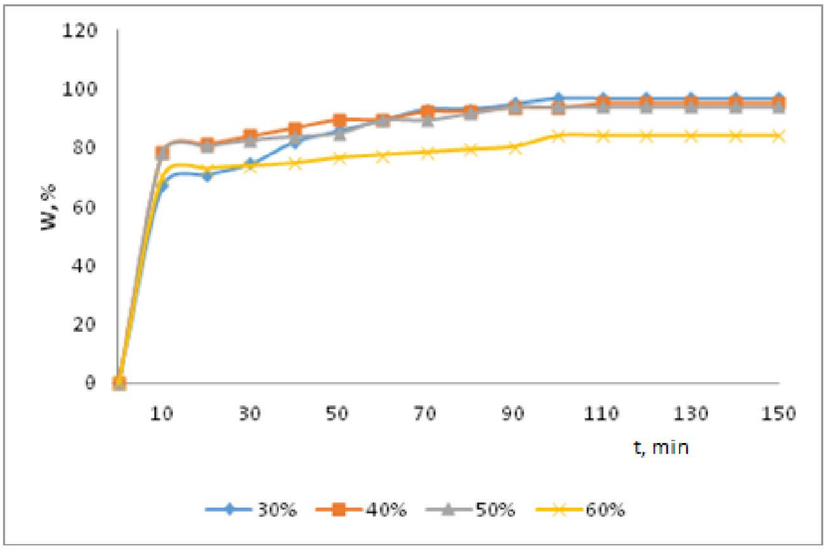


Figure 4 – Degree of dewatering of oil emulsions of different concentration in the presence of the composition Tween-20 - sulfanol. T = 60 ° C

For aqueous mixtures of Tween 80 –sulfanol the degree of water separation at 50 °C for 30-40% of emulsions, the degree of dewatering was 78.43%. For 60% emulsion W = 63.43% at the same temperature. With an increase of temperature till 60 °C for water-oil emulsions of 30-40%, the maximal dehydration degree was 82.09% and 75.63% respectively, for 60% emulsion – 59.7% (Figure 5).

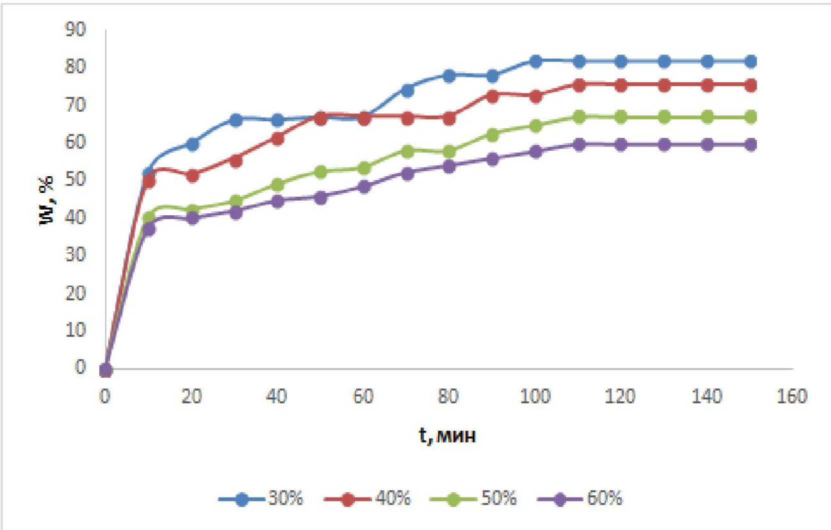


Figure5– Degree of dehydration of water-in-oil emulsions of different concentrations in the presence of the composition Tween-80 –sulfanol. T = 60 ° C

The Tween-20 – sulfanol formulation shows a greater demulsifying effect on oil emulsions in comparison with individual non-ionic surfactants. This occurs probably due to the greater interfacial activity of Tween-20 compared to Tween-80 and higher HLB value and the Tween-20 –sulfanol has an additive demulsifying effect,displacingthe natural stabilizers from oil/water interface.

Conclusion

The demulsifying action of nonionic surfactants Tween-20, Tween-80 with high HLB value and their mixtures with anionic sulfanolwas studied on model emulsions based on the crude oil of North-Western Konys oil field.

The use of Tween-20 for breaking down the oil emulsions did not exceed 63% at 60 °C. The mixture of 1% water solutionsof anionic and non-ionic surfactants at a ratio of 1:1 (vol.) shows a better demulsifying action. According to results, the maximum demulsificationwas observed for the composition of Tween 20 –sulfanol at 60 °C and equals to 97.01% after 100 minutes of thermochemical treatment of artificial water-in-oil emulsions with water content of 30-50%. The research results showed the opportunity of using Tweens mixtures with anionic surfactantsulfanolas effective demulsifying agents.

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МОДЕЛЬДІ МҰНАЙ ЭМУЛЬСИЯЛАРЫНА ИОНДЫ ЕМЕС БАЗ ТВИН-20 ЖӘНЕ ТВИН-80-НІҢ ДЕЭМУЛЬСИЯЛАУ ӘСЕРІ

Аннотация. Мұнайды өңдеуге дайындауда мұнай эмульсияларын бұзу маңызды болғандықтан Қазақстан Республикасы үшін жаңа деэмульсиялаушы композицияларды жасау өзекті мәселе болып табылады. Жоғары гидрофильді-липофильді баланс (ГЛБ) мәніне ие ионды емес БАЗ Твин-20 және Твин-80-нің деэмульсиялау әсері зерттелді. Термохимиялық өңдеуді зерттеу үшін сулы фаза концентрациялары 30%, 40%, 50%, 60 % (көл.) болатын моделді мұнай эмульсиялары қолданылды. Мұнай эмульсиясының сусыздану дәрежесі Твин-20 қатысында 60°С-да 63%-дан аспады. Твин-20, Твин-80 және анионды БАЗ сульфанол 1:1 (көл.) қатынастағы қоспалардың қатысындағы термохимиялық тұндырудың оптималды шарттары анықталды. Твин-20 мен анионды БАЗ сульфанол 1:1 (көл.) қатынастағы композициясы максималды деэмульсиялауды көрсетеді және 30-50% суы бар мұнай эмульсияларында 60°С 100 минут тұндырудан кейін 97,01%-ға тең екені табылды. Деэмульгирлеуші реагенттер ретіде Твиндердің анионды БАЗ сульфанолмен қоспаларын қолдануға болатын мүмкіндігі көрсетілді.

Тірек сөздер: термохимиялық деэмульсиялау, ионды емес беттік-активті заттар, Твин-20, Твин-80, сульфанол, су-мұнайлы эмульсиялар, мұнай эмульсияларын бұзу.

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ДЕЭМУЛЬГИРУЮЩЕЕ ДЕЙСТВИЕ НЕИОННЫХ ПАВ ТВИН-20 И ТВИН-80 НА МОДЕЛЬНЫЕ НЕФТЯНЫЕ ЭМУЛЬСИИ

Аннотация.Разрушение нефтяных эмульсий является важной частью подготовки нефти к переработке, поэтому разработка новых деэмульгирующих композиций является актуальной проблемой для Республики Казахстан. В работе рассмотренодеэмульгирующее действие неионных ПАВ Твин-20, Твин-80, обладающих высоким значение гидрофильно-липофильным балансом (ГЛБ). Для исследования термохимической обработки водонефтяной эмульсии были использованы модельные нефтяные эмульсии на основе нефти месторождения*Северо-Западный Коныс* с концентрацией водной фазы 30%, 40%, 50%, 60 % (объемн.). Степень обезвоживания нефтяной эмульсии в присутствии Твин-20 не превысила 63% при температуре 60°С. Определены оптимальные условия термохимического отстаивания в присутствии смесей неионных ПАВ Твин-20, Твин-80 и анионного ПАВ сульфанолав соотношении 1:1 (объемн.). Максимальная деэмульсация была обнаружена для композиции Твин 20 – сульфанол в соотношении 1:1 (объемн.) при 60°С и равна 97,01% после 100 минут отстаивания для водонефтяных эмульсий с содержанием воды в нефти 30-50%. Результаты подтверждают возможность использования смесей Твинов с анионным ПАВ сульфанолом в качестве деэмульгирующих реагентов для обезвоживания нефти.

Ключевые слова: термохимическое деэмульгирование, неионные поверхностно-активные вещества, Твин-20, Твин-80, сульфанол, водонефтяные эмульсии, разрушение нефтяных эмульсий.