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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 processing and the development of new demulsifying compositions has importance for the Republic of Kazakhstan. In this research, the demulsification effect of 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 Konya with 30%, 40%, 50%, 60% (vol.) of water phase concentration were studied. 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-oil-emulsion was 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-oil emulsions 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 make corrosion of pipelines and equipment used for oil refining due to the presence of water droplets with dissolved chloride salts. It favors an increase in the cost of transportation and refining of oil. In addition, the emulsified water causes changes in 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 Tweens related 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 (CH₂CH₂O)- and polyesters of carboxylic acid provides hydrophilic properties to Tweens and polysorbates favor the lipophilic properties. Tweens are widely used to stabilize the oil-in-water emulsions in practice [1]. Therefore, it was expected that this type of nonionic surfactants can be effective for breaking off the water-in-oil emulsion, i.e. they can be used for the breaking down crude oil emulsions (reverse emulsions) [1, 5]. The polymeric demulsifiers with rather high value of hydrophilic-lipophilic balance (HLB) adsorb on the water/oil interface and destroy the adsorption layer of emulsifiers [1]. The presence of a developed hydrophilic part
contributes to a greater separation of water from oil. Tweens have a suitable HLB due to the large number of ethylene oxides. Oxygenated groups interact with the aqueous phase due to hydrogen bonds and provide a strong hydrophilic part to the surfactant molecule.

It was shown in [6, 7] that a high molecular weight, an increase in 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 crude oil emulsion.

At present, there is no detail research on the demulsifying effect of Tweens and their compositions for the destruction of oil emulsions of local oil fields lacking effective demulsifiers.

Experimental

For demulsification investigation, the nonionic polymer surfactants Tween-20, Tween-80, and anionic surfactant Sodium dodecylbenzenesulfonates(sulfonol) were used.

- Tween-20 - polyethylene (20) sorbitanmonolaurate, C_{30}H_{106}O_{26}, Tween-80 - polyethylene (20) sorbitanmonoooleate, C_{36}H_{122}O_{26}.

Sulfonol is produced as a mixture of related sulfonates. It conforms to the formula R-C_{n}H_{2m+1}SO_{n}Na, where R is a radical corresponding to C_{n}, 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 (1.5 mg/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 carried out using 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 a glass viscometer for oil and oil products by the 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-Farabi Kazakh National University.

To determine the destabilizing ability of demulsifier, 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 demulsifier, 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 ℃ 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 till 50% - 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 naphthenic 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 and paraffins) the stable emulsions can form the basis of the probe of North-West Konys oil [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 sediment under the gravity. The investigated water-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).

![Graph showing the influence of water concentration on kinematic viscosity of oil emulsion. T=20°C](image)

Figure 1– Influence of water concentration on kinematic viscosity of oil emulsion. T=20°C

According to the optical microscopy images, the increasing 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 droplet size in an emulsions results in an increase of water degree and decreasing the emulsion stability. 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.

![Optical microscopy images of oil emulsions with different water concentration](images)

Figure 2 – 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 emulsions of different concentrations and then emulsions were mixed with Tween surfactant for 5 min using the 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 rise in the temperature to 60° C led to the separation of water within 10 minutes and reached a constant value after 120 minutes of observation.

![Graph showing the amount of water separated from oil emulsions of different concentrations at the addition of Tween-20. T = 60°C](image)

**Figure 3** – 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 with other chemical 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 sulfanol was studied. Sulfanol is a more hydrophilic surfactant than non-ionic Tween. Therefore, for increasing the hydrophilic-lipophilic balance the demulsifying effect of the Tween-sulfanol mixture composition was investigated. Composition Tween 20 – sulfanol was used in a ratio of 1: 1 (vol.). In addition, sulfanol refers
to a sufficiently accessible technical anionic surfactant because 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 surfactant composition, 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-ionic it is seen that 60% emulsion has lower water separation in comparison with emulsions with small water concentration.

![Figure 4](image-url) - 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).

![Figure 5](image-url) - 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 – sulphanol 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 – sulphanol has an additive demulsifying effect, displacing the 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 sulphanol was studied on model emulsions based on the crude oil of North-Western Konyys 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 solutions of anionic and non-ionic surfactants at a ratio of 1:1 (vol.) shows a better demulsifying action. According to results, the maximum demulsification was observed for the composition of Tween 20 – sulphanol 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 Tweenes mixtures with anionic surfactants sulphanolas effective demulsifying agents.

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МОДЕЛЬДІ МУНАЙ ЭМУЛЬСИЯЛАРЫНА ИОНДЫ ЕМЕС БАЗ ТВИН-20 ЖӘНЕ ТВИН-80-НІҢ ДЕЗМУЛЬСИЯЛАУ ЭСЕРІ

Аннотация. Мунайды оңдеу ең ізіндегі дәуірде мунай эмulsionларының бұзығы мәңдөгі болғандығы Қазақстан Республикасы үшін жаңа дезмульсиялаушы композицияларды жасау оқиға мәселе болып табылады. Жогары гидрофильді-липофильді баланс (ГЛБ) мөнін ес ионды емес БАЗ Твин-20 және Твин-80-нің дезмульсиялау есері зерттелді. Термохимиялық оңдеуді зерттей үшін сулы фаза концентрациялары 30%, 40%, 50%, 60 % (к.ө.) болатын моделді мунай эмulsionлары колданылды. Мунай эмulsionсының сұсындығы дәрежесі Твин-20 қатысында 60°C-да 63%-дан аспады. Твин-20, Твин-80 және аніонды БАЗ сульфатол 1:1 (к.ө.) қатынастарын коспалардың қатысынаға термохимиялық тұлғырдың оптималды шарттары анықталды. Твин-20 мен аніонды БАЗ сульфатол 1:1 (к.ө.) қатынастары композициясы максималды дезмульсиялауды корсетеді және 30-50% суы бар мунай эмulsionларында 60°C 100 минут тұлғырдан кейін 97.01%-ға тең екені табылады. Дезмульсиялаушы реагенттер ретінде Твиндердің аніонды БАЗ сульфатолмен коспалары колданыға бөлініп мұқымді қорсетілді.

Тірек сөздер: термохимиялық дезмульсиялау, ионды емес беттік-активті заттар, Твин-20, Твин-80, сульфатол, су-мунайды эмulsionлар, мунай эмulsionларына бұзу.

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ДЕЗМУЛЬСИЯЛАУШЫ ДЕЙІНГІ НЕЙОНИНДЫ ПАВ ТВИН-20 И ТВИН-80 ПАНА ЛАТТЕРАЛІ АТЫНБЕЖЕ ТВИН-80 ДЕЗМУЛЬСИЯЛАУ НА МОДЕЛЬНЫЕ НЕФТЯНЫЕ ЭМУЛЬСИИ

Аннотация. Разрушение нефтяных эмульсий является важной частью подготовки нефти к переработке, поэтому разработка новых дезмульгирующих композиций является актуальной проблемой для Республики Казахстан. В работе рассмотрено дезмульгирующее действие нейонных 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 Консас с концентрацией водной фазы 30%, 40%, 50%, 60 % (объем.). Степень обезжоживания нефтяной эмульсии в присутствии Твин-20 не превышала 63% при температуре 60°C. Определены оптимальные условия термохимического отстаивания в присутствии смеси нейонных ПАВ Твин-20, Твин-80 и аннионного ПАВ сульфатол в соотношении 1:1 (объем.). Максимальная дезмульсация была обнаружена для композиции Твин 20 – сульфатол в соотношении 1:1 (объем.) при 60°C 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 аннионным ПАВ сульфатолом в качестве дезмульгирующих реагентов для обезжоживания нефти.

Ключевые слова: термохимическое дезмульгирующее, нейонные поверхностно-активные вещества, Твин-20, Твин-80, сульфатол, водонефтяные эмульсии, разрушение нефтяных эмульсий.