

**DEMULSIFICATION OF NATURAL WATER-IN-OIL EMULSIONS WITH COMPOSITIONAL MIXTURES BASED ON SURFACTANTS**

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**ABSTRACT**

The paper considers the stability of crude oil emulsions in the presence of aqueous solutions of polymers and surfactants and their mixtures. Surfactants of different nature (anionics, cationics and nonionics - sodium dodecylbenzenesulfonates (sulphanol), cetyltrimethylammonium bromide (CTAB), ethoxylated isooctylphenol (OP-10), carboxymethylcellulose (NaCMC) were used for preparation of demulsifying compositions. The behavior of the compositional mixtures at the different interfaces was studied. The compositions studied have a high surface activity (surface tension decreases till 3 mJ/m<sup>2</sup> at the water/oil interface). The demulsifying action of the compositional mixtures was researched. The most effective dewatering compositions were obtained on the base of CTAB and NaCMC at ratio of 1:1. The amount of separated water was equal to 91,95 % after 105 min at 60°C. In addition, the combined action of thermochemical processing and centrifuging showed the increase of dewatering degree of water-in-oil emulsions under action of CTAB/NaCMC mixture (V=97,95 %).

**Keywords:** water-in-oil emulsion, surfactant, polymer, compositional mixtures, interfacial tension, thermochemical dewatering.

**INTRODUCTION**

The stability of crude oil emulsions is determined by oilfields and, consequently, by composition of oil. Water-in-oil emulsions are stabilized by naturally occurring surfactants: carboxylic naphthenic acids, high molecular weight asphaltenes, paraffins, resins. These emulsifiers form at the water-oil interface the adsorption layer with structural viscosity and, hence, provide a high stability of crude emulsions [1]. The stability of oil emulsions formed during petroleum production operations may range from several minutes to several years depending on the nature of crude oil. Therefore, an important objective of the primary oil preparation is a quick and cost-effective breaking down of oil emulsions. The breaking of crude oil emulsions (demulsification) is necessary to avoid problems during the transportation and processing of oil. The presence of water in crude oil is undesirable and can result in pipeline corrosion because of chloride salt content in aqueous phase of emulsion. There are requirements to the amount of emulsified water in crude oil for subsequent processing in a refinery - water content in crude oil must not exceed 1% [2].

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The oil emulsion is characterized by the presence of mechanical impurities - particles of sand and clay, colloidal form of iron sulphide and other particles which relate to the natural emulsifiers also. The large amount of asphaltene and resins and mechanical impurities significantly complicates the oil dewatering processes. The long-term storage of oil recovered can lead to impossibility of dewatering due to the concentrating of surface active high molecular weight components and mechanical impurities at water-oil interface. The stable emulsions may be broken using the special chemical reagents - demulsifiers at appropriate temperatures. The demulsifiers cause a displacement of natural surfactants from adsorption layer, resulting in coalescence of water droplets and, consequently, to the phase separation [3]. The disadvantage of known demulsifiers is their high cost and the necessity of demulsifier selection for crude oil from different oilfields.

Nowadays the development of new effective demulsifiers used for oil dewatering processes has importance. Currently, there are demulsifying compositions obtained by mixing at various ratios of aqueous solutions of surface-active agents and polymers with various functional groups [4]. The aim of the present work is to study the interfacial behaviour of compositions based on surfactant and polymers to develop the efficient formulations for breaking down the natural water-in-oil emulsions. The variation of component ratio of different nature in a surfactant-surfactant and surfactant-polymer mixture allows to obtain systems with wide range of ratios of the hydrophilic and hydrophobic parts, that may cause demulsifying action. It is well known when the hydrophilic - lipophilic balance of the surfactant is varied, a minimum stability of the emulsified system is attained since the surfactant adsorbed at the interface exhibits the same affinity for the oil and water phase [1, 5].

#### EXPERIMENTAL PROCEDURE

**Material and methods.** For formulation of compositional systems the surfactants of various nature (cationics, anionics and nonionics) and water-soluble polymers of industrial production were used. The concentrations of initial components in mixture were 1 % at which low molecular weight surfactants have the greatest surface activity reducing the surface tension of up to 32 mJ/m<sup>2</sup>.

Sulphanol (sodium dodecylbenzenesulfonates) is anion active amphiphile with the formula  $C_{12}H_{25}C_6H_4SO_3Na$ . Cetyltrimethylammonium bromide (CTAB)  $C_{16}H_{33}N(CH_3)_3Br$  is a quaternary ammonium salt. Nonionic oxyethylated isooctylphenol (OP-10) product of joining of ethylene oxide to the alkylphenol with formula  $C_8H_{17}C_6H_4O(CH_2CH_2O)_nH$  [6].

Also water-soluble polymers - sodium carboxymethylcellulose (NaCMC), polyethylene glycol (PEG) were used. Recently it was reported that sodium carboxymethylcellulose  $C_6H_7O_2(OH)_{3-x}(OCH_2COONa)_x$ , (where  $x=1-3$ ,  $n=580$ ) and PEG  $(HO-(CH_2-CH_2-O)_n-H)$  can be used for demulsifying composition formulation [7].

The surface tension of surfactant aqueous solutions and their mixtures with polymers was measured using the modified Wilhelmy method [8].

The oil of Zhanaozen oilfield (Kazakhstan) was used as a natural water-in-oil emulsion. The water amount in crude oil was determined by the Dean-Stark distillation method [9]. The amount of water in crude oil was equal to 24 %, the amount of chlorides was

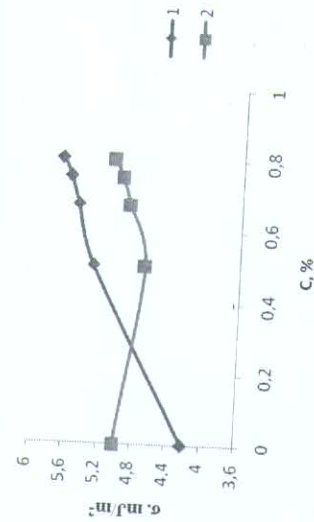
54.8 mg/L. The chloride salts content was determined by extraction and volumetric titration according to the standard procedures [10]. Mechanical impurities content equals 5.22 % according to the standard GOST 6370-83. Determination of asphaltene and resins in Zhanaozen oil was carried out in accordance to ASTM 6560. The method involves the separation of asphaltene with n-heptane or petroleum ether from the oil and their subsequent separation by filtration. Resins dissolved in a filtrate were adsorbed on silica and adsorbed by alcohol-toluene mixture. The heavy oil sample (943 kg/m<sup>3</sup> at 20°C) from Zhanaozen oilfield contains 1.5 % resins, 0.6 % asphaltene.

The stability of the emulsion was studied by observing the sample phase separation with time and at different temperatures. Crude oil was transferred into 50 ml 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 (V, %) was calculated as relation of volume of separated water to the original volume of water in the emulsion. To carry out thermochemical demulsification a demulsifier was added into oil and mixed using an IKA T 10 basic ULTRA-TURAX homogenizer at 8000 rpm for 5 min at 25 °C. All measurements were repeated three times with each sample.

#### RESULTS AND DISCUSSION

In oil emulsion dewatering process the high surface activity of demulsifiers at the water/oil (W/O) is a significant factor. Isotherms of surface tension of aqueous surfactant solutions used correspond to typical isotherms of amphiphile compounds. The surface tension decreases to a constant value (30-33 mJ/m<sup>2</sup>) with growth of surfactant concentrations.

The study of the interfacial behaviour of compositions showed the sufficient surface activity at the water/oil (hexane) (Figure 1, 2). In general, the interfacial tension decreases to 4.5 mJ/m<sup>2</sup> (Figure 1, curve 1). There is an increase of the surface tension of individual surfactants at introduction of polymers due to the increase of mixture viscosity and deceleration of the orientation of surfactant and polymer groups in the adsorbed layer.



1 - sulphanol/PEG, 2 - CTAB/NaCMC

Figure 1. The interfacial tension isotherms of compositional systems at the water/oil interface at various ratio of components.





1 - OP-10/PEG, 2 - OP-10/ sulphanol

**Figure 2. The surface tension isotherms of the compositional systems based on OP-10 at the water/oil interface at different concentrations of the component added.**

This phenomena is observed for a mixture of CTAB/NaCMC where the components are oppositely charged and electrostatic interaction forms associates of components of large size and accordingly increase of the composition viscosity.

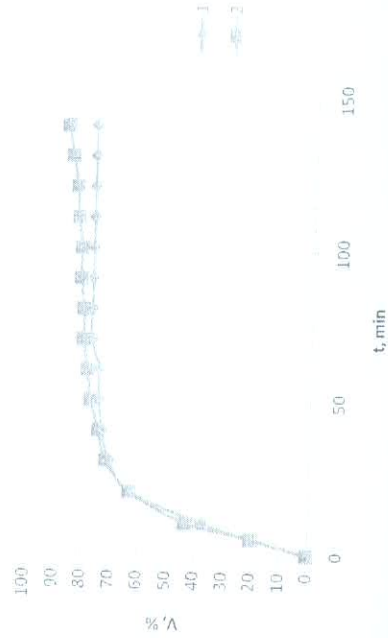
For OP-10/PEG system (Figure 2, curve 1) the increase of surface tension with growth of polymer concentration in the mixture was equal to 0.4 mN/m<sup>2</sup>. Introducing of PEG into OP-10 solution (Figure 2, curve 2) slightly increases the interfacial tension. The presence of hydrophobic groups of different nature in mixture, relatively high molecular weight of OP-10 (646 g), and also the short chain group in PEG macromolecule result in uniform distribution of PEG in the mixture and a slight increase of viscosity. The system OP-10/sulphanol is characterized with the synergistic effect (Figure 2, curve 2). The presence of the organic phase promotes the differentiation of molecules by polarity at the interface. Thus, the compositional mixtures exhibit the high surface activity at the water/oil confirming the possibility of their selective adsorption at the water/oil and reducing the concentration of natural emulsifiers.

The demulsifying action of the compositional systems studied was investigated on samples of water-in-crude oil emulsion form Zhanaozen oilfield.

The individual surfactants and their compositional mixtures were found out not to lead to water separation from water-in-oil emulsion at room temperature. Dilution of the natural oil emulsion with water followed by stirring and adding demulsifiers does not cause the breaking process at room temperature. Hence, the demulsification was carried out at heating, taking into account that the temperature reduces the viscosity of the oil, destroys the adsorption layer of the natural stabilizers and contributes to their displacement from the adsorption layer with more active surfactant.

The optimum temperature of thermal breaking was equal to 60°C. Also the individual surfactants and their mixtures with polymers show the efficient demulsification at

dilution with water by 2 times at this temperature. Dilution by reagent with lower viscosity and density can cause a decrease of structural and mechanical barrier formed by natural stabilizers. Further demulsification of the crude oil emulsion was performed under these optimum conditions. The kinetics of water separation at 60°C under the action of the individual components and the compositional systems is shown on Figures 3, 4.



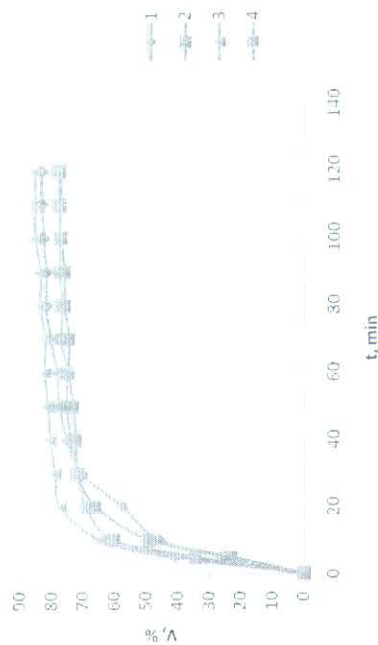
1 - PEG, 2 - sulphanol.

**Figure 3. Kinetics of breaking down the crude oil emulsion in the presence of various surfactants.**

Maximum dehydration at addition of individual sulphanol and PEG was 87.6% and 77.6%, respectively (Figure 3, curves 1, 2). Relatively high demulsifying ability of sulphanol is defined by its effective cleaning action with respect to the asphaltene-resinous oil components. It favours the penetration of sulphanol molecules in the adsorption layer of natural oil stabilizers and further their displacement. As a result of the selective adsorption of demulsifiers the destroying action on the emulsifier solid film can take place. The time of the maximum water phase separation was 140 minutes. PEG is well soluble in water. The surface tension of aqueous solutions of PEG decreases to 64 mN/m<sup>2</sup> only at high concentrations of PEG (> 1 base-mol/L), indicating that there is some debalance of hydrophilic and lipophilic properties to the polar part. PEG macromolecule can simultaneously be adsorbed on a few drops of water, facilitating their coalescence resulting in large droplets formation, followed by phase separation. Time of the maximum separation of water was 70 minutes.

The kinetics of demulsification of water-in-oil emulsion by compositional system based on sulphanol and PEG is shown in Figure 4. The increase of PEG content in the composition of the mixture reduces the amount of released water in comparison with the individual sulphanol. However, at the ratio of the components of 1: 3 the maximum water separation was observed (85.5%), the time of the process - 100 minutes (Figure 4,

curve 3). It follows that the ratio of the components has importance in the formation of the demulsifying mixtures.



Ratio of sulphanol/PEG 1 - 1; 2 - 1; 2; 3 - 1; 3; 4 - 1; 4

Figure 4. Kinetics of oil-water emulsion breaking in the presence of compositional system based on sulphanol and PEG.

It should be noted that the curves on the kinetics of water release from the oil emulsion by compositions are similar and differ by the water separation time, the maximum amount of water and the optimal ratio of components. In the case of compositional systems based on OP-10 and PEG the optimal ratio of OP-10/PEG was 1: 1, the maximum aqueous phase volume (79%) was separated after 110 min. For the systems based on OP-10 and sulphanol the optimal demulsifying ratio was 1: 3, the maximum amount of separated water was 88.5% that much larger compared to individual OP-10 and almost coincides with the value for sulphanol. The maximum amount of water separated reaches during 110 minutes, whereas the time of emulsion breaking for sulphanol was 140 min. Such result can be useful for demulsification of large volumes of water- in-crude oil emulsion.

For compositional systems based on CTAB and NaCMC the optimum ratio was 1: 1, the maximum dehydration degree was equal to 91.95% for 90 minutes. In this system the ion exchange reaction proceeds, positive ions of CTAB and negative NaCMC macroions form associates (polyelectrolyte complexes) due to electrostatic interaction [11]. Mutual neutralization of charges contributes to the formation of hydrophobic complexes which may be considered as hydrophobic demulsifiers, able to penetrate into the adsorption layer and lowering the structural and mechanical properties of oil natural stabilizers. The increase of NaCMC amount in the mixture reduces the breaking down the emulsion caused by growth of viscosity of the mixture and decrease of CTAB/NaCMC associates diffusion to the water - oil interface.

Many experts of the oil processing field reported that only thermochemical processing of oil can not achieve the dehydration of crude oil meeting the requirements. By combined processing of oil with demulsifier, followed centrifuging the time and temperature of breaking down can be and minimized. In the present work after thermochemical processing the crude oil emulsion was also treated by centrifugation. The results of water-oil emulsion treatment by the combined method are presented in the table 1.

Table 1 - Results of combined treatment of water-in-oil emulsions at the presence of compositional systems

Compositional system	Water release, %	Time, min
OP-10/PEG	79	110
OP-10/sulphanol	88,5	140
CTAB/NaCMC (1:1)	91,95	90
CTAB/NaCMC (1:2)	88,5	97,95
	88,8	

The combination of thermochemical treatment and centrifuging allow to achieve the high degree of dehydration. The greatest demulsification effect was shown by the compositional mixture based on sulphanol / PEG (98,4%) at a ratio of 1: 3 and CTAB / NaCMC (97,95%) at a ratio of 1: 1. In general, the combined treatment by compositions results in a high degree of crude oil breaking. The mixtures with any ratio of components at thermochemical processing favour to the destruction of natural emulsifier adsorbed layer and therefore, there is an additional water separation under the centrifuging after the heat treatment.

Thus, the results obtained clearly indicate the efficiency of breaking down water-in-crude oil emulsions using the compositional systems based on surfactant-surfactant and surfactant-polymer.

## CONCLUSION

1. The compositional mixtures showed a high surface activity at the water/oil interface (the interfacial tension was about 3.0 mJ/m<sup>2</sup>).
2. The demulsification of water-in-oil emulsion of Zhanaozen oilfield (Kazakhstan) by compositional systems was carried out. The optimum ratio of the demulsifying components, the maximum amount of water phase separation, the time of the



thermochemical treating were determined. The compositions of NaCMC/CTAB (1: 1, V = 91.95%) and OP-10/sulphanol (1: 3, V = 88.5%) were found to be the most efficient systems for demulsification of water-in-oil emulsion.

3. The combined demulsification (thermochemical processing and centrifuging) demonstrated a high degree of dehydration of water-in-oil emulsion. The most demulsification effect was shown by the mixture based on sulphanol / PEG (98.4%) at a ratio of 1: 3 and CTAB/NaCMC (97.95%) at a ratio of 1: 1.

#### ACKNOWLEDGEMENTS

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## EVALUATION OF BIOREMEDIATION EFFICIENCY IN CRUDE-OIL CONTAMINATED SOILS

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#### ABSTRACT

During oil exploration the contamination of soils with petroleum hydrocarbons (PH) could take place. This is still today one of the major environmental issues. On the other hand, it is already known that bioremediation is cheaper and more efficient than others soil remediation techniques. Consequently, in the framework of the present research, the effect of bioremediation treatment applied to an artificially crude oil-polluted soil was assessed by the decreasing in the PH concentration analysed at different times. The paper presents results regarding the assessment of *ex situ* bioremediation method applied within an experiment conducted for the decontamination of a soil artificially polluted with crude oil, on an impervious platform. Besides the bioremediation efficiency in PH removing from contaminated soil, also soil quality parameters were monitored: pH, total organic carbon content, total nitrogen, C / N ratio, mobile phosphorus and potassium contents and the soil loading degree with inorganic pollutants, heavy metals. The initial concentration of PH in soil was 15,000 mg/kg d.w. The diversity of bacterial genera and species of the native soil was relatively high; 7 taxons were representative, belonging to *Pseudomonas*, *Arthrobacter* and *Flavobacterium* genera that are known for species with high abilities in petroleum hydrocarbons biodegradation. The experiments lasted for ten months and the removing efficiency was evaluated after three, five and respectively, ten months. Across the experimental study, the highest efficiency in PH removing from the crude oil contaminated soil was found in the range of months 3 and 5 since the experiment has started (almost 72%). The petroleum hydrocarbons biodegradation final efficiency was about 92%. The obtained results are demonstrating the potential efficiency of biological remediation method as an environmental friendly solution for a proper management of the crude-oil contaminated sites.

**Keywords:** bioremediation, petroleum hydrocarbons, contaminated soils, crude oil