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# Nonionic surfactants based on polyoxyalkylated copolymers used as demulsifying agents

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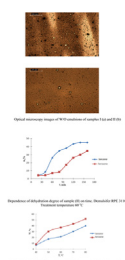
## HIGHLIGHTS

- Physicochemical properties of water-in-crude oil emulsions were studied.
- The effect of the mixture of oil soluble demulsifiers on the water-in-oil (W/O) stability at different temperatures was studied.
- The mixture of two nonionic block copolymers dissolved in kerosene is more efficient for oil emulsion studied in comparison with the mixture dissolved in benzene.
- The result obtained could be useful for formulation of the effective demulsifier composition for the oil emulsions stabilized by asphaltenes and resins.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Demulsification is one of the important stages in the petroleum processing. The breaking of 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 and increase the cost of transportation because of chloride salt content in aqueous phase of emulsion. The physicochemical properties of crude oil of the West Kazakhstan fields (Zhanaozen and Aksaz) which are known by high density and viscosity were studied. Non-ionic block copolymers based on alkoxylated compounds and their mixtures dissolved in organic solvents were used as deemulsifying agents. For the sample of the crude oil from Aksaz field demusification by composition of two demulsifiers dissolved in kerosene is more effective and starts at 40 °C. The most dewatering was observed at 80 °C and the dewatering degree was equaled to 51.95%.



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## 1. Introduction

Demulsification is one of the important stages in the petroleum processing. The breaking of 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 and increase the cost of transportation [1] because of chloride salt content in aqueous phase of emulsion. Therefore, preparation of oil for processing includes primarily dehydration and desalting of oil.

Currently, the Republic of Kazakhstan is one of the major oil-producing countries. Crude oil produced in Kazakhstan varies from light oils to heavy ones. Heavy oil reserves significantly exceed the reserves of light oils with low-viscosity oil. Heavy oils are characterized by high density (>920 $kg/m^3$) and large amount of asphaltenes, resins, and high molecular weight paraffins. It is known that asphaltenes and resins are surface active and form strong structural–mechanical barrier at the water–oil interface and, as a consequence, stable oil emulsions of water-in-crude oil are formed [2,3].

The aim of the present work is to study the physicochemical properties of crude oil of the West Kazakhstan fields (Zhanaozen and Aksaz) which are known by high density and viscosity crudes. Heavy oils of these fields form highly stable oil emulsion. Currently, the research of oil demulsification of the West Kazakhstan fields is of importance for oil processing in our country because these fields are one of the main sources of oil. Surface-active chemicals are used to destabilize water-in crude emulsions (demulsifiers). The most widely applied demulsifier agents are the polyethylene oxide and polypropylene oxide blockcopolymers due to their amphiphilic characteristics. Each crude oil requires the use of a specific demulsifier formulation due to the difference in the chemical composition of each oil [4].

Therefore, non-ionic block copolymers based on alkoxylated compounds and their mixtures dissolved in organic solvents such as benzene and kerosene were studied as demulsifying agents. Benzene as an aromatic solvent favors dissolution of asphaltenes and resins. The stabilization efficiency of asphaltenes and resins was proven to lose after dissolution in aromatic solvents [5]. Also, kerosene can dissolve asphaltenes and resins depending on nature of oils. In addition, kerosene was used due to its low cost and easy of access. Another advantage of oil soluble demulsifiers is that they do not contaminate waste waters of oil processing.

In this work, thermochemical dewatering of samples of crude heavy oil samples was carried out. The destabilization of emulsions was assessed by visual separation of the phases at different temperatures. The results reported herein contribute to a better understanding of the water/oil demulsification mechanism and selection of effective chemical agents.

## 2. Materials and methods

### 2.1. Crude oil characterization

Two samples of crude heavy oil from two fields of the West Kazakhstan region were used in this study: sample I from Zhanaozen field and sample II from Aksaz field. The density of the oil is 943 $kg/m^3$ and 921 $kg/m^3$ respectively. These oils are characterized as heavy oils according to their densities. The water content of the crude oil was determined by the Dean-Stark distillation method [6]. The chloride salts content was determined by extraction and volumetric titration according to the standard procedures [7].

### 2.2. Demulsifier characterization

The demulsifiers used were commercial nonionic surfactants – block copolymers of ethylene oxide and propylene oxide (obtained from "BASF", Germany) – BASAROL PE 6100, BASAROL RPE 3110. These demulsifiers PE 6100, RPE 3110 are oil soluble with low value of RSN characterizing demulsifier HLB. RSN is determined by the demulsifier solubility in water (relative solubility number).

The PE 6100 is a pluronic of PE types. This is block copolymers in which the central polypropylene oxide group is flanked by two polyethylene oxide groups. They conform to the following structural formula:

$$HO(CH_2CH_2O)_x(CH(CH_3)CH_2O)_y(CH_2CH_2O)_zH$$

The pluronic RPE 3110 is nonionic surfactant also. It consists of block copolymers in which the central polyethylene oxide (PEO) block is flanked by two polypropylene oxide (PPO) blocks, as shown by the following formula:

$$HO(CH(CH_3)CH_2O)_x{-}(CH_2CH_2O)_y{-}(CH(CH_3)CH_2O)_xH$$

To demulsify the crude oil the individual demulsifers were dissolved in benzene or kerosene of 1% concentration was added into the crude oil. Also, their mixtures (PE 6100 + RPE 3110) were applied at a ratio of 1:1. Benzene used was of analytical grade. Kerosene was used without any purification.

### 2.3. IR-spectroscopic analysis of oil

To evaluate the composition of the crude oil the IR-spectroscopic analysis was conducted for investigated samples on Fourier IR spectrometer "Specrtum-65" (Perkin Elmer) at 4000–450 $cm^{-1}$ diapason.

### 2.4. Dispersion of 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.

### 2.5. Oil emulsion stability measurements

The stability of the emulsion was studied using the bottle test method 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 (W, %) 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.

## 3. Results and discussion

The stability of water-in-crude oil emulsions is caused by natural surfactants (asphaltenes and resins) in the oil composition. Such components are referred to as natural stabilizers of crude oil emulsions since they adsorb spontaneously at the water–oil interface and form adsorption layer preventing coalescence of water droplets. Asphaltenes and resins are high molecular components of oil which form a strong structural–mechanical barrier at the