

Nonionic surfactants based on polyoxyalkylated copolymers used as demulsifying agents



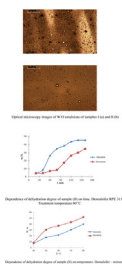
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HIGHLIGHTS

- 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 asphaltene 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 alkoxyated compounds and their mixtures dissolved in organic solvents were used as demulsifying agents. For the sample of the crude oil from Aksaz field demulsification 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 ($>920 \text{ kg/m}^3$) 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 alkoxyated 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

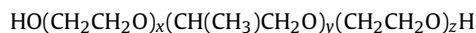
2.1. Crude oil characterization

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].

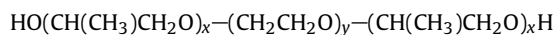
2.2. Demulsifier characterization

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:



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:



To demulsify the crude oil the individual demulsifiers 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 “Spectrum-65” (Perkin Elmer) at $4000\text{--}450 \text{ cm}^{-1}$ 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

Table 1

Characterization of the commercial demulsifiers used in the demulsification tests.

Pluronic	Physical form	Average molar mass (g/mol)	RSN (ml)	Viscosity (23 °C, Brookfield, 60 rpm) (mPa s)	Density, 23 °C (g/cm ³)	Surface tension, (DIN 53914, 1 g/l, 23 °C) (mN/m)	Percentage of polyethylene glycol in molecule (%)
PE 6100	Liquid	Approx. 2000	11.7	Approx. 350	Approx. 1.02	Approx. 40	10
RPE 3110	Liquid	Approx. 3500	9.8	Approx. 600	Approx. 1.03	Approx. 38	10

oil–water interface due to their interfacial activity [8,9]. The content of asphaltenes and resins is equal to 1–2 wt% and 16.6–20 wt%, respectively in the West Kazakhstan oil fields [10]. In the petroleum industry, there is a great variation in the content of such components depending mainly on the oil field. As a consequence, the stability of water-in-oil emulsions from different oil sources could vary also. Therefore, it was necessary first to study the physicochemical properties of the oils to choose an effective demulsifiers. Table 2 demonstrates some physicochemical characteristics of the oil emulsions studied.

As shown in Table 2 the oils of two fields are heavy ones by both density values and water, in addition, the salt and mechanical impurity content exceed significantly their acceptable quantities for oil processing. Currently, both domestic experience and international one show that requirements for oil, arriving at the oil refinery the content of water should be no more than 2%, chloride salts – 3 mg/l, and mechanical impurities – 0.005% [11]. Water, chloride salts dissolved in water and also mechanical impurities exert significant damage, causing corrosion and erosion of equipment. Mechanical impurities can sediment on the walls of equipment and pipelines and decrease their cross section that can lower oil flows. Moreover, mechanical impurities also influence on water-in-crude oil emulsion stability by forming solid stabilizers of oils.

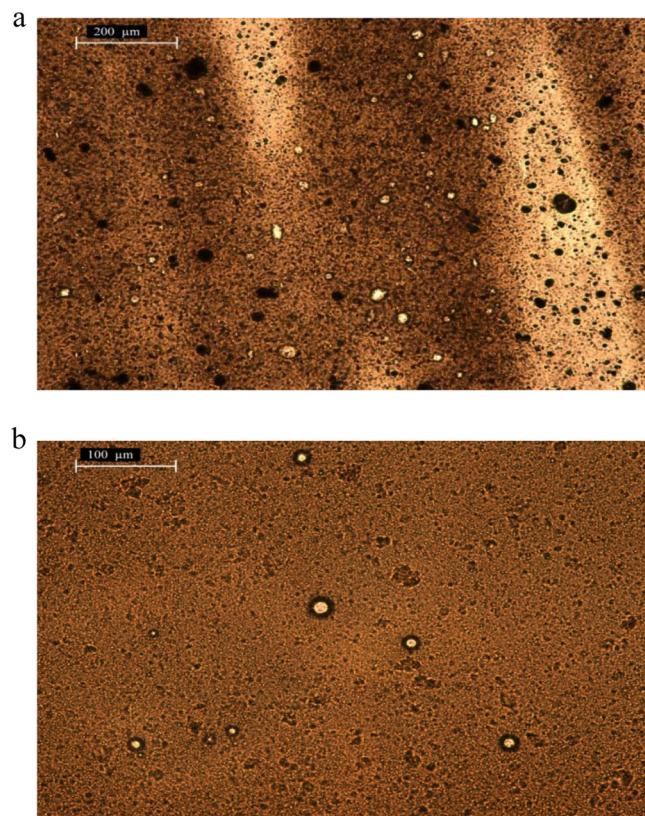
In fact, water, dispersed in crude oil, increases viscosity of the oil and promotes boiling off oil under distillation. The presence of salt in the crude oils also leads to the deactivation of catalysts employed at the refinery.

Therefore, breaking of emulsions is very important in all oil industry operations including crude oil production, transportation and refining [12]. In order to avoid technological problems discussed above, it is necessary to separate oil from water fully, i.e. break down W/O emulsions.

According to optical microscopy images of oil emulsion samples dispersion of water droplets varies within 2–10 μm (sample I) and 3–5 μm (sample II), i.e. oil emulsions are fine dispersed (Fig. 1). Besides, micrographs of W/O emulsions show clearly that the water droplet is surrounded by layer of determined thickness. This could be an adsorption layer formed from solid particles of mechanical impurities of a hydrophobic nature or so called “black emulsifiers” consisting of asphaltenes and resins. At the same time, optical microscopy images show also clearly the presence of black particles (Fig. 1a). These particles may represent also mechanical impurities which can be removed by gravity separation due to their large size. Generally, crude oil emulsions are complex and should be characterized as completely as possible. Water droplet size and amount, compositions of oil, surface active components are important. For this purpose we have studied the IR-spectra of the samples researched in this work.

The IR-spectra confirm the presence of water in crude oil samples: areas of 3436.06 cm^{-1} , 3434.11 cm^{-1} correspond to hydroxylic groups absorbance (Fig. 2a and b). More high intensity of $\nu\text{-OH}$ -groups testifies to high water content in Zhanaozen field oil (sample I) in comparison with sample II. This correlates with data of Table 1 concerning water content.

In addition, the IR-spectrum of the sample I shows the presence of the paraffinic structures of normal and branched chain, long chain paraffins (band at 2954.51 ; 2850.24 ; 1462.87 ; 1377.13 ;

**Fig. 1.** Optical microscopy images of W/O emulsions of samples I (a) and II (b).

719.77 cm^{-1}). Bands at 1162.25 cm^{-1} and 1073.08 cm^{-1} correspond to aromatic structures and at 1631.81 cm^{-1} – naphthenic groups. The IR-spectrum of sample II is similar to the IR-spectrum of the sample I. Sample II also contains paraffinic groups at 2920 , 2850.46 , 1377.14 and 720.03 cm^{-1} ; the band at 1462 cm^{-1} is characteristic of benzene rings. The presence of benzene rings may also confirm the groups including to the asphaltenes and resins, since asphaltenes and resins are polyaromatic and polycyclic condensed ring compounds containing heteroatoms [1].

High density of heavy oils is connected also with high molecular components (asphaltenes, resins, and high molecular weight paraffins) contained in the oil samples. Asphaltenes and resins are known to play an important role in the formation and stability of water-in-crude oil emulsion. Adsorption layer formed by asphaltenes and resins provides the structural–mechanical factor of oil emulsion

Table 2

Physicochemical characterization of heavy crude oils.

Physicochemical characteristics	Crude oil (I) from Zhanaozen field	Crude oil from Aksaz field (II)
$\rho_{20\text{ °C}}$ (kg/m ³)	943.5	921.3
Water content (%)	22.6	2.31
Chloride salts content (mg/l)	154.8	141
Mechanical impurities (%)	5.22	8.39

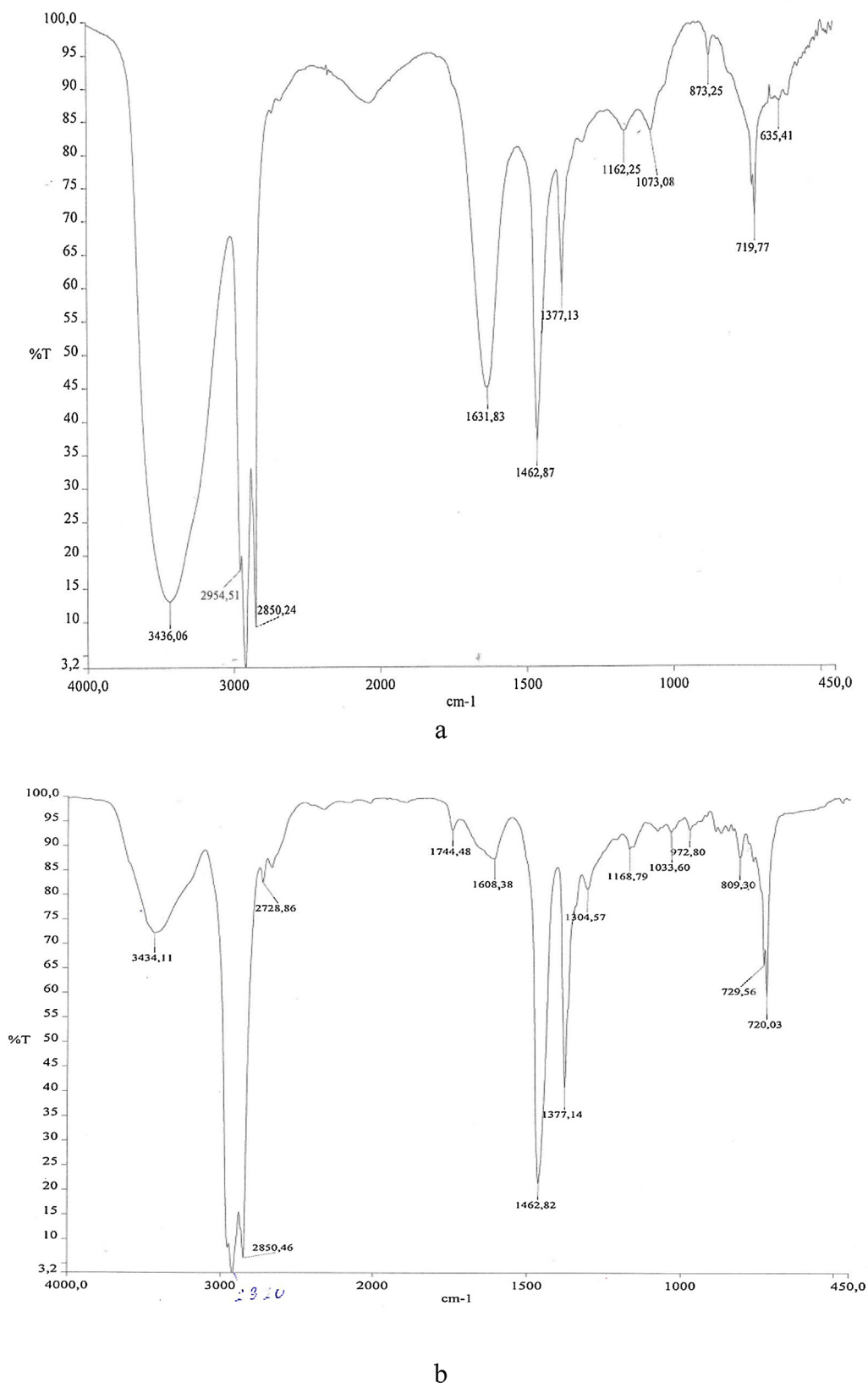


Fig. 2. IR-spectra of oil samples I (a) and II (b).

stabilization. The structural–mechanical barrier (after Rehinder [13]) consisting of high molecular weight asphaltenes, and resins is able to ensure high stability of emulsions due to the structure and mechanical properties of such an adsorption layer.

To break the crude oil emulsions the thermochemical dewatering was carried out using alkylene oxide block copolymers. For dewatering of the crude oil of two samples oil-soluble non-ionic block copolymers PE 6100 and RPE 3110 were used. The

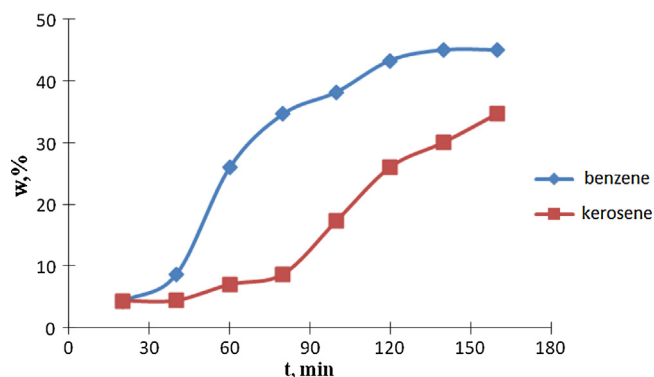


Fig. 3. Dependence of dehydration degree of sample (II) on time. Demulsifier RPE 3110. Treatment temperature 60 °C.

demulsifier PE 6100 represents block copolymers of PPO-PEO-PPO and RPE 3110 is a block copolymer of PEO-PPO-PEO type.

These compounds are oil-soluble and have different HLB (hydrophilic–lipophilic balance) values. HLB for such demulsifiers can be characterized by relative solubility in water RSN (relative solubility number) (Table 1).

In the case when RSN < 13 amphiphilic compounds based on block copolymers are not soluble in water, i.e. HLB displaced to the oil phase. Consequently, adsorption of these nonionic surfactants at the interface leads to displacing natural stabilizers. Adsorption layer of asphaltenes will be displaced to the oil phase and favors water droplet coalescence. Also, organic solvents favor dilution of asphaltenes and resins which lose their stabilizing capability.

Using individual surfactants dissolved in benzene resulted in only 0.44% dehydration of sample I at 40 °C. Increasing the temperature to 70 °C did not result in further separation of the water from the oil emulsion. Mixture of two block copolymers of RPE and PE types at a ratio of 1:1 at 40 °C doubled the dehydration degree (0.88%). Raising the temperature to 70 °C lead to oil emulsion dehydration increase by three times (1.32%). But so low meanings of the dewatering degree show that thermal influence is not enough for sample I and it is necessary to use other methods such as electrical, electromagnetic and others.

While the sample II of Aksaz field undergoes to more thermochemical dehydration. Using of 1% solution of RPE 3110 dissolved in benzene showed that dewatering begins only at 60 °C and reaches 45% after 2 h. Addition of this demulsifier dissolved in kerosene at the same terms destroys the oil emulsion till 34.63% (Fig. 3).

Use of mixtures of two demulsifiers RPE 3110 and PE 6100 at a ratio of 1:1 showed more efficiency of the mixture dissolved in kerosene in comparison with this mixture dissolved in benzene. The separation of water from the oil phase was observed at 40 °C and the dewatering increased to 51.95% at 80 °C (Fig. 4).

The mixture of two block copolymers RPE 3110 and PE 6100 which have similar hydrophilic block content (polyethylene oxide, %) and similar hydrophobic block content (polypropylene oxide, %) but their structure are different (PPO-PEO-PPO and PEO-PPO-PEO). Due to their amphiphilic structure the block copolymers have the high interfacial activity to the oil–water interface. The PEO segment is more hydrophilic and interacts preferably to the water molecules and the PPO segment is more lipophilic and mainly interacts with the oil phase. The mixture of two demulsifiers provides the extensive adsorption of the demulsifier molecules. The more hydrophilic part of the demulsifiers interacts with the water molecules and decreases the interaction between the stabilizer molecules and the water molecules [4]. The hydrophobic part of the demulsifiers (polypropylene oxide blocks) is oriented to the depth of the oil phase. The oil phase spontaneously penetrates on the vacancies at the interface and the stabilizer particles wetted by the oil are

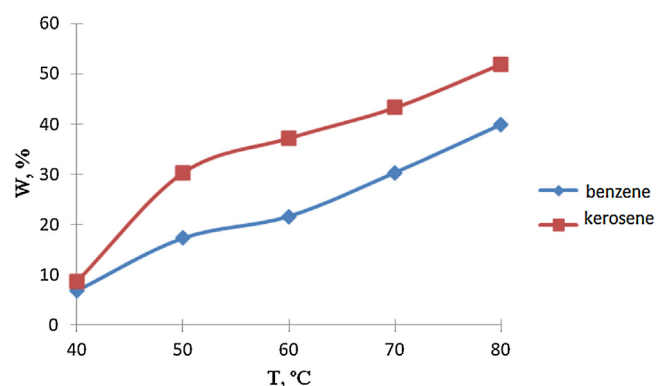


Fig. 4. Dependence of dehydration degree of sample (II) on temperature. Demulsifier – mixtures of RPE 3110 and PE 6100.

displaced from the interface into the oil phase. The water globules are deprived of the protective layers. As a result of the collision of dispersion phase particles water droplets can coalesce into larger ones.

In addition, the solvents influence on the efficiency of the demulsifier [14]. The experimental results showed the higher demulsification efficiency of the demulsifier solution in kerosene than the destabilizing action of the demulsifier dissolved in benzene. It is known that kerosene consists of 60% of saturated hydrocarbons and has relatively low density (0.75–0.80 g/cm³). Due to this kerosene is rapidly distributed in the organic medium and delivers the demulsifiers to the interface. Benzene is characterized by greater density of about 0.87 g/cm³ and, apparently, by lesser degree of mixing with the oil. Accordingly, not all of the demulsifier macromolecules are distributed at the interface and their efficiency decreases.

4. Conclusion

In this work crude oil of two fields of West Kazakhstan region (Zhanaozen and Aksaz) were investigated. Water-in-crude oil emulsions contain different amount of water of different dispersions. Demulsification of these heavy oils is complicated by high molecular components which stabilize oil emulsions. The influence of oil-soluble demulsifiers was studied with respect to these oils for the first time. Zhanaozen heavy oil emulsion (sample I) had a very high stability and separation of water from oil was poor (less than 2% at 70 °C). For demulsification of this crude oil the heating with addition mix of two oil-soluble demulsifying agents is not enough. For second sample from the Aksaz field demulsification 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%. The use of mixtures of two surfactants based on oil-soluble alkylene oxide block copolymers allows to enhance assortment of demulsifying agents and decrease cost of demulsifiers.

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