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Study on the effect of new compositions on the breakdown of stable water-in-oil emulsions

Badanie wpływu nowych kompozycji na rozpad stabilnych emulsji typu woda w oleju

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ABSTRACT: The increase in the production of high-viscosity crude oils often leads to the formation of persistent water-in-oil emulsions, mainly due to the presence of formation water during extraction. These emulsions hinder transportation and processing because they contain high levels of asphaltenes, resins, paraffins, salts, and mechanical impurities. These components act as natural emulsifiers, increasing viscosity and corrosiveness, raising operational costs, reducing processing efficiency, and accelerating equipment wear. This study evaluates the effectiveness of newly developed multifunctional KA-series compositions (KA-1, KA-2, KA-3) in breaking persistent emulsions under laboratory conditions. The formulations were developed using BAF-1, gossypol resin (a corrosion inhibitor), and commercial demulsifiers (ND-12, Difron-9426, Alkan-415), and were tested on crude oil from the Absheron (35% water), Sangachal (30%), and Dashgil (32%) fields in Azerbaijan. Experiments were carried out at temperatures of 20–50°C, reagent concentrations of 50–500 g/t, and contact times of 40–120 minutes. Demulsification efficiency increased with both temperature and reagent concentration, reaching optimal values at 50°C after 120 minutes. For all three fields – Absheron, Sangachal, and Dashgil – the optimal dosages of the KA-series demulsifiers ranged from 150 to 500 g/t, providing approximately 98–99% separation efficiency in the tested samples. The KA compositions also reduced residual water, mechanical impurities, and chloride content. For example, KA-2 lowered chloride concentration in the Absheron sample from 417.4 to 103.4 mg/L and reduced mechanical impurities from 1.63% to 0.05%, with similar trends observed in other samples. This study demonstrates that multifunctional demulsifiers tailored to the specific challenges of heavy crude oils outperform single-component reagents. The findings provide a scientific basis for improving oil-treatment processes, especially in fields with high water content and stable emulsion formation. The KA-series formulations show strong potential for industrial application in such reservoirs. The novelty of this study lies in the development and laboratory validation of multifunctional KA-series demulsifier formulations specifically tailored for high-viscosity crude oils, ensuring both high separation efficiency and reduced residual water content. These results contribute to the optimization of crude oil dehydration processes, enabling more efficient and environmentally sustainable oil production.

Keywords: KA-series compositions, water-in-oil emulsions, individual reagents, chloride salts, mechanical impurities, high-viscosity crude oils.

STRESZCZENIE: Wzrost wydobycia ropy naftowej o wysokiej lepkości często prowadzi do powstawania trwałych emulsji typu woda w oleju, głównie wskutek obecności wody złożowej podczas wydobycia. Emulsje te utrudniają transport i przetwarzanie, ponieważ zawierają znaczne ilości asfaltenów, żywic, parafin, soli oraz zanieczyszczeń mechanicznych. Składniki te działają jak naturalne emulgatory, zwiększając lepkość i korozyjność, podnosząc koszty eksploatacji, zmniejszając wydajność przetwarzania i przyspieszając zużycie sprzętu. W niniejszym badaniu oceniono skuteczność nowo opracowanych wielofunkcyjnych kompozycji serii KA (KA-1, KA-2, KA-3) w rozbijaniu trwałych emulsji w warunkach laboratoryjnych. Formuły zostały opracowane przy użyciu BAF-1, żywicy gossypolowej (inhibitora korozji) oraz komercyjnych demulgatorów (ND-12, Difron-9426, Alkan-415). Badania przeprowadzono na próbkach ropy naftowej ze złóż Apszeron (35% wody), Sangaczal (30%) i Dashgil (32%) w Azerbejdżanie. Eksperymenty przeprowadzono w temperaturze 20–50°C, przy stężeniach odczynników 50–500 g/t i czasie kontaktu 40–120 minut. Skuteczność demulgacji wzrastała wraz z temperaturą i stężeniem odczynnika, osiągając optymalne wartości w temperaturze 50°C po 120 minutach. W przypadku wszystkich trzech złóż – Apszeron, Sangaczal i Dashgil – optymalne dawki demulgatorów serii KA wynosiły od 150 do 500 g/t, zapewniając około 98–99% skuteczność separacji w badanych próbkach. Kompozycje KA przyczyniły się również do obniżenia zawartości wody resztkowej, zanieczyszczeń mechanicznych oraz chlorków. Przykładowo, w próbce ze złoża Apszeron kompozycja KA-2 obniżyła stężenie chlorków z 417,4 do 103,4 mg/l oraz zmniejszyła zanieczyszczenia mechaniczne z 1,63% do 0,05%. Podobne tendencje zaobserwowano w pozostałych próbkach. Przeprowadzone badania wykazały, że wielofunkcyjne demulgatory dostosowane do specyfiki ciężkiej ropy naftowej przewyższają skutecznością odczynniki jednoskładnikowe. Wyniki badań stanowią naukową podstawę do doskonalenia procesów uzdatniania ropy naftowej, szczególnie w złożach o wysokiej zawartości wody i skłonności do tworzenia trwałych emulsji.

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Preparaty z serii KA wykazują duży potencjał do zastosowań przemysłowych w takich złożach. Innowacyjność niniejszego badania polega na opracowaniu i laboratoryjnej walidacji wielofunkcyjnych preparatów demulgujących serii KA, zaprojektowanych specjalnie do ropy naftowej o wysokiej lepkości, zapewniających wysoką skuteczność separacji przy jednoczesnym obniżeniu zawartości wody resztkowej. Wyniki te przyczyniają się do optymalizacji procesów odwadniania ropy naftowej, umożliwiając bardziej wydajną i zrównoważoną środowiskowo produkcję ropy.

Słowa kluczowe: kompozycje serii KA, emulsje typu woda w oleju, indywidualne odczynniki, sole chlorkowe, zanieczyszczenia mechaniczne, ropa naftowa o wysokiej lepkości.

Introduction

In recent years, the decline in light oil production and the increase in the extraction of highly viscous and heavy crude oils have significantly raised the water content in produced oil. This, in turn, leads to the formation of stable physicochemical systems with formation water, commonly known as emulsions. The presence of such emulsions not only complicates processing operations but also intensifies corrosion risks in pipelines and equipment, making the issue of demulsification particularly relevant (Ali and Alqam, 2000; Gurbanov and Sardarova, 2022).

The chemical reagents used during enhanced oil recovery operations – especially surfactants and polymers – often result in the formation of water-in-oil emulsions with both aggregative and kinetic stability. In most cases, demulsifiers are applied to break these emulsions. However, the excessive use of diverse and expensive demulsifiers not only increases production costs but also creates operational challenges during refining (Lutfullin et al., 2005; Nebogina et al., 2008; Bakhtizin et al., 2016). Furthermore, the application of individual demulsifiers often fails to achieve deep demulsification of stable emulsions, particularly in heavy and high-viscosity crude oils. Therefore, the development of new, highly efficient multifunctional formulations has become essential for preparing such oils for transportation (Matiyev et al., 2016).

Currently, the effective breakdown of highly stable emulsions formed by highly viscous crude oils is considered one of the most technically complex challenges in oil production. Emulsion stability depends on various factors, including droplet size, oil viscosity and density, the content of light hydrocarbon fractions, the physicochemical properties of the water phase, temperature, pressure, mixing rate, and duration. Stability plays a critical role in determining the appropriate processing technologies and the extent of phase separation. It is commonly evaluated based on the dispersity and temporal equilibrium of the dispersed phase (Mukhamadiyev and Notov, 2008; Gurbanov and Gasimzade, 2023).

Water remains one of the most valuable and limited resources on the planet. One of the main threats to environmental safety is oil and petroleum products, and stable water-in-oil emulsions are among the most persistent and challenging pollutants. These emulsions are often resistant to mechanical separation and present significant environmental, technical, and economic risks. Therefore, the advancement of oil preparation and treatment technologies is crucial for improving both the quality of final petroleum products and overall technical-economic efficiency (Schubert and Armbruster, 1989; Al-Sahhaf et al., 2008; Verruto and Kilpatrick, 2008; Gurbanov and Gasimzade, 2022).

This article is devoted to the development of new multifunctional compositions designed to break down water-in-oil emulsions with aggregative stability, particularly those formed in highly viscous heavy oils. The study also evaluates the effectiveness of these formulations under laboratory conditions. Previous research has provided the foundation for this work: Pal et al. (2021) studied the performance of naturally derived demulsifiers; Nurullayev et al. (2022) analyzed the geological and technological development of the Siyazan monocline oil field; Iskandarov (2024) examined structural changes in complex pipeline systems; and Gurbanov and Sardarova (2022) explored microbiological protection methods for underground facilities.

Objective of the study

The purpose of this research is to examine the application of new compositions in the demulsification of water-in-oil emulsions with aggregative and kinetic stability under laboratory conditions.

Research methodology

Preparation of crude oil samples with highly viscous properties for transportation was carried out under laboratory conditions in accordance with the methodology described in previous work (Gurbanov and Gasimzade, 2022).

Additionally, during the preparation process, experimental results and established mathematical expressions were used to determine the percentage of residual water, ballast water, mechanical impurities, and chloride salts, as well as to evaluate the demulsification efficiency of the newly developed KA-series compositions (Gasimzade, 2024).

A commonly applied method for evaluating the demulsification efficiency of individual reagents and their formulated compositions is the bottle test (static settling) procedure. In this method, the demulsifying agent or its composition is first dissolved in an appropriate solvent and then introduced into pre-selected crude oil samples at varying concentrations. The mixture is then vigorously agitated for approximately 1 minute to ensure uniform dispersion of the reagent. Subsequently, the emulsified oil samples are placed in a thermostated water bath under controlled temperature conditions. The calculation of demulsifier doses is carried out based on the initial water content of the water-in-oil emulsions without taking into account the concentration of the demulsifier and the oil.

The tested water-in-oil emulsion samples are placed in a specially graduated 100 mL conical-bottom precipitating vessel, and a pre-calculated amount of commercial demulsifier is added to each of them using micro-dosing syringes. The vessels are tightly sealed and shaken by hand for 10 minutes to ensure even distribution of the demulsifier within the oil phase and thorough mixing.

After mixing, the vessels containing the water-in-oil emulsions treated with demulsifiers are placed in a thermostat for the period of time corresponding to their residence time in pipelines and technological oil production facilities. The thermostatic temperature corresponds to the technological temperature of oil dehydration. The volume of separated water is recorded at preselected time intervals. In addition, the quality of the separated water after oil dehydration is visually analyzed. Subsequently, using a special sampler, an oil sample is taken at a level of 10 mm above the oil-water phase separation boundary to determine the residual water content (GOST 2477-2014). Based on the volume of separated water over time, the dehydration degree of the emulsions is calculated using the initial water content of the water-in-oil emulsions:

$$W = V_0/V \cdot 100\% \quad (1)$$

where W is the demulsification efficiency [%], V_0 is the volume of separated water, [mL], V is the initial water content, [mL] (Gurbanov and Gasimzade, 2022).

Additionally, the amount of ballast water (B) in the oil sample after demulsification is calculated using the following empirical formula, based on the amount of water separated from the emulsion and the initial water content of a 100 g oil sample at various temperatures over a two-hour period:

$$S = [(m_1 - m_2)/(m_3 - m_2)] \cdot 100\% \quad (2)$$

where S is the percentage of ballast water after demulsification [%], m_1 is the amount of water in the oil before demulsification [mL], m_2 is the amount of water separated from the oil during demulsification [mL], m_3 is the volume of the oil sample [mL].

The efficiency of the demulsification process was calculated based on the difference between the initial water content of the emulsion and the amount of water separated during treatment. The residual water (R) content (Δm) was determined using the following expression:

$$\Delta m = m_1 - m_2 \quad (3)$$

The water content of crude oil samples was determined according to ASTM D4006 using a Dean–Stark apparatus.

The amounts of mechanical impurities and chloride salts in crude oil samples were determined under laboratory conditions in accordance with standard procedures. Mechanical impurities were quantified based on the known mass of the oil. The oil samples were filtered using filter paper, and the retained solid phase was dried at 105°C to a constant weight. The difference in weight before and after filtration was used to calculate the percentage of mechanical impurities. This procedure followed GOST 6370-83 (Gasimzade, 2024; Nurullayev et al., 2023).

The chloride salt content was determined using the water extraction method in accordance with GOST 21534-76. The crude oil sample was mixed and homogenized with distilled water, and the resulting aqueous phase was separated and analyzed. The concentration of chloride ions in the aqueous extract was determined by argentometric titration (Mohr method). The results were expressed in mg/L, and variations in concentration were recorded at different reagent dosages.

Each measurement was performed in triplicate, and the average values were reported. All reagents used during the experiments were of analytical grade, and the tests were conducted under identical conditions to ensure accuracy and reproducibility (Gasimzade, 2024).

Chemical nature and classification of reagents

To carry out the laboratory demulsification of crude oil samples with stable water-in-oil emulsions and highly viscous properties, new KA-series compositions, with code names KA-1, KA-2, and KA-3 were developed. These compositions were prepared using gossypol resin as a corrosion inhibitor, the BAF-1 reagent and the demulsifiers ND-12, Difron-9426, and Alkan-415.

In this study, the KA-series multifunctional compositions were formulated to evaluate their demulsification performance against stable water-in-oil emulsions formed by heavy crude oils. Each KA composition consists of a combination of surface-active agents and functional additives with complementary physicochemical properties:

- ND-12 – nonionic surfactant produced in Azerbaijan for crude oil demulsification;

- Difron-9426 – block copolymer of ethylene and propylene oxides dissolved in methanol;
- Alkan-415 – nonionic ethoxylated alcohol-based surfactant for crude oil dehydration;
- Gossypol resin – by-product of cottonseed oil processing, exhibiting corrosion-inhibiting and surface-active properties;
- BAF-1 – multifunctional composition with high surface activity and dispersing ability, effective against asphaltene–resin–paraffin structures, improving oil flow and reducing corrosion.

When used in combination within the KA-series compositions, these components provide synergistic action, enhancing the demulsification process and the overall stability of oil treatment systems under laboratory conditions.

Detailed information about the KA-series compositions is presented in Table 1.

Table 1. Code names and components of the compositions (by volume)

No.	Code name of the composition	Components of the compositions	Component ratio
1	KA-1	BAF-1 + Difron-9426 + Gossypol resin	13:19:6
2	KA-2	BAF-1 + ND-12 + Gossypol resin	14:18:6
3	KA-3	BAF-1 + Alkan-415 + Gossypol resin	16:16:6

Table 2 presents the physicochemical characteristics of the crude oil samples used in the research (ASTM D, 2017; ASTM D, 2024; ASTM D, 2020; ASTM D, 2022; ASTM D, 2019a; ASTM D, 2019b; GOST, 1976; GOST, 1983; GOST, 1985; GOST, 2014).

To carry out the laboratory demulsification of crude oil samples containing stable water-in-oil emulsions formed with formation water, new KA-series compositions with code names KA-1, KA-2, and KA-3 were developed. These samples included oil from the Absheron field with an emulsified water content of 35%, the Sangachal field with 30%, and the Dashgil field with 32%. The experiments were conducted at varying durations of 40, 80, and 120 minutes and at temperatures of 20, 30, 40, and 50°C. During the tests, KA-series compositions were applied at concentrations of 100, 200, 300, 400, and 500 g/t for the Absheron emulsion sample; 50, 100, and 150 g/t for the Sangachal sample; and 50, 100, 150, 200, and 250 g/t for the Dashgil sample.

Analysis and discussion of results

In the first stage, the demulsification of stable water–oil emulsions was carried out without the use of chemical reagents, under the influence of temperature alone. Experiments were conducted in the temperature range of 20–60°C for durations of 40, 80, and 120 minutes (Table 3).

Table 3. Demulsification of stable water–oil emulsions without reagents

Oil sample	T [°C]	Demulsification efficiency [%]		
		40 min	80 min	120 min
Absheron	20	12.4	21.6	33.1
	30	15.2	28.5	37.3
	40	20.5	36.4	45.6
	50	26.8	40.3	57.6
	60	37.2	55.1	72.4
Sangachal	20	18.5	31.3	47.6
	30	24.2	40.7	55.4
	40	30.3	48.5	63.1
	50	37.2	56.6	75.8
	60	45.4	68.5	83.2
Dashgil	20	15.3	27.8	44.5
	30	18.7	38.6	51.2
	40	25.3	44.5	57.8
	50	30.7	52.4	66.1
	60	38.5	66.3	78.4

Table 2. Physicochemical characteristics of crude oils

No.	Indicators	Absheron	Sangachal	Dashgil	Indicated methods
1	Density at 20°C [kg/m^3]	915.1	856.3	897.2	ASTM D1298 (Hydrometer method)
2	Kinematic viscosity at 20°C [cSt]	122.0	27.3	756	ASTM D445 (Capillary viscometer)
3	Water content, mass [%]	35	30	32	ASTM D4006 (Distillation)
4	Chloride salt content [mg/l]	534.3	152.1	326.2	ASTM D6470 GOST 21534 (Extraction method)
5	The content of mechanical impurities [% (*m*/*m*)]	5.86	1.9	3.76	GOST 6370 (Filtration method)
6	Resin content [% (*m*/*m*)]	10.7	8.96	2.5	ASTM D2007 (Solvent precipitation)
7	Asphaltene content [% (*m*/*m*)]	5.6	0.35	3.8	ASTM D6560 (n-heptane precipitation)
8	Paraffin content [% (*m*/*m*)]	4.4	9.3	12.7	GOST 11851 (Cooling and filtration method)

The results clearly show that demulsification efficiency increased significantly with temperature for all samples. The lowest efficiencies were recorded at 20°C, while the highest values were obtained at 60°C. Nevertheless, even at the optimal temperature without reagents, complete phase separation did not occur (e.g., in the Absheron sample, the maximum efficiency was 72.4%). This underlines the necessity of using chemical reagents to achieve higher separation levels.

In the next stage, the effect of individual reagents — Difron-9426, ND-12, and Alkan-415 — which are components of the KA-series compositions, was studied. Experiments were conducted at 60°C, identified as the most favorable temperature in the reagent-free stage (Table 4–6).

All individual reagents significantly improved demulsification efficiency compared to the reagent-free process. For example, in the Absheron sample at 60°C and 120 minutes, efficiency increased from 72.4% without reagents to 92.1% with Difron-9426, 93.9% with ND-12, and 93.6% with Alkan-415. Similar improvements were observed for the Sangachal and Dashgil samples. Although the differences among the three reagents were relatively small, ND-12 and Alkan-415 demonstrated slightly higher efficiencies in some cases. This indicates their potential for enhanced performance when used in combination formulations.

The results showed that at 20°C, the demulsification efficiency of KA-1 composition increased with increasing concentration in all three studied emulsified crude oil samples. The highest efficiency was observed at the optimal concentration of the composition. Over 120 minutes, KA-1 composition demonstrated efficiencies of 63.9%, 71.8%, and 59.9% for the Absheron, Sangachal, and Dashgil emulsified oil samples, respectively. At 20°C and 120 minutes, at the optimal concentration of KA-1, the residual and ballast water contents were 12.6% and 16.3% for the Absheron sample, 8.5% and 10.8% for the Sangachal sample and 10.8% and 13.8% for the Dashgil sample.

Table 4. Demulsification of oil samples with Difron-9426 at 60°C

Oil sample	$C_{reagent}$ [g/t]	Demulsification efficiency [%]		
		40 min	80 min	120 min
Absheron	150	39.4	57.8	74.7
	250	41.7	59.4	76.9
	350	44.5	62.5	80.5
	450	47.8	65.8	84.2
	550	51.7	69.0	88.7
	750	56.4	73.7	92.1
Sangachal	100	47.1	70.0	85.4
	200	49.6	72.5	87.8
	250	52.3	74.8	89.4
	300	55.8	78.2	92.8
	350	59.7	83.6	95.5
Dashgil	150	40.2	68.0	80.8
	250	43.6	72.4	83.7
	400	46.7	75.8	87.2
	550	50.8	79.2	91.3
	650	55.7	84.4	94.0

Table 5. Demulsification of oil samples with ND-12 at 60°C

Oil sample	$C_{reagent}$ [g/t]	Demulsification efficiency [%]		
		40 min	80 min	120 min
Absheron	150	39.7	58.4	75.3
	250	42.3	60.0	77.5
	350	45.2	63.2	82.4
	450	48.4	66.3	84.8
	550	55.6	69.8	89.5
	750	57.0	74.4	93.9
Sangachal	100	47.7	70.6	85.9
	200	50.3	73.2	88.4
	250	52.9	75.4	90.0
	300	56.4	78.8	93.7
	350	60.4	84.2	96.4
Dashgil	150	40.8	69.5	81.0
	250	44.3	73.0	84.4
	400	47.4	76.5	87.8
	550	51.6	79.8	91.9
	650	56.5	85.0	95.7

Table 6. Demulsification of oil samples with Alkan-415 at 60°C

Oil sample	$C_{reagent}$ [g/t]	Demulsification efficiency [%]		
		40 min	80 min	120 min
Absheron	150	39.5	58.1	75.0
	250	42.0	59.6	77.2
	350	44.9	63.0	82.2
	450	48.1	66.1	84.5
	550	55.3	69.5	89.1
	750	57.7	74.1	93.6
Sangachal	100	47.5	70.4	85.4
	200	50.0	73.0	88.2
	250	52.6	75.1	89.7
	300	56.1	78.5	93.5
	350	60.0	84.0	96.1
Dashgil	150	40.5	69.3	80.6
	250	44.0	72.7	84.2
	400	47.2	76.2	87.5
	550	51.3	79.5	91.6
	650	56.3	84.6	95.3

At 30°C, the demulsification efficiency of the KA-1 composition similarly increased with increasing concentration, reaching the highest values at the optimal concentration. Over 120 minutes, the KA-1 composition demonstrated efficiencies of 69.6%, 79.3%, and 72.4% for the Absheron, Sangachal, and Dashgil samples, respectively. At 30°C and 120 minutes, the residual and ballast water contents were 10.6% and 14.1% for the Absheron sample, 6.8% and 8.1% for the Sangachal sample, and 8.8% and 11.5% for the Dashgil sample.

At 40°C, a similar trend was observed – demulsification efficiency increased with concentration. Over 120 minutes, KA-1 composition exhibited efficiencies of 85.6%, 94.0%, and 87.3% for the Absheron, Sangachal and Dashgil samples, respectively. During the demulsification process at 40°C and 120 minutes, the residual and ballast water contents were 5.0% and 7.2% for the Absheron sample, 1.8% and 2.5% for the Sangachal sample, and 4.1% and 5.6% for the Dashgil sample.

At 50°C, the KA-1 composition reached the highest efficiency values across all studied samples. Over 120 minutes, the composition demonstrated efficiencies of 97.8%, 98.4%, and 98.0% for the Absheron, Sangachal, and Dashgil emulsified oil samples, respectively.

Figures 1–3 illustrate the dependence of residual and ballast water content on the concentration of the KA-1 composition at 50°C for the studied oil samples.

From the values shown in the graphs, it is evident that at 50°C, demulsification with KA-1 composition reached its optimal efficiency. Over 120 minutes, the residual and ballast water content for the Absheron, Sangachal, and Dashgil emulsified oil samples were 0.8% and 1.2%, 0.5% and 0.7%, and 0.6% and 0.9%, respectively.

At 20°C, the demulsification efficiency of KA-2 composition increased with increasing concentration in all three emulsified oil samples, with the highest efficiency observed at the optimal concentration. Over 120 minutes, the KA-2 composition demonstrated efficiencies of 64.9%, 72.5%, and

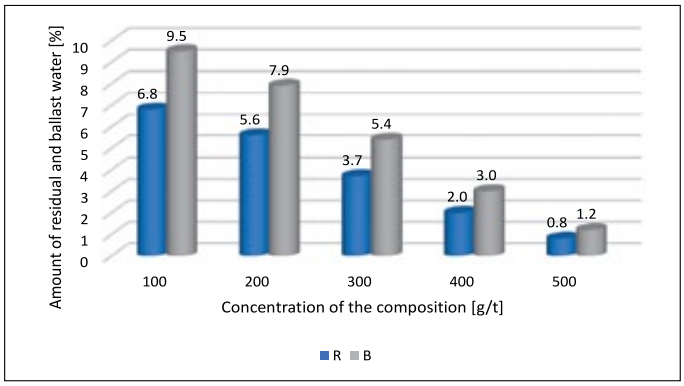

Figure 1. Dependence of residual water (R) and ballast water (B) content on the concentration of the KA-1 composition applied at 50°C (for Absheron oil)

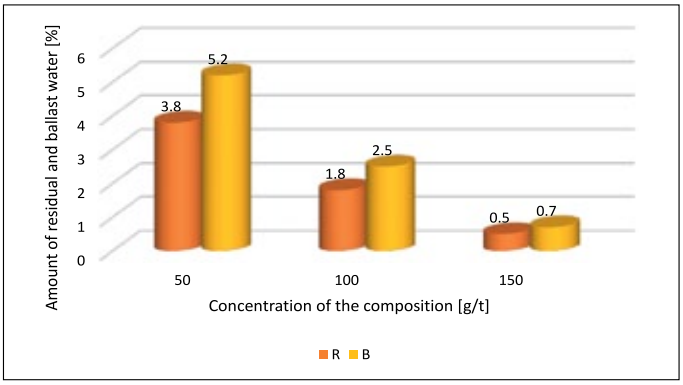

Figure 2. Dependence of residual water (R) and ballast water (B) content on the concentration of the KA-1 composition applied at 50°C (for Sangachal oil)

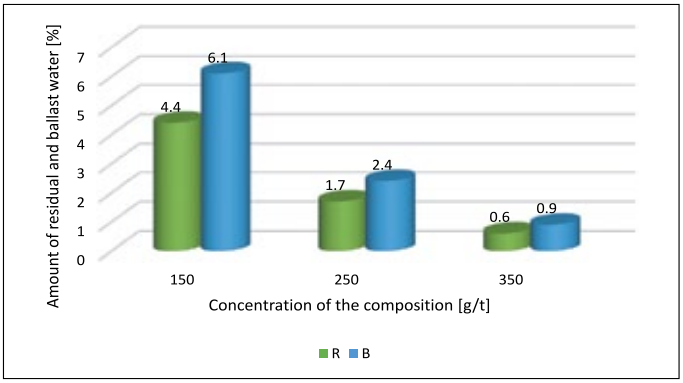

Figure 3. Dependence of residual water (R) and ballast water (B) content on the concentration of the KA-1 composition applied at 50°C (for Dashgil oil)

67% for the Absheron, Sangachal, and Dashgil samples, respectively. At 20°C and 120 minutes, at the optimal concentration of KA-2 composition, the residual and ballast water contents were 12.3% and 15.4% for the Absheron sample, 8.3% and 10.5% for the Sangachal sample, and 10.6% and 13.4% for the Dashgil sample.

At 30°C, the demulsification efficiency of the KA-2 composition also increased with increasing concentration, reaching the highest values at the optimal concentration. Over 120 minutes, the composition showed efficiencies of 70.1%, 80.1%, and 73.3% for the Absheron, Sangachal and Dashgil samples, respectively. At 30°C and 120 minutes, the residual and ballast water contents were 10.5% and 13.9% for Absheron, 6.0% and 7.9% for Sangachal, and 8.5% and 11.2% for Dashgil.

At 40°C, the demulsification efficiency of the KA-2 composition increased with increasing concentration, with the optimal concentration yielding the best results. Over 120 minutes, efficiencies were 86.5%, 94.6%, and 88.5% for Absheron, Sangachal, and Dashgil samples, respectively. At 40°C and 120 minutes, the residual and ballast water contents were 4.7% and 6.8% for Absheron, 1.6% and 2.3% for Sangachal, and 3.7% and 5.1% for Dashgil.

At 50°C, the highest efficiency values were again achieved at the optimal concentration. Over 120 minutes, the KA-2 composition demonstrated efficiencies of 99.1%, 99.5%, and 99.2% for the Absheron, Sangachal, and Dashgil samples, respectively.

Figures 4–6 show the dependence of residual and ballast water contents on the concentration of KA-2 composition at 50°C.

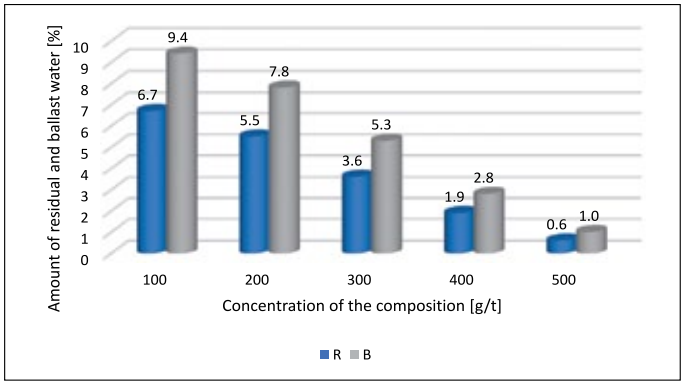

Figure 4. Dependence of residual water (R) and ballast water (B) content on the concentration of the KA-2 composition applied at 50 °C (for Absheron oil)

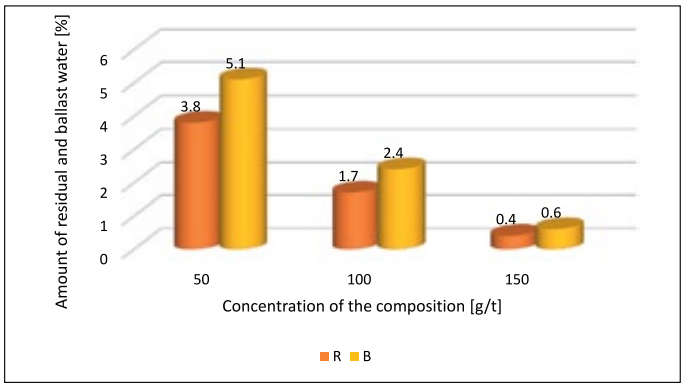

Figure 5. Dependence of residual water (R) and ballast water (B) content on the concentration of the KA-2 composition applied at 50°C (for Sangachal oil)

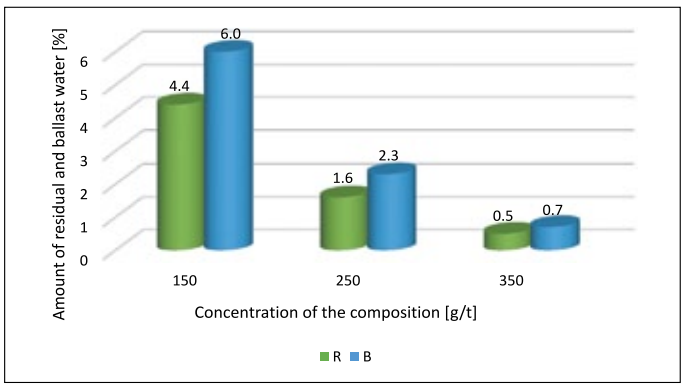

Figure 6. Dependence of residual water (R) and ballast water (B) content on the concentration of the KA-2 composition applied at 50°C (for Dashgil oil)

From the values shown in the graphs, it is evident that at 50°C, demulsification with the KA-2 composition reached its optimal efficiency. Over 120 minutes, the residual and ballast water contents were 0.3% and 0.5% for Absheron, 0.15% and 0.2% for Sangachal, and 0.25% and 0.4% for Dashgil.

At 20°C, the demulsification efficiency of the KA-3 composition increased with increasing concentration in all three emulsified oil samples, with the highest efficiency observed at the optimal concentration. Over 120 minutes, the KA-3 composition showed efficiencies of 64.0%, 72.0%, and 66.3% for Absheron, Sangachal, and Dashgil, respectively. At 20°C and 120 minutes, the residual and ballast water contents, were 12.6% and 16.2% for Absheron, 8.4% and 10.7% for Sangachal, and 10.8% and 13.7% for Dashgil.

At 30°C, the demulsification efficiency of the KA-3 composition also increased with increasing concentration, reaching the highest values at the optimal concentration. Over 120 minutes, the composition exhibited efficiencies of 69.8%, 79.4%, and 72.6% for the Absheron, Sangachal, and Dashgil samples, respectively. At 30°C and 120 minutes, the residual and ballast water contents were 10.6% and 14% for Absheron, 6.2% and 8.1% for Sangachal, and 8.8% and 11.4% for Dashgil.

At 40°C, the demulsification efficiency of the KA-3 composition increased with increasing concentrations, with the optimal concentration yielding the best results. Over 120 minutes, the efficiencies were 86%, 94.1%, and 87.7% for Absheron, Sangachal, and Dashgil, respectively. The residual and ballast water contents were 4.9% and 7.0% for Absheron, 1.8% and 2.5% for Sangachal, and 3.9% and 5.5% for Dashgil.

At 50°C, the highest efficiency values were again achieved at the optimal concentration. Over 120 minutes, the KA-3 composition exhibited efficiencies of 98.2%, 98.7%, and 98.4% for Absheron, Sangachal, and Dashgil, respectively.

Figures 7–9 illustrate the relationship between the concentration of the KA-3 composition and the residual and ballast water content at 50°C.

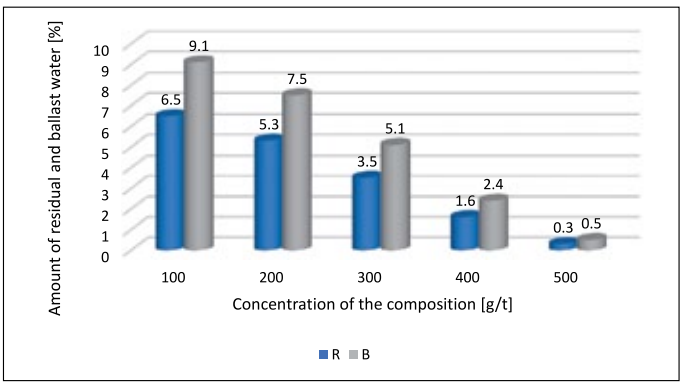

Figure 7. Dependence of the percentage of residual water (R) and ballast water (B) on the concentration of the KA-3 composition applied at 50°C (for Absheron oil)

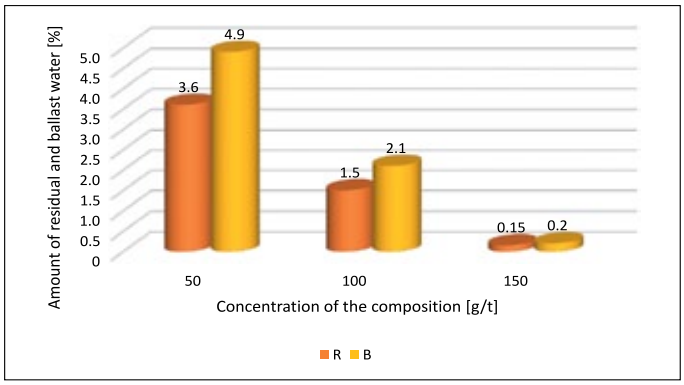

Figure 8. Dependence of the percentage of residual water (R) and ballast water (B) on the concentration of the KA-3 composition applied at 50°C (for Sangachal oil)

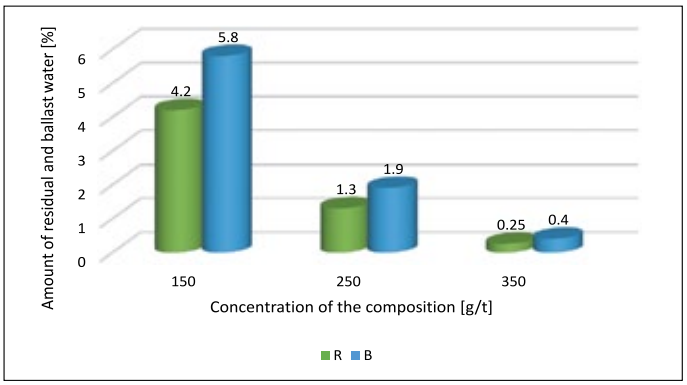

Figure 9. Dependence of the percentage of residual water (R) and ballast water (B) on the concentration of the KA-3 composition applied at 50°C (for Dashgil oil)

From the values shown in the graphs, it is evident that at 50°C, demulsification at the optimal concentration of the KA-3 composition resulted in residual and ballast water contents of 0.6% and 1.0% for Absheron, 0.4% and 0.6% for Sangachal, and 0.5% and 0.7% for Dashgil samples over 120 minutes.

In addition, the effects of varying concentrations of KA--series compositions at 50°C on the contents of chloride salts and mechanical impurities in the Absheron, Sangachal, and Dashgil oil samples were studied. When the concentrations of the KA-1, KA-2, and KA-3 compositions varied between 100–500 g/t at 50°C, the chloride salt and mechanical impurity contents in the Absheron sample decreased in the following ranges: 417.4–139.5 mg/L, 412.9–103.4 mg/L, 410.9–107.8 mg/L for chloride salts, and 1.6243–0.2453%, 1.6304–0.0532%, 1.4686–0.0993% for mechanical impurities.

Similarly, at 50°C, when the concentrations of the KA-1, KA-2, and KA-3 compositions in the Sangachal sample varied between 100–500 g/t, the chloride salt and mechanical impurity contents decreased in the following ranges: 91.8–54.7 mg/L, 80.6–43.4 mg/L, 84.7–50.8 mg/L for chloride salts and 0.2954–0.0678%, 0.2754–0.0368%, 0.2796–0.0616% for mechanical impurities. For the Dashgil sample, when the concentrations of the KA-1, KA-2, and KA-3 compositions at 50°C ranged between 100–500 g/t, the chloride salt and mechanical impurity contents decreased in the following ranges: 218.4–143.7 mg/L, 198.2–98.6 mg/L, 209.8–108.7 mg/L for chloride salts and 0.9321–0.0731%, 0.8964–0.0493%, 0.8996–0.0586% for mechanical impurities.

Using these results, the effectiveness of the KA-series compositions (KA-1, KA-2, KA-3) in the demulsification process was calculated and presented in comparative form in Table 7.

Table 7 shows that the highest effect of the new KA-series compositions occurred at 50°C. At this temperature, the optimal concentrations for the KA-1, KA-2, and KA-3 compositions in the demulsification of Absheron, Sangachal, and Dashgil emulsified oils were 500 g/t, 150 g/t, and 300 g/t, respectively. Among the KA-series compositions, KA-2 showed the best results in the demulsification of all three crude oil samples.

The effectiveness of the KA-series compositions, as shown in Table 2, can be summarized as follows:

1. The effectiveness of the KA-1 composition at 50°C, with optimal concentrations of 500 g/t, 150 g/t, and 300 g/t, for the Absheron, Sangachal, and Dashgil oil samples is 97.8%, 98.4%, and 98.0%, respectively.

Table 7. Comparative analysis of the efficiency rates during demulsification at the optimal concentration of KA series compositions

Oil sample	Composition	Concentration [g/t]	Time [min]	Temperature [°C]	Ballast water [%]	Efficiency rate [%]
Absheron	KA-1	500	120	50	1.2	97.8
Sangachal		150			0.7	98.4
Dashgil		350			0.9	98.0
Absheron	KA-2	500			0.5	99.1
Sangachal		150			0.2	99.5
Dashgil		350			0.4	99.2
Absheron	KA-3	500			1.0	98.2
Sangachal		150			0.6	98.7
Dashgil		350			0.7	98.4

2. The effectiveness of the KA-2 composition at 50°C, with optimal concentrations of 500 g/t, 150 g/t, and 300 g/t, for the Absheron, Sangachal, and Dashgil oil samples is 99.1%, 99.5%, and 99.2%, respectively.
3. The effectiveness of the KA-3 composition at 50°C, with optimal concentrations of 500 g/t, 150 g/t, and 300 g/t, for the Absheron, Sangachal, and Dashgil oil samples is 98.2%, 98.7%, and 98.4%, respectively.

Thus, the effects of the new compositions on the breakdown of aggregate and kinetically stable water-in-oil emulsions formed in high-viscosity crude oils were studied in laboratory conditions, and effective results were obtained. The analysis showed that the compositions provided more thorough demulsification of stable water-in-oil emulsions than individual demulsifiers.

Figure 10 presents the visual results of the demulsification of high-viscosity crude oil samples after treatment with the KA-3 and KA-2 compositions. The experiments were conducted at optimal concentrations and a temperature of 50°C. As shown in Figure 10, application of the compositions resulted in clear separation of the emulsions into water and oil phases.

Figure 10. Visual results of crude oil demulsification after treatment with the KA-3 and KA-2 compositions at the optimal concentration

The results show that application of the KA-2 and KA-3 compositions significantly increased the volume of the water phase and reduced the thickness of the emulsion layer. This confirms that the demulsification process proceeded with high efficiency. The visual observations are also consistent with the laboratory analysis results and demonstrate that both compositions are effective in breaking high-viscosity crude oil emulsions. The KA-3 composition was distinguished by faster phase separation, whereas KA-2 allowed the formation of a more stable and transparent water phase.

The results indicate that all KA-series compositions demonstrated high demulsification efficiency; however, different crude oil samples required different optimal dosages. This difference can be attributed primarily to the physicochemical properties of the samples, particularly their paraffin, asphaltene, and resin content, initial water content, and the degree of emulsion stability.

In the Absheron sample, higher viscosity and more stable emulsions necessitated a higher dosage to achieve maximum separation efficiency. The Sangachal sample, with a lower initial water content, reached high efficiency at a lower dosage. The Dashgil sample exhibited moderate emulsion stability, resulting in intermediate optimal dosages.

Trend analysis showed that for all samples, increasing the composition concentration increased efficiency up to an optimal threshold, beyond which no significant improvement was observed. This indicates that once the optimal concentration is reached, conditions for reducing interfacial tension and promoting droplet coalescence are fully met.

Furthermore, the reduction in ballast water content indicates that the compositions not only facilitated the separation of the water phase but also improved the quality of the separated water by reducing mechanical impurities. This is a significant advantage in commercial processing, as it can reduce the costs associated with additional purification steps.

Conclusion

1. The demulsification performance of three newly developed KA-series compositions (KA-1, KA-2, and KA-3) was evaluated under laboratory conditions using high-viscosity crude oil samples from Absheron (35% water content), Sangachal (30%), and Dashgil (32%). The optimal concentrations for these compositions were 500 g/t for KA-1, 150 g/t for KA-2, and 300 g/t for KA-3, respectively.
2. The analysis of multiple experimental results showed that at 50°C over 120 minutes, the demulsification efficiency of the optimal concentration of the KA-1 composition was 97.8% for Absheron, 98.4% for Sangachal, and 98.0% for Dashgil. Furthermore, at the same concentration, the percentage of ballast water in the Absheron sample was 1.2%, 0.7% in Sangachal, and 0.4% in Dashgil.
3. At 50°C over 120 minutes, the optimal concentration of the KA-2 composition demonstrated a demulsification efficiency of 99.1% for Absheron, 99.5% for Sangachal, and 99.2% for Dashgil. Under the same conditions, the ballast water content was 0.5% for Absheron, 0.2% for Sangachal, and 0.4% for Dashgil.
4. At 50°C over 120 minutes, the optimal concentration of the KA-3 composition exhibited a demulsification efficiency of 98.2% for Absheron, 98.7% for Sangachal, and 98.4% for Dashgil. The ballast water content was 1.0% for Absheron, 0.6% for Sangachal, and 0.7% for Dashgil.

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