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DEMULSIFICATION BEHAVIOR OF CRUDE OIL EMULSIONS İN THE PRESENCE OF MULTICOMPONENT DEMULSIFIERS

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Abstract

In the present study, the demulsification of 35 % water-in-oil Muradkhanli crude oil emulsions was investigated using both individual reagents and their composite formulations. The individual reagents included ALKAN-318, ALKAN DE-202, Separol, Demin-8411, and Dissolvan-3359. Demulsification experiments were conducted at 40 °C and 50 °C for 2 hours using the bottle-test method. To enhance demulsification efficiency, demulsifier-based composite formulations were developed under laboratory conditions. These compositions consisted of the studied demulsifiers combined with ethanol, which was added to reduce interfacial tension. The optimal dosage for the composites was determined to be 500 g/t; therefore, both the individual reagents and the composites were compared within the concentration range of 150–500 g/t, and the results were presented in graphical and tabular forms. Since the formulations were based on demulsifiers, they were conventionally denoted as deemulsifier compositions (DC), and a total of ten compositions (DC-1 to DC-10) were synthesized. Along with the demulsification of 35 % water-cut Muradkhanli crude oil emulsions, the effects of both the individual reagents and the composite systems on surface tension, interfacial tension, viscosity, HLB index, and salt content were also studied, and the obtained results were comparatively analyzed. Experimental findings revealed that the highest demulsification efficiency was achieved with the DC-5 composition.

Keywords: reagent; composition; demulsification; water-oil emulsion; surface tension; efficiency.

ОСОБЛИВОСТІ ДЕЕМУЛЬГАЦІЇ НАФТОВИХ ЕМУЛЬСІЙ У ПРИСУТНОСТІ БАГАТОКОМПОНЕНТНИХ ДЕМУЛЬГАТОРІВ

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Анотація

У цьому дослідженні був вивчений процес деемульгації водонафтових емульсій сирої нафти родовища Мурадханли з вмістом води 35 % із використанням як індивідуальних реагентів, так і їхніх композицій. До індивідуальних реагентів належали ALKAN-318, ALKAN DE-202, Separol, Demin-8411 та Dissolvan-3359. Деемульгаційні експерименти проводили за температур 40 °C і 50 °C протягом 2 год із застосуванням методу пляшкових випробувань (bottle test). З метою підвищення ефективності деемульгації в лабораторних умовах були розроблені композиційні формуляції на основі деемульгаторів. Ці композиції складалися з досліджуваних деемульгаторів у поєднанні з етанолом, який додавався для зниження міжфазного натягу. Оптимальне дозування композицій було визначено на рівні 500 г/т; відповідно, як індивідуальні реагенти, так і композиції порівнювали в діапазоні концентрацій 150–500 г/т, а отримані результати були подані в вигляді графіків і таблиць. Оскільки формуляції базувалися на деемульгаторах, їх умовно позначали як деемульгаторні композиції (DC), і загалом було синтезовано десять композицій (DC-1 – DC-10). Одночасно із дослідженням деемульгації водонафтових емульсій сирої нафти Мурадханли з вмістом води 35 % також був вивчений вплив як індивідуальних реагентів, так і композиційних систем на поверхневий натяг, міжфазний натяг, в'язкість, індекс HLB та вміст солей, а отримані результати були проаналізовані в порівняльному аспекті. Експериментальні дані показали, що найвища ефективність деемульгації була досягнута для композиції DC-5.

Ключові слова: реагент; композиція; деемульсація; водонафтова емульсія; поверхневий натяг; ефективність.

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Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

Introduction

Crude oil emulsions are one of the most persistent and costly challenges in petroleum production, transportation, and refining. These emulsions are typically stabilized by natural surface-active compounds such as asphaltenes, resins, and fine solids, which form viscoelastic interfacial films at the oil–water boundary, preventing coalescence of water droplets. Their presence leads to increased viscosity, pipeline corrosion, emulsion carryover, and inefficient dehydration processes, all of which negatively impact operational and economic performance of oil production facilities[1–5].

The Muradkhanli crude oil, characterized by a high content of polar components and water cut up to 35 %, exhibits strong emulsion stability that complicates phase separation. Conventional demulsifiers often show limited efficiency under such conditions, especially at moderate temperatures (below 60 °C), due to the complex interactions between the natural stabilizers and the chemical additives. Therefore, the development of multi-component or composite demulsifiers with synergistic performance has become a promising strategy for improving dehydration efficiency and reducing processing time [6–10].

Recent studies have demonstrated that the combination of different surfactant types—for instance, nonionic and amphiphilic agents—can enhance the breaking of emulsions through a balance of hydrophilic–lipophilic (HLB) properties and interfacial tension reduction. The addition of polar solvents such as ethanol can further promote the diffusion and adsorption of demulsifying molecules at the oil–water interface, accelerating coalescence. However, the selection of optimal component ratios and the assessment of their combined effects require systematic laboratory evaluation [11–14].

In this study, the demulsification behavior of 35% water-cut Muradkhanli crude oil emulsions was investigated using both individual demulsifiers (ALKAN-318, ALKAN DE-202, Separol, Demin-8411, Dissolvan-3359) and their composite formulations (DC-series). The prepared ten composite systems (DC-1 to DC-10) were designed to exploit synergistic effects among the individual reagents and ethanol. The work aims to identify the most effective formulation, assess its influence on demulsification efficiency, viscosity, surface and interfacial tension, hydrophilic–lipophilic balance (HLB), and salt removal, and provide insights for optimizing chemical dehydration of highly emulsified crude oils.

Research methodology

One of the widely used methods to evaluate the demulsification ability of reagents and their compositions is the bottle test (static settling) method. For this, reagents or compositions are first dissolved in a solvent and then added to the packaged oil samples to be investigated in various concentrations. After the reagents are added, they are mixed thoroughly for 1 minute and then left in a water bath. Depending on the demulsification ability of the tested demulsifier, the separation of water is recorded at various time intervals. The amount of separated water is calculated based on the following mathematical relation [17]:

$$X\% = \frac{w}{w_0} 100\% \quad , \qquad (1)$$

where, w_0 – is the initial amount of water in the emulsion, %, w – is the amount of water separated during demulsification, %.

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

$$S\% = \frac{m_1 - m_2}{m_3 - m_2} 100\% \quad , \qquad (2)$$

where, S – is the percentage of ballast water after demulsification %, m_1 – is the amount of water in the oil before demulsification (%), m_2 is the amount of water separated from the oil during demulsification (%), m_3 is the amount of the oil sample (%).

The amount of residual water in the oil is determined using the Din-Stark apparatus in accordance with the GOST 2477-2014 standards.

The oil sample used in the study is heavy emulsified oil from the Muradkhanli field, and its physical-chemical properties are shown in the following table [18]:

Table 1

Physical-chemical properties of Muradkhanli oil

1	Density 20 °C, kg/m³	965
2	Viscosity 20 °C, mP·s,	2249
3	Water content, % by mass	35
4	Chloride salts content, mg/L	448.4

Continued from Table 1

5	Mechanical impurities content, % by mass	6.29
6	Resins content, % by mass	16.4
7	Asphaltenes content, % by mass	5.3
8	Paraffins content, % by mass	7.0
9	Freezing temperature, °C	+18

Five commercial demulsifiers — ALKAN-318, ALKAN DE-202, Separol, Demin-8411, and Dissolvan-3359 — were used as the base reagents (table 2).

Table 2

Composition, physicochemical parameters, and application characteristics of individual demulsifiers used in this study.

Characteristics	ALKAN-318	ALKAN-202	Demin-8411	Separol NF-36	Dissolvan-3359
Composition	Non-ionic and anionic surfactants	Non-ionic and anionic surfactants	Mixture of anionic and non-ionic surfactants	Mixture of anionic and non-ionic surfactants	Mixture of ethylene/propylene oxide block copolymers and oxyethylated resins
Appearance	Transparent liquid from light yellow to dark brown	Light yellow or transparent liquid	Dark yellow or brown liquid	Dark yellow or brown liquid	Liquid from yellow to brown
Density (at 20 °C), g/cm^3	0.92 – 0.96	0.95 – 1.02	1.00 – 1.05	1.02 – 1.06	0.89 ± 0.02
Viscosity (at 25 °C)	180 – 300 mPa·s	150 – 250 mPa·s	250 – 300 mPa·s	220 – 280 mPa·s	123 mPa·s (at 20 °C)
pH (at 20 °C)	6.0 – 7.5	6.0 – 7.0	5.0 – 6.5	5.0 – 6.0	≈ 9.0 (1% in water)
Freezing point, °C	–30	–14 … –10	–20 … –25	–20 … –25	< –36
Flash point, °C	≥ +12	≥ +12	≥ +25	≥ +25	28
Initial boiling point, °C	≥ +63	≥ +63	≥ +70	≥ +70	–
Mass fraction of non-volatile matter, %	55 – 58	50 – 55 (typical)	–	–	–
Solubility	Well soluble in water and oil	Partially soluble in water and oil	Soluble in water and organic solvents	Well soluble in water and oil	Forms emulsions in water and organic solvents
Optimal temperature, °C	40 – 70	40 – 60	60 – 80	60 – 80	40 – 70
Application field	Heavy and highly viscous emulsions	Medium and highly viscous emulsions	Heavy and highly stable emulsions	Heavy and highly stable emulsions	Demulsifier for emulsions with high resin/asphaltene content
Stability and reactivity	Stable under normal conditions, no decomposition	Stable under normal conditions	Stable	Stable	Stable, complies with EQG test
Storage and transportation	In metal or plastic container, 12 months	12 months in sealed container	12 months	12 months	2 years, minor effect of temperature changes
Country of origin	Azerbaijan	Azerbaijan	Germany	distributed by a Nigerian supplier	Germany

Surface tension (γ) and interfacial tension (IFT) were measured using the du Noüy ring method in accordance with GOST 1770 and ASTM D971 standards. All measurements were performed at 25 °C under atmospheric conditions [15].

The dynamic viscosity of the emulsions, both before and after demulsifier treatment, was determined using a rotational viscometer (Reotest-2) at a controlled temperature of 20 °C. Rheological measurements were conducted to evaluate changes in flow behavior induced by the applied formulations.

The hydrophilic–lipophilic balance (HLB) values of the individual demulsifiers and composite formulations were estimated according to Griffin's method, based on the relative molecular weights of the hydrophilic and lipophilic moieties [16].

The chloride salt content in the separated water phase was determined by titrimetric

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

analysis following GOST 21534 and ASTM D6470 standards, enabling an assessment of the desalting efficiency of the investigated formulations [18].

Results and their discussion

Experimental investigations were initially focused on studying the demulsification process under the influence of individual reagents. The tests were conducted at a temperature of 40 °C, for a duration of 120 minutes, and at dosages of 150, 300, and 500 g/t.

It is well known that stable water–oil emulsions cannot be effectively broken by temperature alone. Therefore, the present study employed an experimental approach based directly on reagent application.

According to the obtained results, the quantities of both ballast water and residual water were determined, and the corresponding data are presented in Figures 1 and 2.

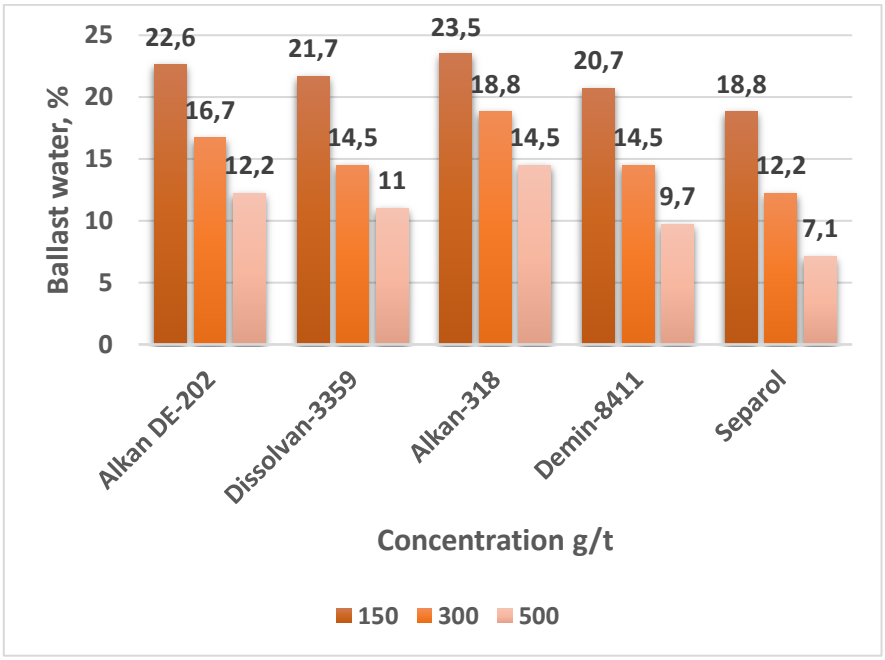

Fig. 1. Variation of ballast water content during the demulsification of crude oil using individual reagents (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411 and Separol) at different dosages (150, 300 and 500 g/t), 40 °C, 120 min

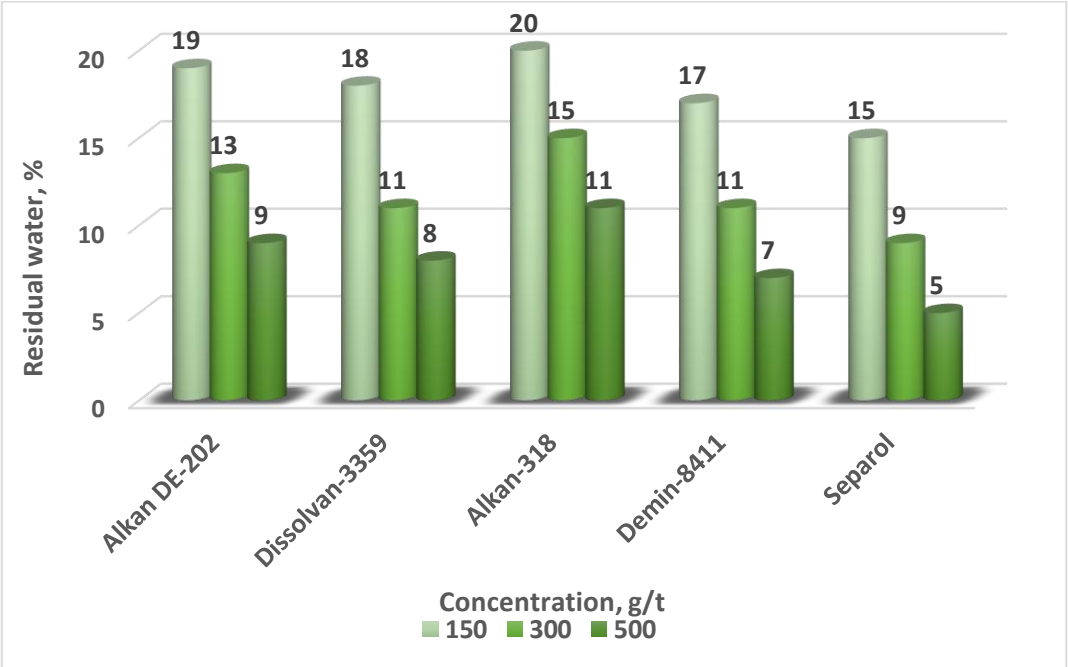

Fig. 2. Variation of residual water content during the demulsification of crude oil using individual reagents (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411 and Separol) at different dosages (150, 300 and 500 g/t), 40 °C, 120 min

The obtained results indicate that, although each of the five individual reagents influenced the demulsification process to some extent, the best performance was observed with the Separol reagent.

It should be noted that a temperature of 40 °C is relatively low for the efficient breakdown of stable water–oil emulsions. Consequently, the residual water content remained somewhat elevated in all cases.

The low rate of demulsification can be attributed primarily to the high interfacial and surface tension between the water and oil phases, which hinders the coalescence of dispersed water droplets.

Therefore, further experiments were carried out to examine how the reduction of water content affects both surface tension and interfacial tension. The corresponding results are presented in Figures 3 and 4.

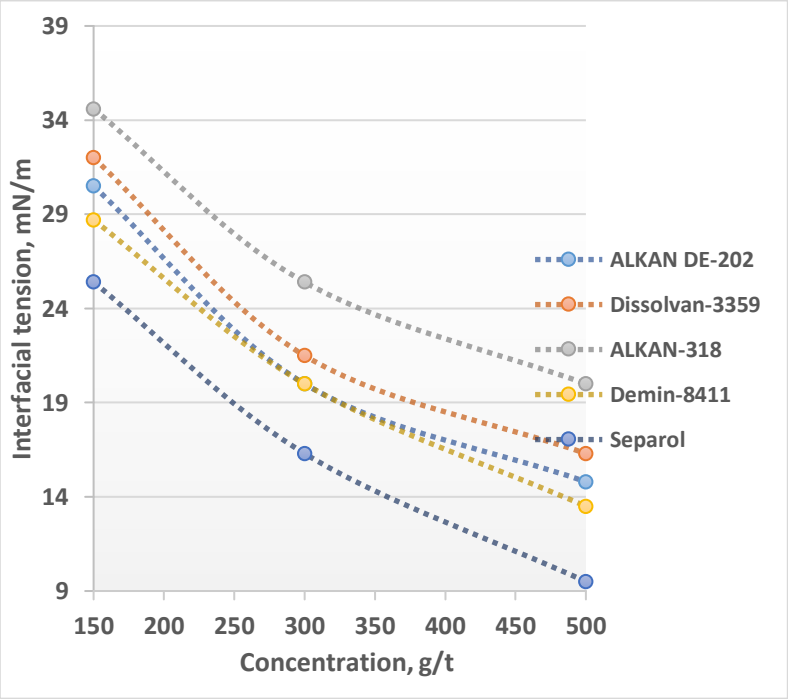

Fig. 3. Variation of interfacial tension during demulsification of crude oil using individual reagents (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411 and Separol) at different dosages (150–500 g/t)

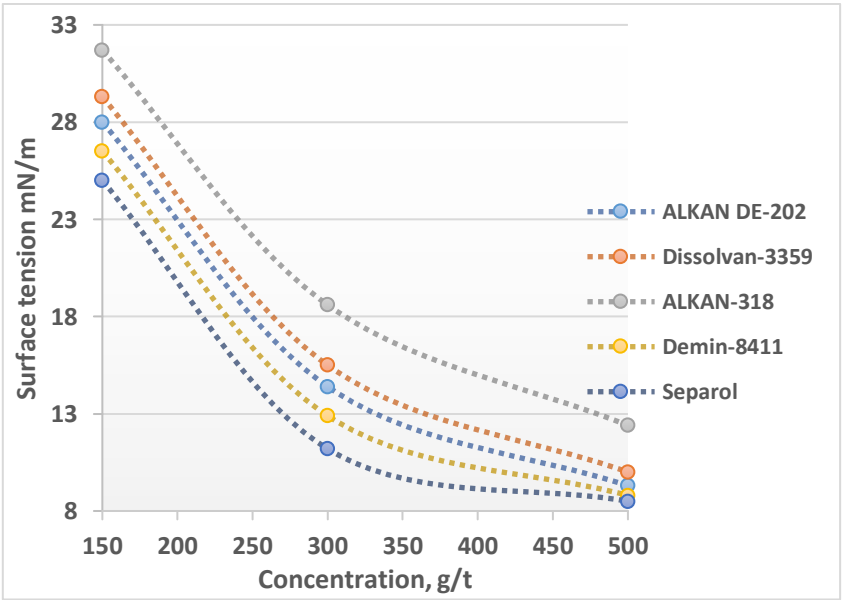

Fig. 4. Variation of surface tension during demulsification of crude oil using individual reagents (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411 and Separol) at different dosages (150–500 g/t)

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

As shown in Figures 3 and 4, the Separol reagent produced the lowest values of surface and interfacial tension, indicating a faster and more efficient demulsification process.

The temperature of 40 °C is considered a critical or threshold temperature for water–oil emulsions, since under these conditions their viscosity often exhibits anomalous behavior. Therefore, an additional investigation was conducted to examine the intensity of viscosity variation in crude oil emulsions under the influence of individual reagents, and the obtained results are presented in Figure 5.

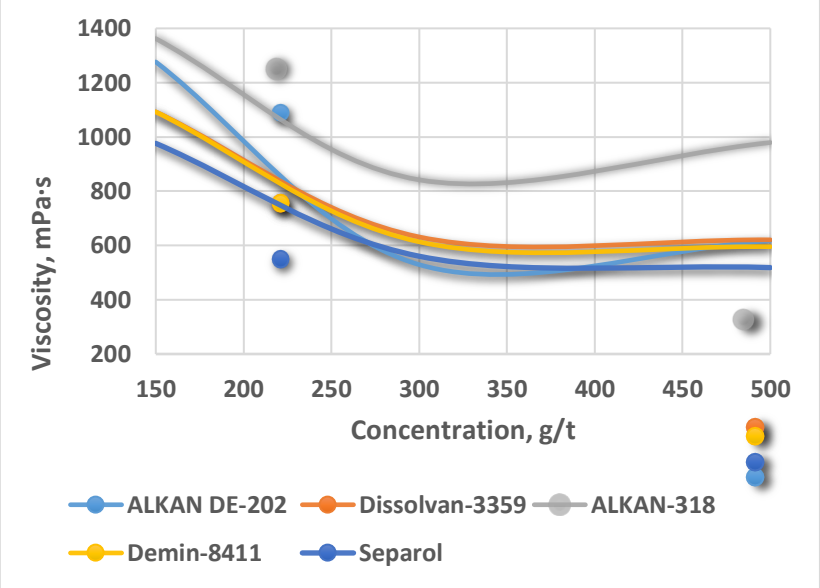

Fig. 5. Concentration-dependent changes in dynamic viscosity of emulsions treated with individual demulsifiers at 20 °C

As shown in Figure 5, under the influence of ALKAN DE-202, ALKAN-318, and Dissolvan-3359 reagents, certain anomalies in viscosity variation are observed due to the emulsion being at its critical temperature. This phenomenon can be attributed to partial disruption of structural stability and the non-uniform distribution of dispersed phase particles.

For Demin-8411 and Separol, such anomalies were not detected; however, their viscosity values remained relatively high, indicating incomplete stabilization of the dispersed system.

Another important parameter influencing the rheological behavior of crude oil emulsions is the hydrophilic–lipophilic balance (HLB index), which characterizes the surface activity and orientation of demulsifiers at the oil–water interface. Therefore, the study was continued with the determination of the HLB index, and the obtained results are illustrated in Figure 6.

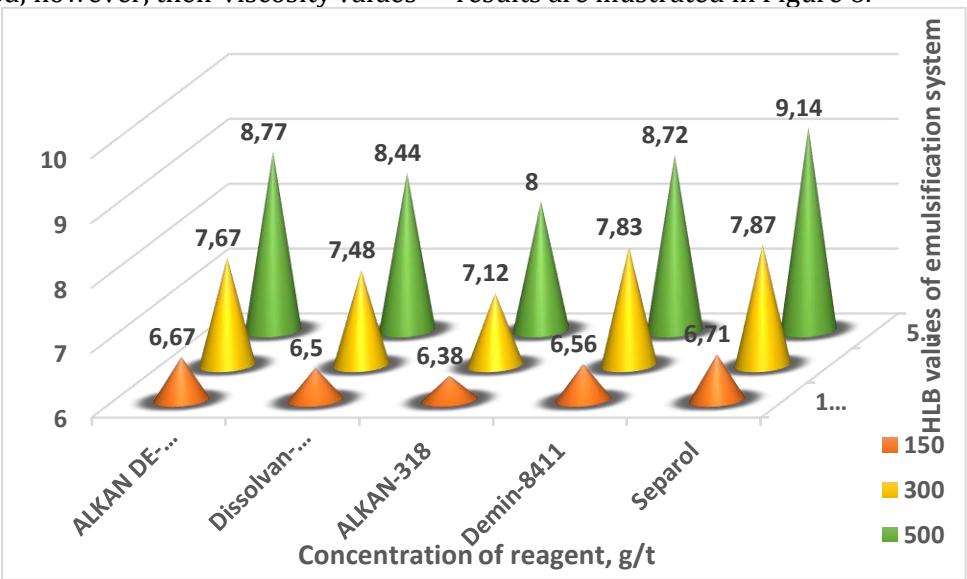

Fig. 6. Variation of HLB values of the emulsification system under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at different concentrations (150–500 g/t)

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

As illustrated in Figure 6, the HLB values of the emulsification system increase progressively with reagent concentration, indicating enhanced surface activity and a shift toward greater hydrophilicity in the emulsifier structure.

Among the tested reagents, Separol and Dissolvan-3359 exhibited the highest HLB values (9.14 and 8.77, respectively), suggesting superior interfacial orientation and improved coalescence of water droplets, which contributes to more efficient demulsification. In contrast, Alkan-318, Alkan DE-202, and Demin-8411 displayed relatively lower HLB values, reflecting their stronger lipophilic tendencies and weaker interaction with the aqueous phase.

Overall, the optimal HLB range was determined to be between 8.5 and 9.0, where the demulsifiers exhibit the most balanced combination of surface activity and interfacial destabilization, leading to enhanced emulsion breakdown efficiency.

Under identical experimental conditions — using the same reagents, exposure time, and water–oil emulsion system — the studies were conducted at 50 °C. The increase in temperature significantly influenced the demulsification kinetics and coalescence behavior of the emulsion. The obtained results are presented in Figures 7 and 8.

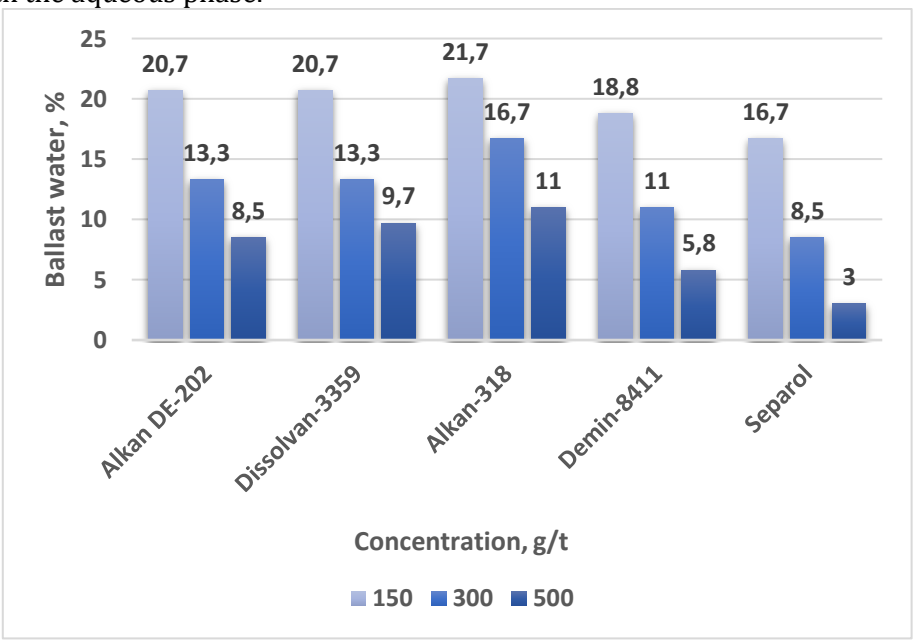

Fig. 7. Variation of ballast water content at 50 °C under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at different concentrations (150–500 g/t)

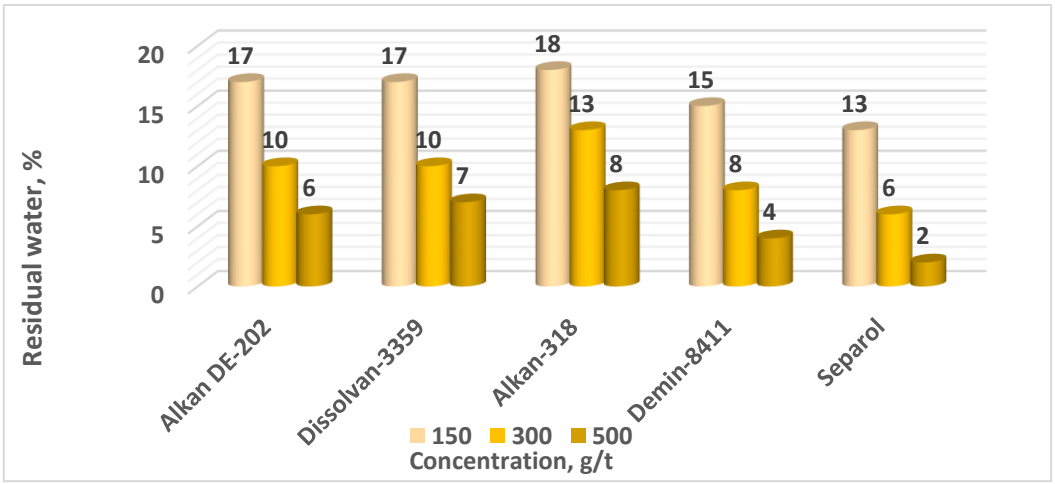

Fig. 8. Variation of residual water content at 50 °C under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at different concentrations (150–500 g/t)

As illustrated in Figures 7 and 8, an increase in temperature to 50 °C significantly enhanced the efficiency of the demulsification process for all reagents tested. Both ballast water and residual water contents decreased markedly compared to the experiments conducted at 40 °C, confirming

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

that elevated temperature accelerates coalescence kinetics and reduces both surface and interfacial tension at the oil–water boundary.

Among all reagents, Separol demonstrated the highest performance, achieving only 3 % ballast water and 2 % residual water at a dosage of 500 g/t. This superior effect is attributed to its balanced hydrophilic–lipophilic properties and enhanced interfacial activity, which promote rapid droplet coalescence and phase separation.

Other reagents such as Alkan DE-202 and Dissolvan-3359 also contributed to a reduction in water content, though their efficiency remained moderate compared to Separol. Overall, the experiments indicate that increasing temperature not only improves reagent activity but also reduces emulsion viscosity and weakens interfacial stability, thereby accelerating demulsification. Nevertheless, achieving maximum separation efficiency likely requires the use of composite reagent systems with synergistic effects.

Subsequently, at a temperature of 50 °C, the surface and interfacial tensions between the oil and water phases were measured. The results of these measurements are presented in Figures 9 and 10.

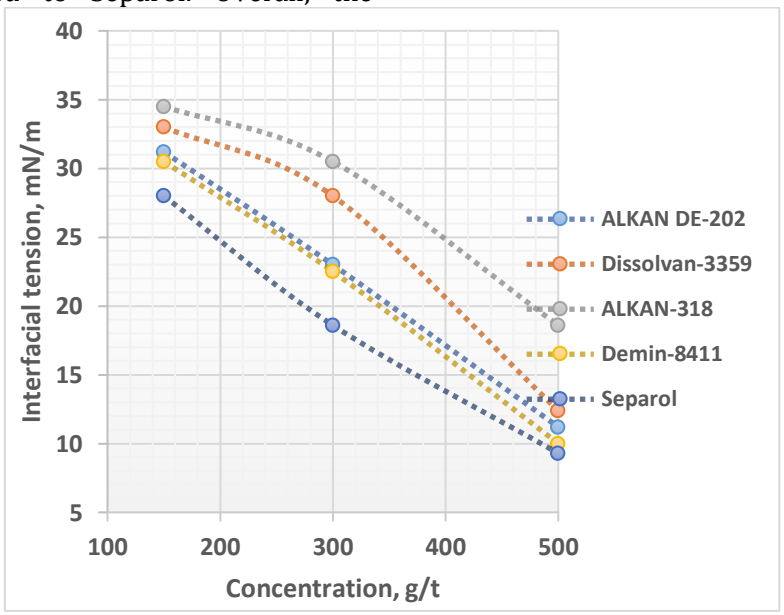

Fig. 9. Variation of interfacial tension between oil and water phases under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at 50 °C and different concentrations (150–500 g/t)

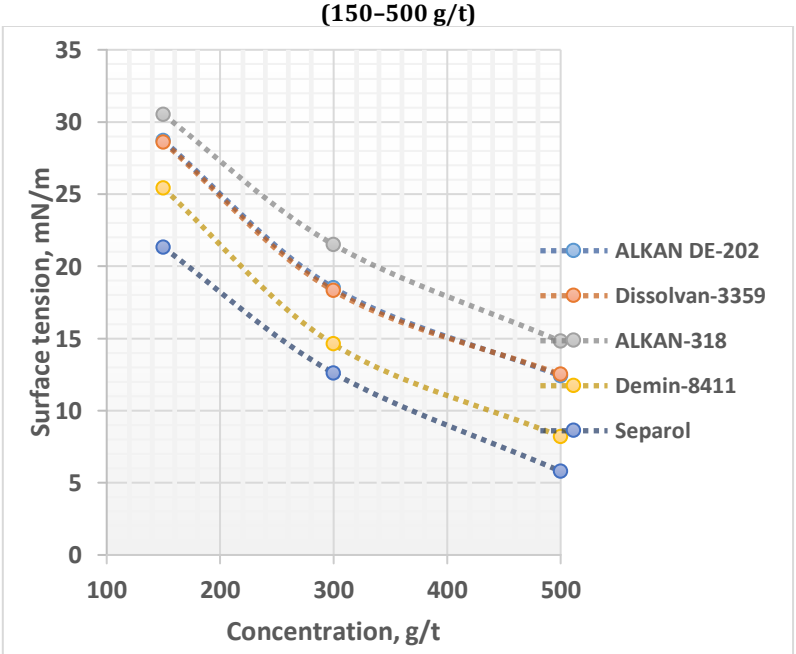

Fig. 10. Variation of surface tension of oil–water emulsions under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at 50 °C and different concentrations (150–500 g/t)

As shown in Figures 9 and 10, both interfacial and surface tensions decrease consistently with increasing reagent concentration, indicating a progressive enhancement of surface activity and interfacial adsorption. The reduction is most pronounced for Separol, which achieves the lowest interfacial tension value of approximately 10–11 mN/m and a surface tension of about 7–8 mN/m at a dosage of 500 g/t.

This behavior confirms that Separol molecules exhibit strong interfacial orientation and efficiently displace natural stabilizers such as resins and asphaltenes from the oil–water boundary. As a result, the film surrounding water droplets becomes less rigid, facilitating droplet coalescence and accelerating phase separation.

In contrast, Alkan-318 maintains relatively high interfacial and surface tension values even at increased concentrations, which explains its weaker demulsification efficiency observed in earlier tests. Demin-8411, Dissolvan-3359, and Alkan DE-202 show moderate performance, but their ability to reduce interfacial resistance remains inferior to that of Separol.

Overall, the experimental data demonstrate that at elevated temperature (50 °C), the adsorption–desorption dynamics at the oil–water interface are intensified. The temperature rise enhances molecular mobility and allows surface-active reagents to more effectively orient themselves at the interface, thus reducing interfacial tension and promoting faster demulsification kinetics.

Subsequently, in accordance with the experimental sequence, the variation intensity of viscosity was determined in parallel with the demulsification process. The results of these tests are presented in Figure 11.

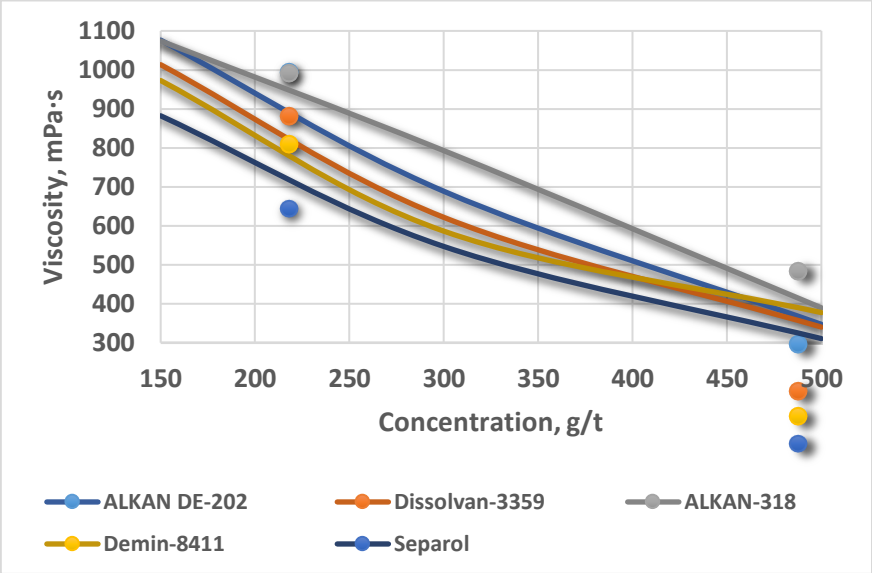

Fig. 11. Variation of emulsion viscosity at 50 °C under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at different concentrations (150–500 g/t)

As shown in Figure 11, increasing the concentration of all demulsifiers leads to a steady decrease in emulsion viscosity, confirming their positive influence on the rheological behavior and stability of the oil–water system.

At low concentrations (150–300 g/t), the viscosity reduction occurs moderately, reflecting partial destabilization of the interfacial film around water droplets. As the concentration reaches 500 g/t, the viscosity decreases sharply for all reagents due to enhanced interfacial activity and improved coalescence dynamics.

Among the studied reagents, Separol exhibited the strongest viscosity-reducing effect, achieving a minimum of approximately 390–410 mPa·s, followed by Demin-8411 and Dissolvan-3359, while Alkan-318 showed the weakest performance. This indicates that Separol not only promotes demulsification but also effectively reduces internal friction and weakens structural viscosity, which are key for improving the flowability of emulsified crude oil.

Overall, the obtained data confirm a direct correlation between interfacial tension reduction and viscosity decrease, demonstrating that reagents with higher surface activity contribute to more efficient demulsification and rheological improvement.

The next stage of the study focused on determining the hydrophilic–lipophilic balance (HLB) index of the system. The results obtained under the influence of different reagents are presented in Figure 12.

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

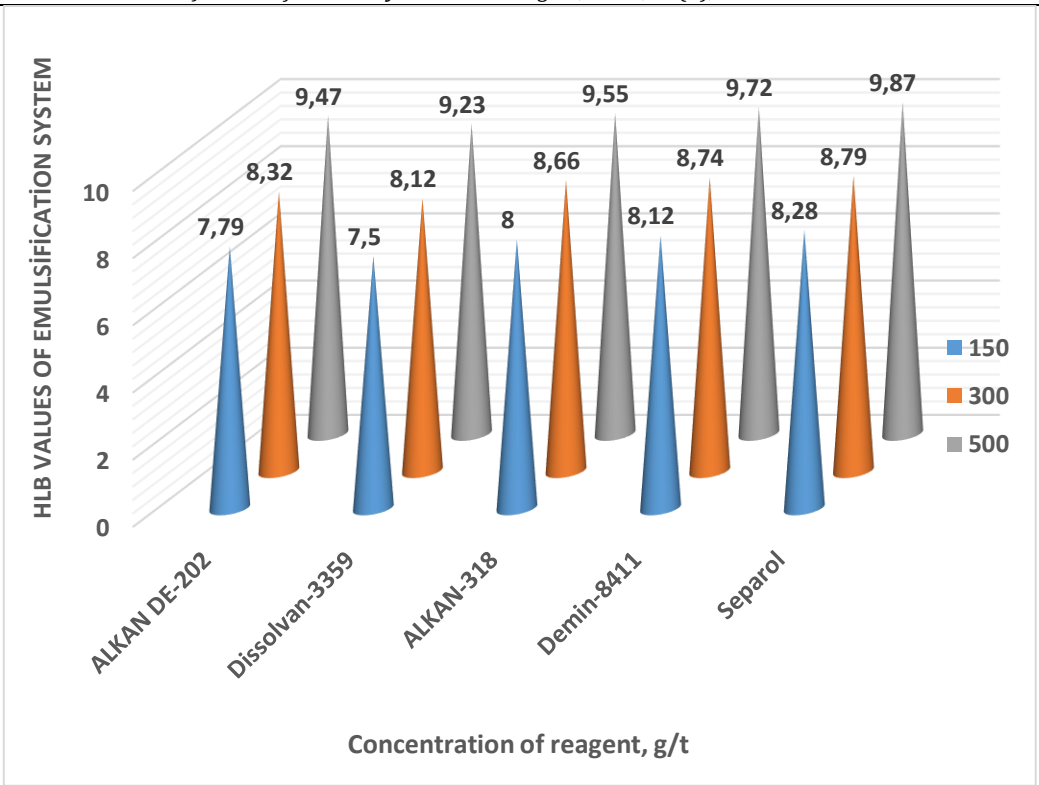

Fig. 12. Variation of HLB values of the emulsification system at 50 °C under the influence of individual demulsifiers (Alkan DE-202, Dissolvan-3359, Alkan-318, Demin-8411, and Separol) at different concentrations (150–500 g/t).

As shown in Figure 12, increasing the concentration of each reagent results in a progressive rise in the HLB index, indicating a stronger hydrophilic character and improved surfactant alignment at the oil–water interface.

At low concentrations (150 g/t), the HLB values remain below 8.3, which corresponds to insufficient interfacial orientation and relatively weak demulsifying efficiency. When the concentration is increased to 300 g/t and further to 500 g/t, HLB values rise sharply, reaching 9.23–9.87 for the most active reagents. This range is considered optimal for destabilizing water-in-oil emulsions, as it promotes effective film disruption and rapid coalescence of dispersed water droplets.

Among all reagents, Separol displayed the highest HLB value (9.87 at 500 g/t), confirming its excellent interfacial activity and balanced hydrophilic–lipophilic nature. Demin-8411 and Dissolvan-3359 also exhibited strong surface activity, while Alkan-318 and Alkan DE-202 maintained moderately lower values, indicating a higher lipophilic bias.

Overall, the results demonstrate that increasing the reagent concentration enhances the hydrophilic component of the system, leading to reduced emulsion stability, improved coalescence dynamics, and greater demulsification efficiency at elevated temperatures.

Summarizing the experimental results obtained with individual reagents, it can be concluded that for such highly stable water–oil emulsions, temperatures of 40 °C and 50 °C are considered relatively low. Under these conditions, the observed parameters – viscosity, surface tension, interfacial tension, HLB index, as well as the amounts of ballast and residual water — cannot be regarded as fully satisfactory.

This indicates the necessity to develop alternative chemical approaches aimed at improving demulsification efficiency without further temperature increase, ensuring that the mentioned parameters remain within technologically acceptable limits.

In this context, the development of effective composite formulations became a key research priority. These compositions were designed based on the previously studied demulsifiers, maintaining identical component ratios to allow a reliable comparative analysis.

The optimal ratios and formulations demonstrating the best results are presented in Table 3. As shown, a total of ten different compositions were synthesized and conventionally denoted as the DC series. Although demulsifiers served as the main base of these systems, the addition of ethanol as a surface-active co-agent significantly enhanced the overall efficiency of the compositions.

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

Table 3

Composition and component ratios of the investigated demulsifier-based formulations (DC series)

Composition name	Components	Ratio (mass ratio)
DC-1	ALKAN DE-202+Dissolvan-3359+etanol	6:3:0.5
DC-2	ALKAN DE-202+ ALKAN-318 +etanol	6:3:0.5
DC-3	ALKAN DE-202+ Demin-8411+etanol	6:3:0.5
DC-4	ALKAN DE-202+ Separol +etanol	6:3:0.5
DC-5	Dissolvan-3359+ ALKAN-318 +etanol	6:3:0.5
DC-6	Dissolvan-3359+ Demin-8411+etanol	6:3:0.5
DC-7	Dissolvan-3359+ Separol +etanol	6:3:0.5
DC-8	ALKAN-318 + Demin-8411+ etanol	6:3:0.5
DC-9	ALKAN-318 +Separol+ etanol	6:3:0.5
DC-10	Demin-8411+ Separol +etanol	6:3:0.5

The same experimental procedures were carried out using the DC-series composite formulations, and the results were compared with those obtained for individual reagents. The first stage of the study involved conducting the demulsification process and determining the amounts of residual and ballast water.

The experiments were performed at 50 °C for 120 minutes, and the obtained results are presented in Figures 13 and 14.

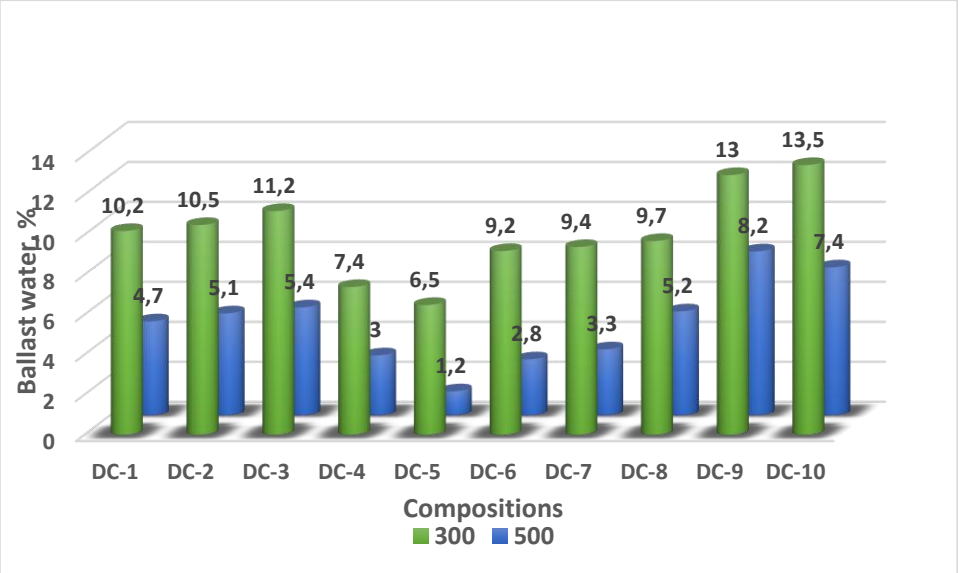

Fig. 13. Effect of DC-series compositions on the demulsification process at 50 °C — Variation of ballast water content

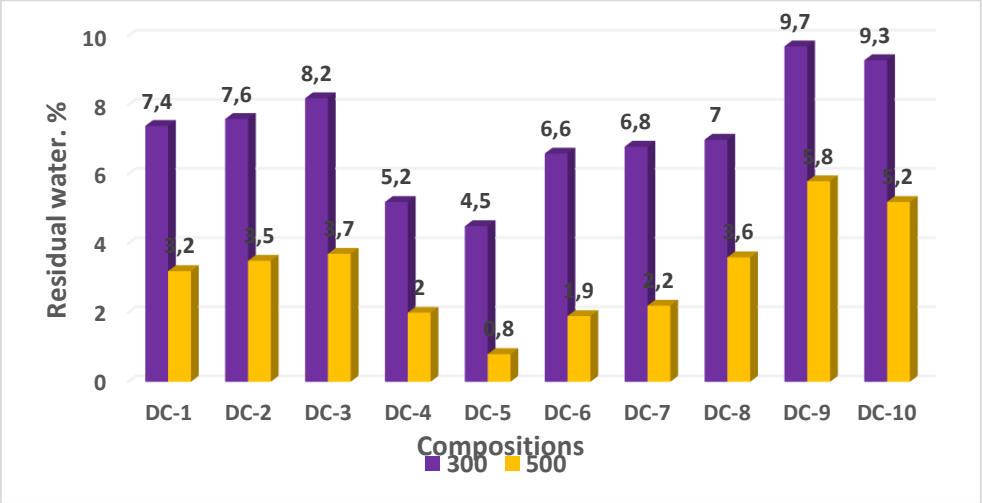

Fig. 14. Effect of DC-series compositions on the demulsification process at 50 °C — Variation of residual water content

Experimental results demonstrated that the application of DC-series composite formulations provides significantly higher efficiency in breaking stable water–oil emulsions compared to individual demulsifiers. Among the ten tested formulations, eight exhibited a marked

improvement in phase separation by considerably reducing both residual and ballast water contents. In particular, DC-5 composition showed the best performance, achieving only 0.8 % residual water and 1.2 % ballast water at a dosage of 500 g/t. Such outstanding efficiency can be attributed to the synergistic interaction between its constituent reagents. This synergy enhances the adsorption of surfactant molecules at the oil–water interface, leading to a substantial decrease in surface tension and coalescence energy barrier, which accelerates the merging of dispersed droplets. Other formulations such as DC-4, DC-6, and DC-7 also displayed good results, though slightly less pronounced. Their moderate performance can be explained by HLB index values that slightly deviate from the ideal balance range (8–9), which is crucial for efficient phase separation. Nevertheless, these systems maintained a more stable demulsification kinetics compared to individual reagents.

Conversely, DC-9 and DC-10 exhibited an antagonistic effect, likely caused by incompatibility between some components, resulting in the suppression of interfacial activity and reduced water separation efficiency. Such effects are typically associated with the dominance of one reagent at the interface, which inhibits the adsorption and cooperative function of the other components.

Overall, the study confirms that the optimal ratio and interaction of reagents are key factors in achieving high demulsification efficiency. The inclusion of ethanol also played an important role by adjusting the hydrophilic–lipophilic balance and facilitating phase separation in viscous systems. Although the studied crude oil contains approximately 7 % paraffins, the maximum experimental temperature was intentionally limited to 50 °C. This temperature was selected to perform a comparative evaluation under partially wax-structured conditions rather than under complete wax dissolution.

At 50 °C, individual demulsifiers exhibited limited efficiency, likely due to the persistence of paraffin crystal networks affecting droplet coalescence. However, the composite formulation demonstrated significantly improved performance under the same conditions. This indicates that the enhanced demulsification efficiency of the composite system is not merely temperature-driven, but is associated with synergistic interactions between its components, enabling effective destabilization of the emulsion even in the presence of residual wax structures.

Therefore, the selected temperature provides a more stringent and practically relevant evaluation of demulsifier performance, highlighting the superiority of the composite formulation over individual reagents.

Hence, the superior performance of eight out of ten DC-series formulations compared to individual demulsifiers highlights their strong potential for industrial application.

In the next stage of the study, the influence of these compositions on surface tension and interfacial tension was investigated, and the results are presented in Figures 15 and 16.

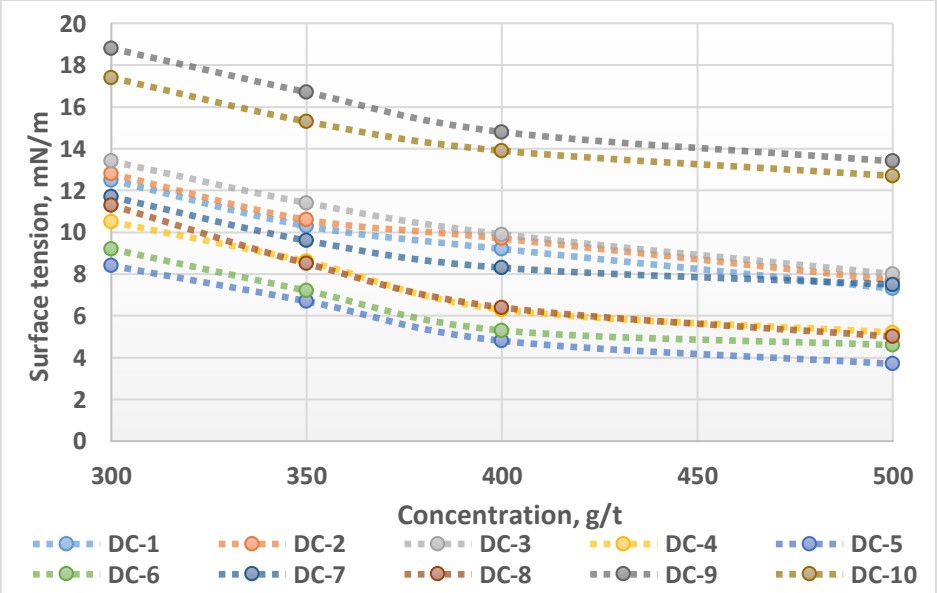

Fig. 15. Effect of DC-series compositions on surface tension at 50 °C

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

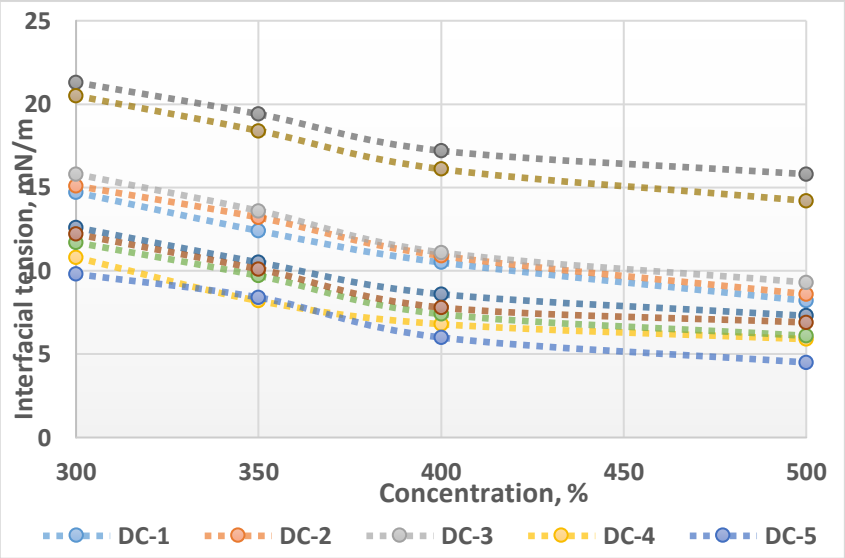

Fig. 16. Effect of DC-series compositions on interfacial tension at 50 °C

The obtained results show a strong correlation between the effects of the DC-series compositions on surface and interfacial tension and their demulsification performance. In other words, the compositions that achieved higher separation efficiency also demonstrated the greatest reduction in both surface and interfacial tensions.

Among all formulations, DC-5 composition exhibited the most remarkable performance, reducing the surface tension to approximately 5–6 mN/m and the interfacial tension to 9–10 mN/m at 50 °C. This significant reduction reflects a pronounced synergistic effect among its components. The presence of ethanol enhances the adsorption of both polar and nonpolar molecules at the phase boundary, forming a denser molecular layer that lowers interfacial energy and facilitates droplet coalescence—thereby accelerating the demulsification process.

Other formulations – particularly DC-4, DC-6, DC-7, and DC-8 – also produced favorable outcomes, maintaining surface tension values within the 7–9 mN/m range. This indicates that their hydrophilic-lipophilic balance (HLB) values are near the optimal range for stable yet easily separable emulsions.

However, as observed in previous experiments, DC-9 and DC-10 showed a mild antagonistic interaction, likely due to the uneven adsorption of active agents at the oil–water interface. This imbalance weakened surface activity and resulted in relatively higher tension values compared to other systems.

Overall, these findings confirm that the compatibility and proportional ratio of reagents in composite systems play a decisive role in controlling both the kinetics of demulsification and the thermodynamic balance of interfacial phenomena.

The next stage of the study focuses on assessing the effect of the 10 laboratory-prepared compositions on viscosity variation as a function of demulsification rate, and the results are presented in Figure 17.

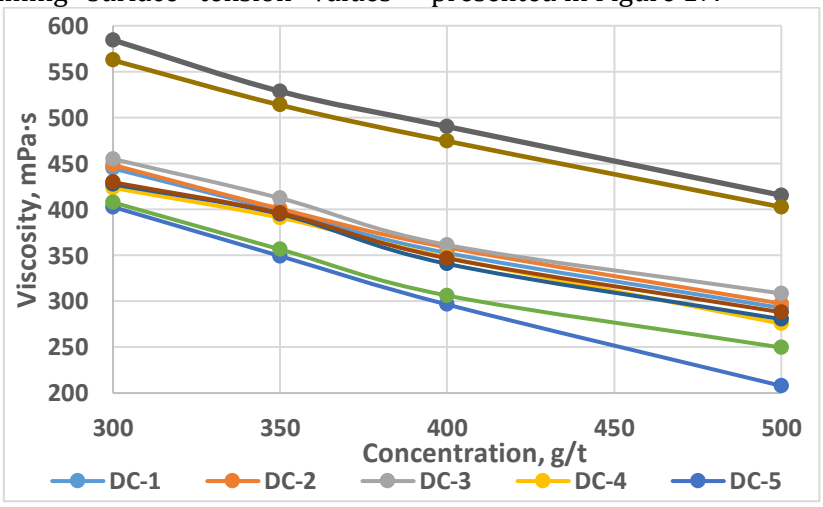

Fig. 17. Effect of DC-series compositions on the viscosity of the oil emulsion as a function of concentration (at 50 °C)

The experimental results demonstrated that the water content in the emulsion plays a crucial role in determining its viscosity. A higher proportion of the aqueous phase increases internal friction within the emulsion, thereby raising its overall rheological resistance. Consequently, as the demulsification process becomes more efficient and water separation proceeds faster, the viscosity of the system decreases proportionally.

This trend was clearly observed in the experiments conducted with the DC-series compositions. As illustrated in Figure 17, eight of the ten formulations (DC-1 through DC-8) significantly enhanced demulsification rates, which in turn caused a corresponding decrease in viscosity. Among them, DC-5 exhibited the most pronounced effect, reducing the viscosity to the lowest level at 50 °C. The superior performance of DC-5 can be attributed to the synergistic interaction between its components, which act cooperatively through adsorption and diffusion mechanisms at the oil–water interface. This weakens the interfacial barrier, increases permeability, and consequently reduces internal friction within the emulsion.

In contrast, DC-9 and DC-10 showed relatively weaker performance. This may be due to an antagonistic effect between their components, where one reagent inhibits the surface activity of the other, preventing sufficient reduction of interfacial stability. Despite being tested under identical experimental conditions (50 °C, the same dosage, and the same exposure time), their viscosity values remained comparatively higher.

Overall, both viscosity and interfacial/surface tension are directly dependent on the rate of demulsification. The faster the separation of phases, the weaker the structural resistance and molecular interactions within the system. Therefore, compositions such as DC-5, DC-4, DC-6, and DC-7 demonstrated the most efficient performance, achieving superior results compared to individual reagents due to their strong synergistic balance.

Conversely, the absence of such synergy, as observed in DC-9 and DC-10, resulted in less favorable outcomes, underscoring the critical importance of formulation design and component compatibility in composite reagent systems.

Finally, the study also examined the influence of both individual reagents and composite formulations on salt removal from the crude oil sample at 50 °C, as shown in Figure 18. The desalting process is closely related to demulsification; a reduction in viscosity and interfacial tension promotes easier separation of brine droplets carrying salts. This directly improves the quality and stability of the treated crude oil.

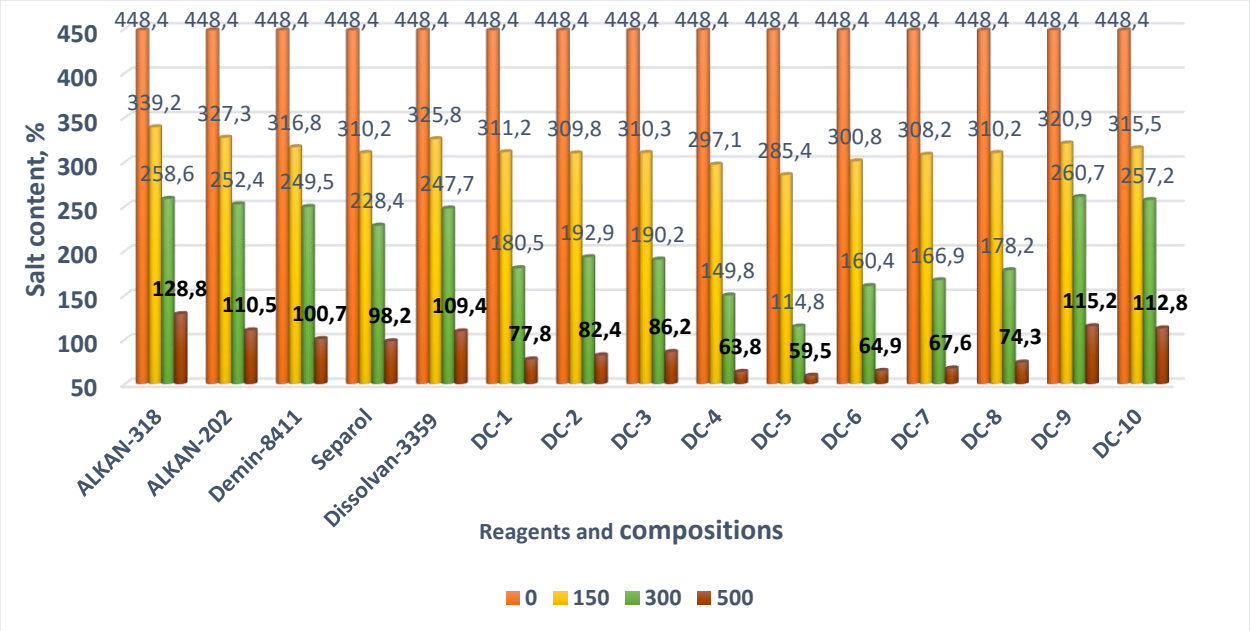

Fig. 18. Effect of individual reagents and DC-series compositions on the salt content of the crude oil sample as a function of concentration (at 50 °C)

The results of the study indicate that the settling rate of salts, which play a crucial role in stabilizing the water phase within crude oil, varies significantly under the influence of both individual reagents and composite formulations. Salt ions (mainly Na^+, Ca^{2+}, and Mg^{2+}) form an electric double layer around water droplets, preventing their coalescence and thereby maintaining the

Journal of Chemistry and Technologies, 2026, *34*(2), 482-498

long-term stability of the emulsion. Consequently, efficient salt removal is essential for both effective demulsification and enhancement of crude oil quality.

As illustrated in Figure 18, all reagents and compositions contributed to a decrease in salt content to varying extents. However, the most pronounced effect was observed with the DC-5 composition at a dosage of 500 g/t, where the salt content was reduced by approximately 63.8%. This significant improvement demonstrates that the interfacial structure between oil and water phases was almost completely disrupted under the action of DC-5.

The superior performance of DC-5 can be attributed to the synergistic adsorption and dispersion mechanisms among its active components. The surfactant molecules weaken the electrostatic barriers formed by salt ions, reduce interfacial tension, and promote the coalescence of water droplets. As a result, the aqueous phase separates more rapidly, facilitating the sedimentation and removal of salts from the oil matrix.

In contrast, compositions such as DC-9 and DC-10 showed weaker performance, likely due to antagonistic interactions between components, where one reagent inhibits the interfacial activity of the other, maintaining partial stabilization of hydrated salts.

Overall, the findings confirm that salt separation efficiency is closely linked to demulsification kinetics. The reduction of both viscosity and interfacial tension enhances the coalescence of brine droplets and accelerates salt removal. Among all formulations, DC-5, DC-4, and DC-6 demonstrated the highest efficiency, confirming their practical relevance for improving the desalting and purification performance of crude oil systems. The economic efficiency of individual demulsifiers and the DC-5 composite formulation, which exhibited the strongest performance enhancement, is illustrated in Figure 19.

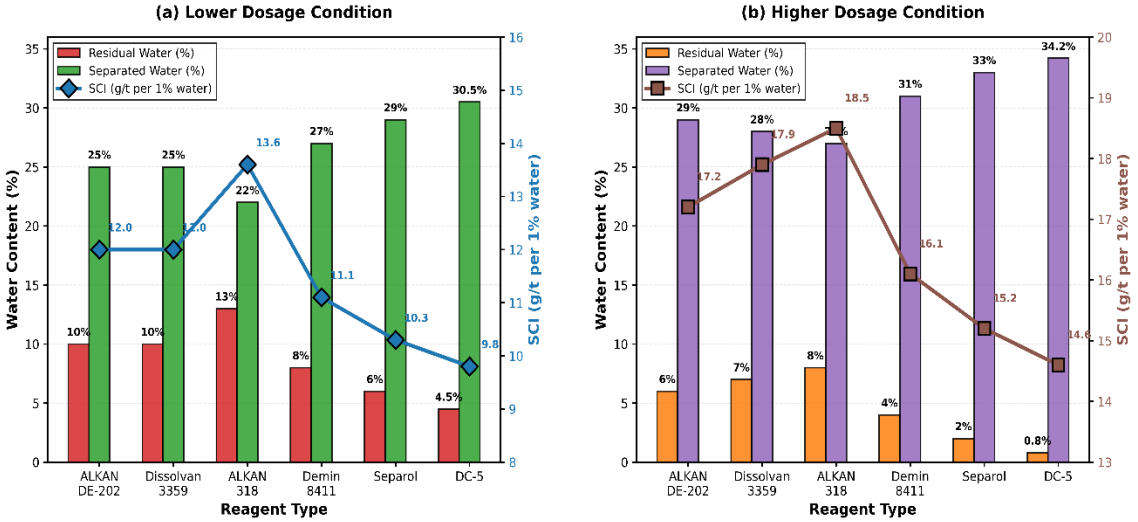

Fig.19. Comparison of residual water content, separated water fraction, and specific consumption index (SCI) for individual demulsifiers and the DC-5 composite formulation under (a) lower-dosage and (b) higher-dosage conditions. Lower SCI values correspond to improved economic efficiency

Figure 19 illustrates the relationship between demulsification performance and economic efficiency for the individual demulsifiers and the DC-5 composite formulation. At both dosage levels, the reduction in residual water content is accompanied by a corresponding increase in the separated water fraction, reflecting improved dehydration efficiency. This trend is particularly pronounced for the DC-5 formulation, which consistently achieves the lowest residual water content among all tested systems.

The specific consumption index (SCI), defined as the reagent dosage required to remove 1 % of water, provides a practical measure of economic efficiency. As shown in Figure 19, DC-5 exhibits the lowest SCI values under both lower- and higher-dosage conditions, indicating that less chemical is required to achieve the same degree of water separation compared with the individual demulsifiers. This behavior demonstrates that the enhanced demulsification performance of DC-5 is directly translated into improved cost-effectiveness.

In contrast, individual demulsifiers display higher SCI values, particularly under lower-dosage conditions, where incomplete separation leads to less efficient reagent utilization. The superior performance of DC-5 therefore reflects not only synergistic interfacial effects but also a tangible economic advantage, as improved

separation efficiency reduces the specific chemical consumption required for dehydration.

Conclusion

1.The individual reagents — ALKAN-318, ALKAN DE-202, Separol, Demin-8411, and Dissolvan-3359 – were tested at concentrations of 150–500 g/t using a 35 % water-cut Muradkhanli crude oil sample at 40 °C for 120 minutes. The results indicated a generally weak demulsification performance, with only Separol showing comparatively satisfactory efficiency.

2.When the temperature was increased to 50 °C, the separation rate and coalescence degree of water droplets in the 35 % water-cut Muradkhanli crude oil sample increased notably, while both surface and interfacial tensions decreased, and the viscosity exhibited a downward trend. Nevertheless, these results remained insufficient for highly stable emulsions, indicating a need for more active systems.

3.For the first time, DC-series composite formulations were developed based on individual demulsifiers with the addition of ethanol as a co-surfactant. The presence of ethanol enhanced the surface activity of the system, promoting adsorption at the oil–water interface and facilitating the phase separation process.

4.The highest efficiency was achieved with the DC-5 composition (Dissolvan-3359 + ALKAN-318 + ethanol, 6 : 3 : 0.5). At 50 °C, 500 g/t concentration, and 120 minutes of testing, this formulation minimized the residual and ballast water contents, significantly reduced surface and interfacial tensions, and accelerated the coalescence rate within the emulsion.

5.The application of DC-5, DC-4, DC-6, and DC-7 compositions resulted in a substantial increase in the salt sedimentation rate in the 35 % water-cut Muradkhanli crude oil sample, demonstrating that these formulations simultaneously enhance both demulsification and desalting processes.

6.Based on the experimental results, the DC-5 composition (Dissolvan-3359 + ALKAN-318 + ethanol) is recommended for industrial-scale application under operational conditions of 45–55 °C and 450–550 g/t dosage for the efficient treatment of 35 % water-cut Muradkhanli crude oil emulsions.

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