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Synthesis and characterization of new Gemini surfactants and used there to treatment W/O emulsions in heavy crude oil

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Selected cationic Gemini surfactants were effective in separating water-oil emulsions, whereas cationic Gemini surfactants are (R1 and R2) with alkyl chain lengths of 5 and 6. Their characterization was done by FTIR, ^{1}H-NMR, and ^{13}C-NMR characters of these "new Gemini surfactants". These Gemini surfactants' basic surface properties were investigated by measuring the relationship between electrical conductivity and surfactant concentration to determine critical micelles concentration CMC. Demulsification (emulsion breaking) is necessary in many practical applications as the petroleum industry and wastewater treatment in environmental technology. Demulsifiers with amine were used for breaking of water in crude oil emulsion in this study. The relative rate of water separation was determined via breaker tests. The demulsifier which has longer alkyl chain length had a better performance on breaking emulsion than demulsifier which has shorter alkyl chain length.

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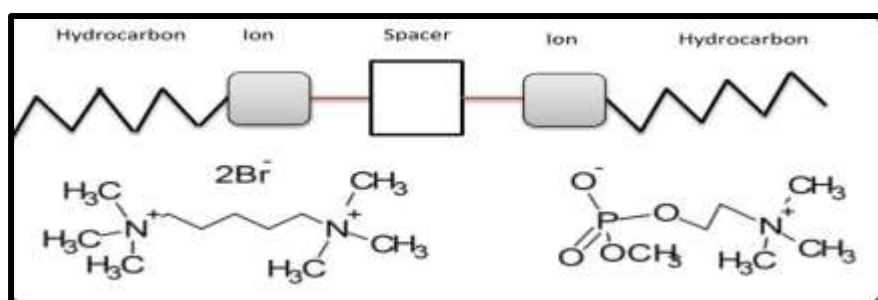Email: rabab-laf.ch@sci.utq.edu.iq
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Introduction

Gemini surfactant is a molecule resulting from a link of two, three, four, or five normal surfactants (traditional) by a bridge called (spacer). It has a special behavior with two polar groups at least and have greater effectiveness of traditional surfactants, as shown in Scheme 1 [21].

SCHEME 1 Gemini surfactants [21]

Geminis are surfactants that consist of two monomeric surfactants (two hydrophilic and two hydrophobic groups) joined by a spacer. Gemini surfactants have superior properties due to their unique structure, such as higher Surface activity and lower Critical Micelle Concentration (CMC) [1-2], improved oil/water interfacial tension reduction efficiency, unusual aggregation morphologies, and improved wetting, solubilizing, foaming, and antibacterial activities [3-4]. Because cationic surfactants are widely used in the chemical industry and also in everyday cosmetic as well as cleaning products, they are present in wastewater, groundwater, and soil. Furthermore, cationic surfactant has been proposed as additive reagents in organic contaminated soil mitigation and remediation [5-6]. The water in oil emulsion forms during the manufacturing of crude oil, which is frequently accompanied by water. The stability of the emulsion varies from little minutes to years, depending on the crude oil and to a lesser extent, water [7]. Water can become intimately dispersed throughout the crude oil as small droplets under production conditions. The natural petroleum emulsion produced by the secondary production is composed of crude oil as a dispersion medium and brine as a dispersed phase, which is typically stabilized by natural chemicals such as asphaltenes, resins, and solids such as dlays and waxes [8]. At the water-oil interface, these components may clump together, preventing droplets from re-forming a distinct phase. Asphaltenes are regarded as the most important component in emulsion stabilization. Asphaltenes adsorb at the water in crude oil interfaces, forming a rigid film around the water droplet and preventing it from rupturing during droplet-

droplet collisions [9-10]. In these investigations, we have found that novel quaternary ammonium Gemini Surfactants with hydroxyl groups [11-12]. Alkyl trimethylammonium bromide is one of cationic surfactants used to test the effect of these Gemini Surfactants on water and oil separation [water in oil [W/O]] [13].

Experimental

Materials and methods

Sigma-Aldrich Company provided the following materials: 1,5 -di bromo bentane (98% purity), 1,6 -di bromo hexane (98% purity), 4-dimethyl amino benzaldehyde (99.5% purity), ethyl acetate (99% purity), chloroform (99% purity), ethanol (99.8% purity), and silica gel high-purity Grade 40. (35-70 mesh). All solutions were prepared with twice-distilled water.

A Bruker AM 500 Spectrometer was used to record the ^{1}H-NMR and ^{13}C-NMR spectra. The prepared Gemini surfactants' NMR spectra were recorded in CDCl$_3$, and the chemical shifts recorded were internally referenced to TMS [0 ppm]. Fourier transform infrared (FT-IR) Spectroscopy was used to confirm the structural properties of these new Gemini surfactants on a Thermo - Electron Corporation Nicolet 380 FT-IR spectrophotometer.

TLC was performed on aluminum sheets covered by a homogeneous silica gel sorbent layer of 90 - 120 m thickness, 5-17 Sorbent size (m). The surfactant solution's CMC values were calculated using electrical conductivity And a WTW Inolab cond 740 conductivity meter [Germany].

Preparation of gemini surfactant (R1)

N^1,N^5-bis(4-formylphenyl)-N^1,N^1,N^5,N^5-tetramethylpentane-1,5-diaminium dibromide

The synthesized Gemini surfactant was obtained by reaction between alkyl halide; namely, 1,5 di Bromo pentane, (0.025 mol),

(5.75 g) and 4-dimethyl amino benzaldehyde (0.050 mol), (7.45 g) in 50 mL ethanol. The reaction mixture was reflexed for (24 hours)

and left for complete precipitation of the Gemini compounds. The produced Gemini surfactants were filtered off and recrystallized three times from ethanol to produce the desired Gemini surfactant to obtain (light brown crystals) with a yield of 80% and a melting point of (63 °C)[14].


N^1,N^6-bis(4-formylphenyl)– N^1,N^1,N^6,N^6-tetramethylpentane-1,5-diaminium dibromide
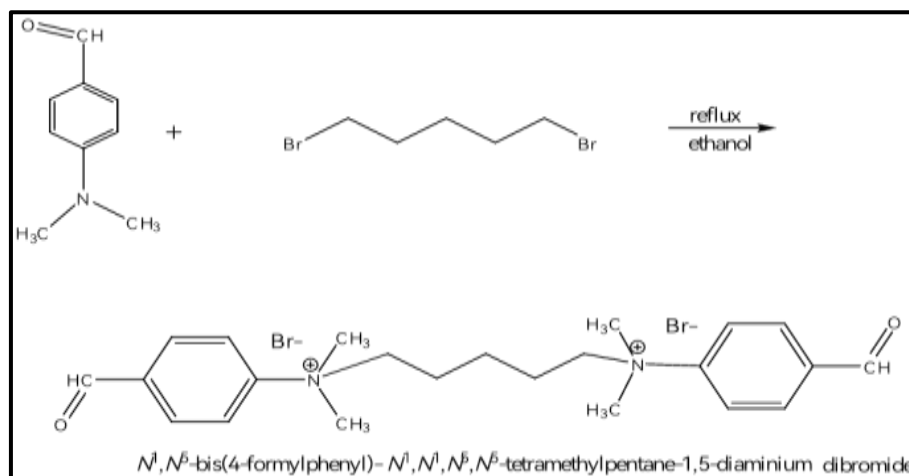
EQUATION 1 R1 synthesis

Preparation of Gemini surfactant (R2)

N^1,N^6-bis(4-formylphenyl)-N^1,N^1,N^6,N^6-tetramethylhexane-1,6-diaminium di bromide

: (0.025 mol), (6 g) of 1,6 di Bromo hexane reaction with (0.05 mol), (7.45 g), from 4-dimethyl amino benzaldehyde in 50 mL ethanol. The reaction mixture was reflexed for (22 h) and left for complete precipitation of the Gemini compounds. The produced Gemini surfactants were filtered off and recrystallized three times from ethanol to produce the desired Gemini surfactant to obtain (dark green crystals) with a yield of 80% and a melting point of (65 °C) [14].

N^1,N^6-bis(4-formylphenyl)-N^1,N^1,N^6,N^6-tetramethylhexane-1,6-diaminium di bromide (M6)
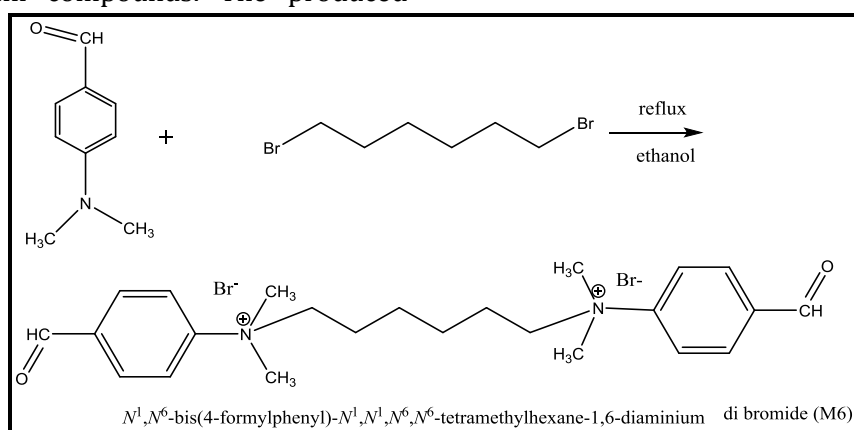
EQUATION 2 R2 synthesis

Results and discussion

FTIR spectrum of Gemini surfactant

The infrared spectrum of the Gemini surfactant (R1) C-H (Ar.) (3085 cm^{-1}) and C-H (Aliph) at (2918 cm^{-1}) and two stretching bands for (C=O) aldehyde at (1665 cm^{-1}).

The infrared spectrum of the Gemini surfactant (R2) C-H (Ar.) (3092 cm^{-1}) and C-H (Aliph) at (2903 cm^{-1}) and two stretching bands for (C=O) aldehyde at (1660 cm^{-1}).

Nuclear magnetic resonance

^{1}H- NMR spectrum of the R1 in CDCl$_3$ peak assignments was characterized by the presence of (O = CH) appeared to signal at δ (9.73) ppm, the signal at δ (6. 68-7.74) ppm was belonging to the aromatic protons and signal at δ (3.08) ppm due to (N-CH$_3$) and (N-CH$_2$) protons seemed at δ (1.91) ppm, and also (CH2) aliphatic protons were appeared at δ (1.29) ppm.

^{13}C-NMR spectrum of the R1 peaks assignments of chemical shifts are characterized by the peak associated with δ (HC=O) appearing at δ (190.3) ppm. In addition, the aromatic carbon rings was exhibited at range δ (116.1-125.8) ppm, (N-CH3) at (110.96), (N-CH2) at (77.37), and (CH2) aliphatic at (40.7).

^{1}H- NMR spectrum of the R2 in CDCl$_3$ peak assignments was characterized by the presence of (O = CH) appeared to signal at δ (9.74) ppm, the signal at δ (6. 73-7.75) ppm belonging to aromatic protons and signal at δ (3.09) ppm due to (N-CH$_3$), (N-CH$_2$) protons were appeared at δ (1.91) ppm, and (CH2) aliphatic protons were seemed at δ (1.3) ppm. ^{13}C-NMR spectrum of the R2 peaks assignments of chemical shifts was characterized by the peak associated with δ (HC=O) appearing at δ (190.3) ppm. In addition, the aromatic carbon rings was exhibited at range δ (125.8-154.1) ppm, (N-CH3) at (111.96), (N-CH2) at (77.37), and (CH2) aliphatic at (40.29).

CMC determination by conductivity method

A different dilute concentration was used of prepared surfactant (0.1x10^{-3} M) to (1x10^{-3} M) and the values were recorded by electrical conductivity (G) for prepared solutions at (25 °C). As depicted in Figures 1- 4, values were converted into specific conductivity (L) using the relationship (1) and plotted with the change in concentration and CMC extraction from Plot (4).

L=K G --------------1

Where,

 L= specific conductivity, **K**=cell constant, and **G**= electrical conductivity.

We observe that conductivity increases linearly with concentration due to an increase in the released amphiphilic number in the solution to reach a critical micelles concentration point (CMC). The increase in the number of free ions in the solution causes a significant change.
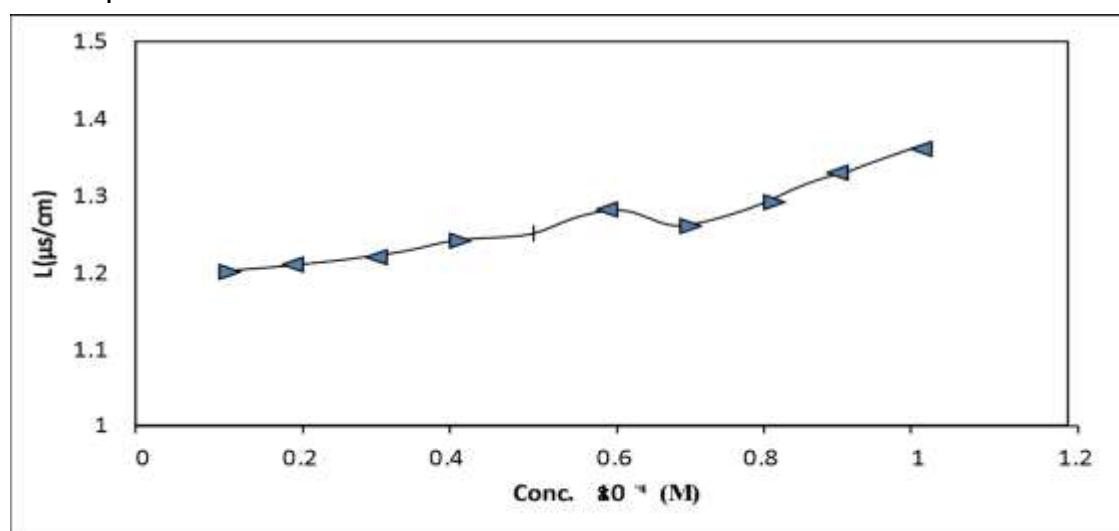

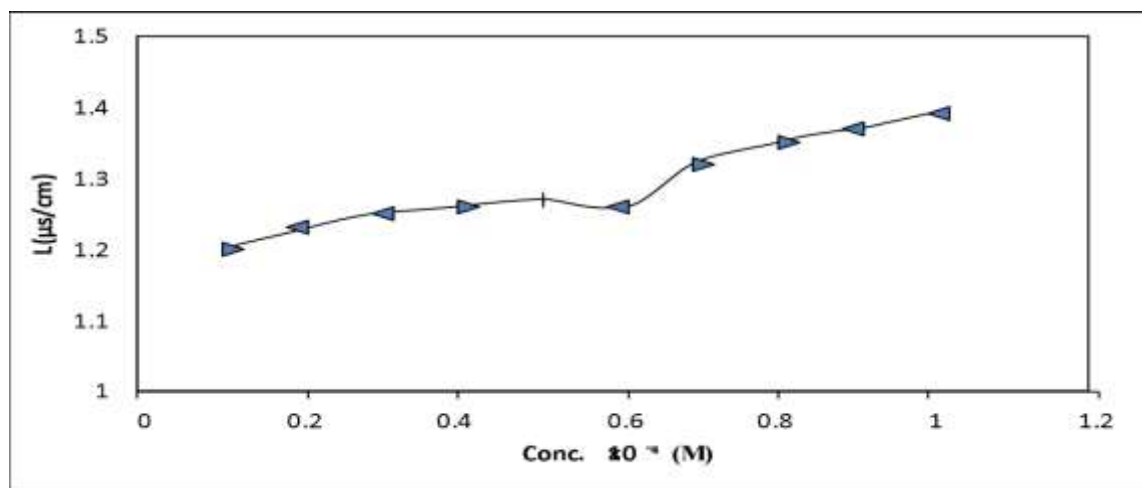**FIGURE 1** CMC of (R1) surfactants

FIGURE 2 CMC of (R2) surfactants

Studying the efficiency of Gemini surfactants as demulsifier by bottle tests

Demulsifiers are one of the most important factors influencing the efficiency of water separation from oil and the stability of emulsions by breaking the film surrounded by the continuous phase and allowing the mixed phases to be separated from each other. Efficiency of emulsions depends on the structure of Gemini surfactant and additives used in the composition of demulsifier [15,16]. The separation efficiency of water from crude oil can be calculated as a function of concentration, time, and temperature from Equation 2 [17,18] :

% E Separation = (VS/VT) x 100 ......   (2)

Also, it can be calculated emulsion stability using Equation 3:

% Emulsion stability = [1 – (VS/VT)] x 100 (3)

Where, % E Separation: the percentage of separation efficiency of water from crude oil.
V S: Volume of water separated (mL).

V T: Total volume of brine (2.7 mL) in crude oil. The objective of a Demulsifiers

"bottle test" is to investigate the performance of a demulsifier in a series of tests designed to replicate the conditions found in the actual production system as closely as possible. It is, however, impossible to simulate everything. Over many years of worldwide testing, it has been discovered that the concentration of demulsifiers in the process can differ from that in the laboratory bottle test [19 -20].

In this study, crude oil was distributed in glass tubes (capacity tube: 10 mL) and was placed in a water bath at 30 °C and 60 °C for 120 minutes, during which there were separate water readouts using nanocomposites concentrations (50,100, and 150) ppm. The separation efficiency of prepared demulsifiers from M5 and M6 surfactants was studied. We are using several factors that have a direct impact on the percentage of water separation. These are the following factors: (i) demulsifier concentration, (ii) temperature effect, and (iii) settling time effect (Tables 1 and 2, Figures 5 and 6).

TABLE 1 Separated water using demulsifier (R1) with crude oil

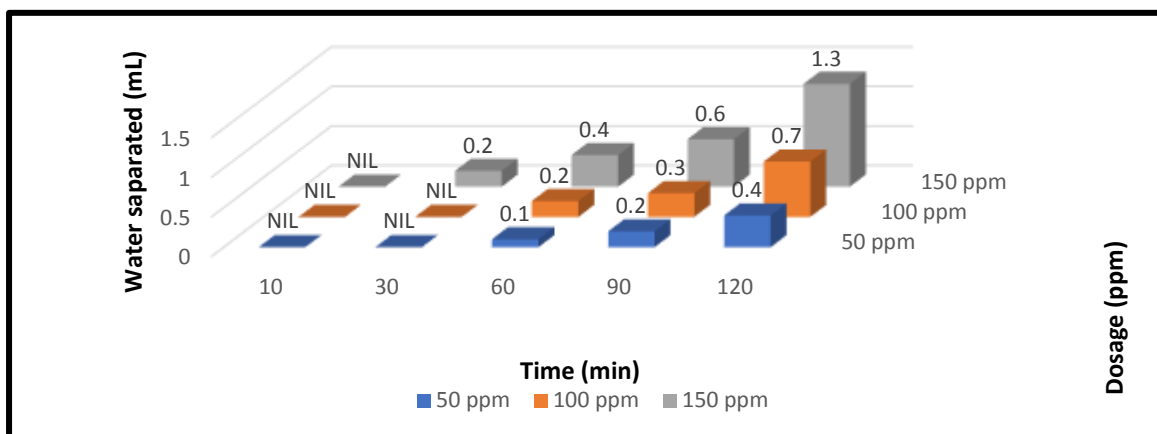| Temperature	Dosage ppm	Water Separated (mL)					%E Separation	% Emulsion Stability
		After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.		
30 °C	50	Nil	Nil	0.1	0.2	0.4	15%	85%
	100	Nil	Trace	0.2	0.3	0.7	26%	74%
	150	Nil	0.2	0.4	0.6	1.3	48%	52%
60 °C	50	Nil	0.1	0.2	0.5	0.8	30%	70%
	100	Nil	0.2	0.4	0.7	0.9	33%	67%
	150	Nil	0.4	0.7	1	1.5	56%	44%

FIGURE 3 Effects of demulsifier R1 dosage and settling time on separated water at 30 °C with crude oil
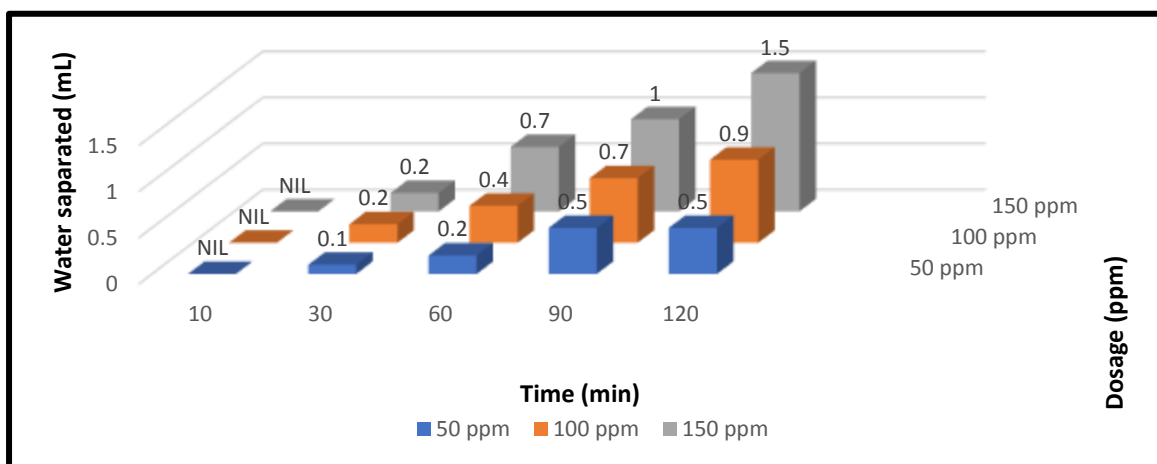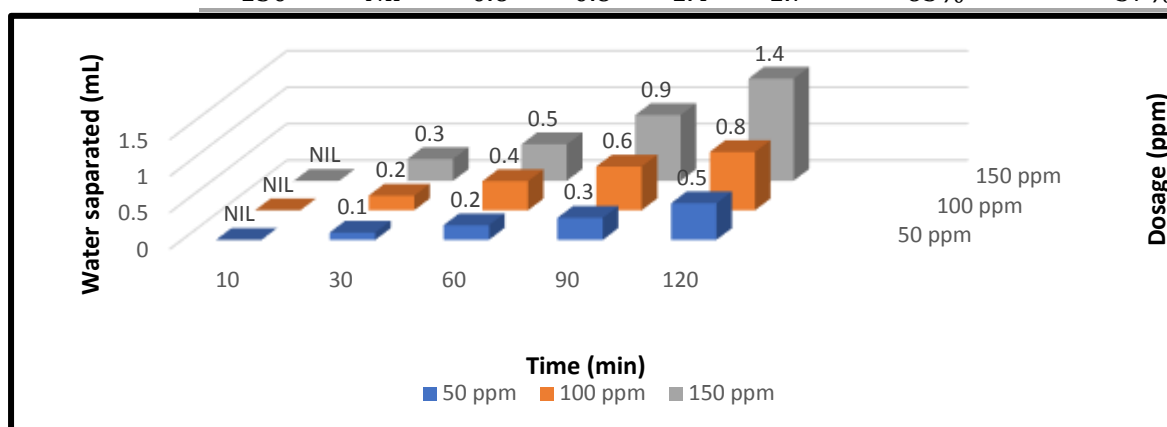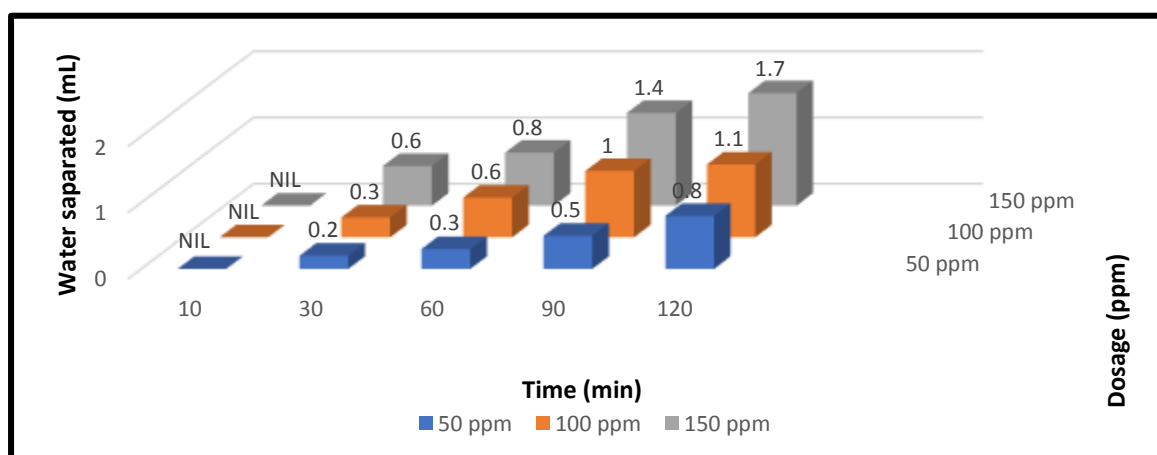

FIGURE 4 Effects of demulsifier R1 dosage and settling time on separated water at 60 °C with crude oil

TABLE 2 Separated water using demulsifier (R2) with crude oil

Temperature	Dosage ppm	Water Separated (mL)					%E Separation	% Emulsion Stability
		After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.		
30°C	50	Nil	0.1	0.2	0.3	0.5	19%	81%
	100	Nil	0.2	0.4	0.6	0.8	30%	70%
	150	Nil	0.3	0.5	0.9	1.4	52%	48%
60 °C	50	Nil	0.2	0.3	0.5	0.8	30%	70%
	100	Nil	0.3	0.6	1	1.1	41%	59%
	150	Nil	0.6	0.8	1.4	1.7	63%	37%

FIGURE 5 Effects of demulsifier R2 dosage and settling time on separated water at 30 °C with crude oil

FIGURE 6 Effects of demulsifier R2 dosage and settling time on separated water at 60 °C with crude oil

Conclusion

Emulsion breaking was generally caused by supplied demulsifiers and water separation efficiency increased with maximizing the dose of prepared demulsifiers. High temperatures cause an increase in separation efficiency at lower concentrations, where separation efficiency enhances with increasing temperature, and water separation efficiency increases with increasing separation time for all types of demulsifiers with the maximum separation obtained at high temperatures (120 min).

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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