Synthesis and characterization of new surfactants and its application in treatment of W/O emulsions in heavy crude oil

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ABSTRACT

In this study, two new types of surfactants formed from a reaction of dimethyl amino benzaldehyde with 1- Bromo tetradecane and 1- Bromo decane were prepared and characterized. the structure of the synthesized compounds was confirmed using infrared FTIR and nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR). Demulsifiers were applied to emulsions (water in oil) to separate water. The results showed high efficiency in separating water from crude oil.

Keywords: Surfactants, Demulsifiers, Crude oil.
Article type: Short Communication.

INTRODUCTION

Surfactants are amphiphilic compounds that contain a tail, which is insoluble in water, presenting hydrophobic groups and a water-soluble head with hydrophilic groups (Desai & Banat 1997; Tadros 2014). Due to this structure, these substances have the ability to diffuse in water and to place themselves between air/water or oil/water interfaces (Banat *et al.* 2000; Soberón Chávez 2011; Faizulina *et al.* 2023), solubilizing hydrophobic compounds in water and giving stable emulsions with many applications in different industrial sectors including the agrochemical (Singh & Cameotra 2011; López Prieto *et al.* 2019), agriculture (Sachdev & Cameotra 2013), food (Nitschke & Costa 2007; López Prieto *et al.* 2018), pharmaceutical (Gharaei Fa 2011) and cosmetic industries (Varvaresou & Iakovou 2015; Vecino *et al.* 2017) as well as therapeutic (Gudiña *et al.* 2013), medicine (Rodrigues *et al.* 2006) and oral-health related (Elshikh *et al.* 2016) applications.

Surfactants can be classified on the basis of charge carrying by the polar (hydrophilic) part of the surfactant molecule and the literature study. Generally, surfactant, are four types as follows:

(i) Cationic: The hydrophilic group carries a positive charge, for example, quaternary ammonium chloride, $RN(CH_3)_3{}^+Cl^-$.

(ii) Anionic: The hydrophilic group carries a negative charge, for example, alkyl benzene sulfonate, $RC_6H_4SO_3{}^-Na^+$.

(iii) Nonionic: The hydrophilic group carries no apparent ionic charge for example polyoxyethylene alkylphenol $R(OC_2H_4)_xOH$.

(iv) Zwitterionic: The hydrophilic group carries both positive and negative charge for example sulfobetaine, $RN^+(CH_3)_2CH_2CH_2SO_3{}^-$. (Shachi *et al.* 2018)

Alkyl dimethylammonium bromide is one of these investigations, which we have found ammonium surfactants. Herein we report the synthesis and the efficiency of breaking the emulsions.

MATERIALS AND METHODS

Materials and instruments

The following materials were purchased from Sigma – Aldrich Company: 1-Bromo tetradecane (98 % purity), 1-Bromo decane (98% purity), 4-dimethyl amino benzaldehyde (99.5% purity), ethyl acetate (99% purity),

chloroform (99% purity), ethanol (99.8 % purity), 1-bro purity, silica gel high-purity grade 40 (35-70 mesh). Twice distilled water was used in the preparation of all solutions. The characterization by [1] H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer. The NMR spectra of the prepared Gemini surfactants were recorded in CDCl$_3$ and chemical shifts recorded were internally referenced to TMS (0 ppm) and Fourier transform infrared (FT-IR) verified the structural characters of these new surfactants on a Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Thin layer chromatography (TLC) was conducted on aluminum sheets covered by the homogeneous silica gel sorbent layer of 90 - 120 μm thickness, 5-17 Sorbent size (μm). The CMC values of the surfactant solution were determined from electrical conductivity with a WTW Inolab cond 740 conductivity meter (Germany).

Preparation of Synthesis of 4-formyl-N,N-dimethyl-N-tetradecylbenzenaminium bromide (M1)

The synthesized surfactant was obtained by reaction between alkyl halide namely: 1-
Bromo tetradecane (0.1 mol), and 4-dimethyl amino benzaldehyde (0.1 mol) 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 surfactant to obtain Green crystals with a yield of 85% and a melting point of 66 °C (14).
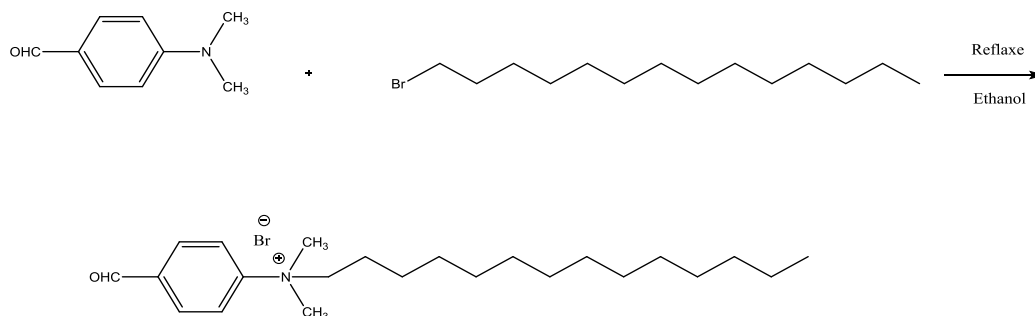

Fig. 1. Synthesis of M1.

Preparation of N-decyl-4-formyl-N,N-dimethylbenzenaminium bromide (M2):

The synthesized surfactant was obtained by reaction between alkyl halide namely:1-
Bromo decane: (0.1 mol), of 1,6 di Bromo hexane reaction with 0.2 mol 4-dimethyl amino benzaldehyde in 50 mL ethanol. The reaction mixture was reflexed for 24 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 surfactant to obtain Dark green crystals with a yield of 82% and a melting point of 69 °C (14).
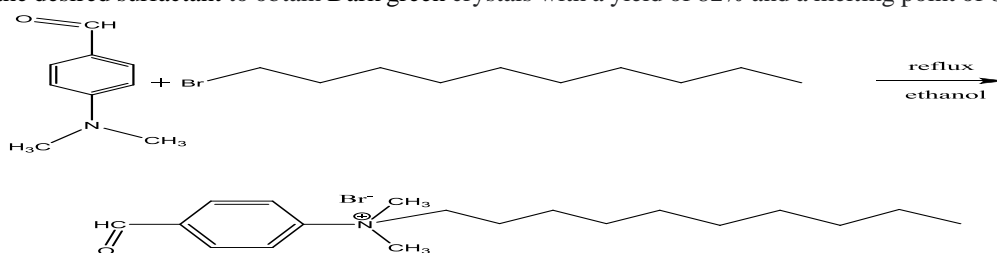

Fig. 2. Synthesis of R2.

RESULTS AND DISCUSSION

FT-IR spectrum of surfactant

The infrared spectrum of the surfactant (M1) C-H (Ar.) at 3366 cm^{-1} and C-H (Aliph) at 2951 cm^{-1} and two stretching bands for (C=O) aldehyde at 1700 cm^{-1}. The infrared spectrum of the surfactant (M2) C-H (Ar.) at 3045 cm^{-1} and C-H (Aliph) at 2910 cm^{-1} and two stretching bands for (C=O) aldehyde at 1665 cm^{-1}.

Nuclear Magnetic Resonance

^{1}H- NMR spectrum of the M1 in CDCl$_3$ peak assignments characterized by the presence of (O = CH) appeared to signal at δ 9.75 ppm, the signal at δ 6. 713-7.756 ppm belonging to aromatic protons and signal at δ 3.98 ppm due to (N-CH$_3$), (N-CH$_2$) protons seemed at δ 1.257 ppm, (CH$_2$) aliphatic protons seemed at δ 1.244 ppm.

^{13}C-NMR spectrum of the **M1** 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 exhibited at range δ 131.94-125.31 ppm, (N-CH$_3$) at 111.96, (N-CH$_2$) at 77.37, (CH$_2$) aliphatic at 40.4.

^{1}H- NMR spectrum of the **M2** in CDCl$_3$ peak assignments characterized by the presence of (O = CH) appeared to signal at δ 9.75 ppm, the signal at δ 6. 80-7.76 ppm belonging to aromatic protons and signal at δ 3.09 ppm due to (N-CH$_3$), (N-CH$_2$) protons seemed at δ .91) ppm, (CH$_2$) aliphatic protons seemed at δ 1.3 ppm.

^{13}C-NMR spectrum of the **M2** 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 exhibited at range of δ 125.8-154.1 ppm, (N-CH$_3$) at 111.96, (N-CH$_2$) at 77.37, (CH$_2$) aliphatic at 40.29.

3-4 Determine CMC by conductivity method

A different dilute concentration was used of prepared surfactant 0.1×10^{-3} to 1×10^{-3} and the values were recorded by electrical conductivity (G) for prepared solutions at 25 °C. The values were converted to the specific conductivity (L) through the relationship 1 and plot with the change in concentration and extraction of CMC from the plot (as shown in Figs. 5 and 6).

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

where: **L**= specific conductivity; **K** = cell constant; **G** = electrical conductivity.

We note that the conductivity changes linearly by the concentration elevation, because of an upraise in the released amphiphilic number in the solution to reach a critical micelles concentration point (CMC). Then the change is big because of the elevation in the number of free ions in the solution.
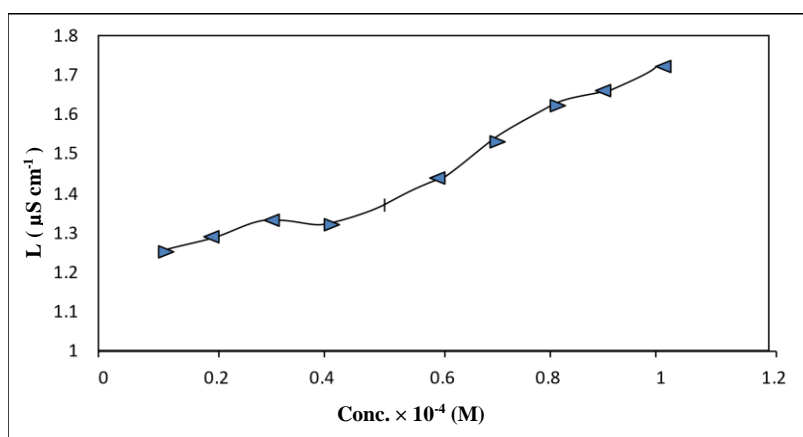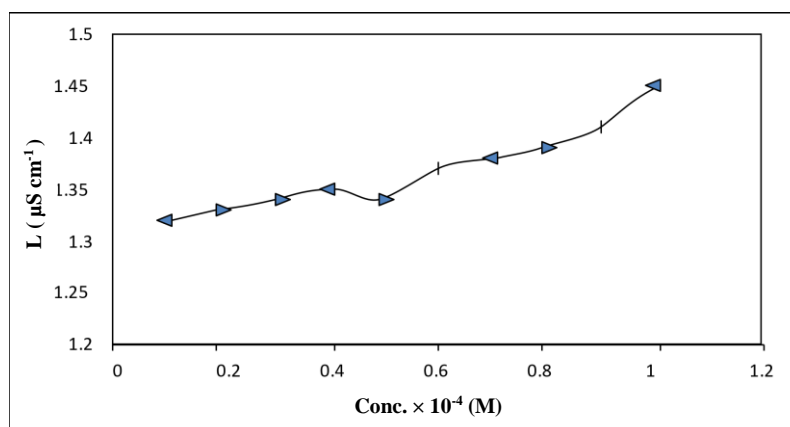

Fig. 3. CMC of M1 surfactant.

Fig. 4. CMC of M2 surfactants.

Examing the efficiency of gemini surfactants as demulsifier by bottle tests

Demulsifiers of the most important factors affecting the separation efficiency of water from oil and the stability of emulsions through break the film which is surrounded by the continuous phase, and allowing the mixed phases to be separated from each other, where the separation efficiency of emulsions depends on the structure of Gemini

surfactant and additives used in the composition of demulsifier. The separation efficiency of water from crude oil can be calculated as a function of concentration, time, and temperature from equation 2 (Azim *et al.* 2010; Mosayebi & Abedini 2013):

E separation (%) = (VS∕VT) × 100 ……   .. **(2)**

 Also can be calculated emulsion stability by using equation 3

Emulsion stability (%) = [1 − (VS∕VT)] × 100 …….. **(3)**

where: E Separation (%): The percentage of separation efficiency of water from crude oil.
VS: 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 that are designed to duplicate the conditions found in the actual production system as closely as possible. However, it is impossible to simulate everything. It has been found over many years of worldwide testing that the concentration of demulsifier in the process can be different from that in the laboratory bottle test (Nuraini *et al.* 2011). 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 min, 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.

Table 1. Separated water usig demulsifier (M1) with crude oil.

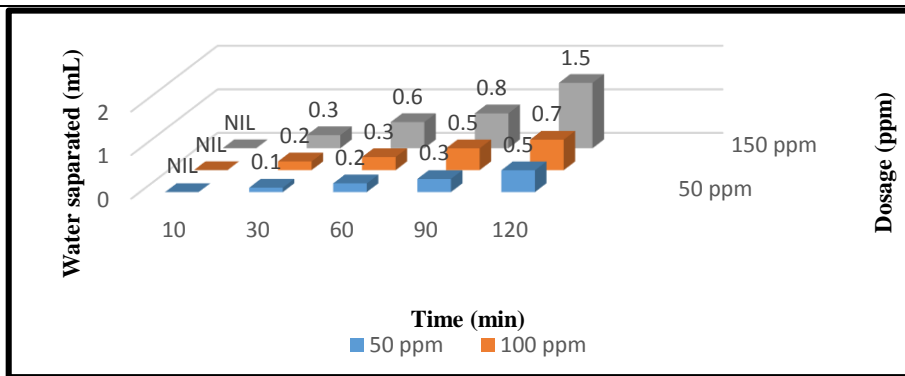| Temperature	Dosage (ppm)	Water Separated (mL)					E separation (%)	Emulsion stability (%)
		After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.		
30 °C	50	Nil	0.1	0.2	0.3	0.5	18.5	81.5
	100	Nil	0.2	0.3	0.5	0.7	26	74
	150	Nil	0.3	0.6	0.8	1.5	56	44
60 °C	50	Nil	0.2	0.3	0.4	1	37	63
	100	Nil	0.3	0.5	0.8	1.2	44	56
	150	Nil	0.4	0.6	1	1.9	70	30

Fig. 5. Effects of the demulsifier M1 dosage and settling time on separated water at 30 °C with crude oil.

CONCLUSION

Generally, emulsion breaking occurred by supplied demulsifiers, where water separation efficiency increases with increasing dose of prepared demulsifiers. At high temperatures will be leads to increase in separation efficiency at lower concentrations, where the separation efficiency is increased with increased temperature, also water separation efficiency increases with increasing separation time for all types of demulsifiers, where maximum separation obtained is at (120 min).
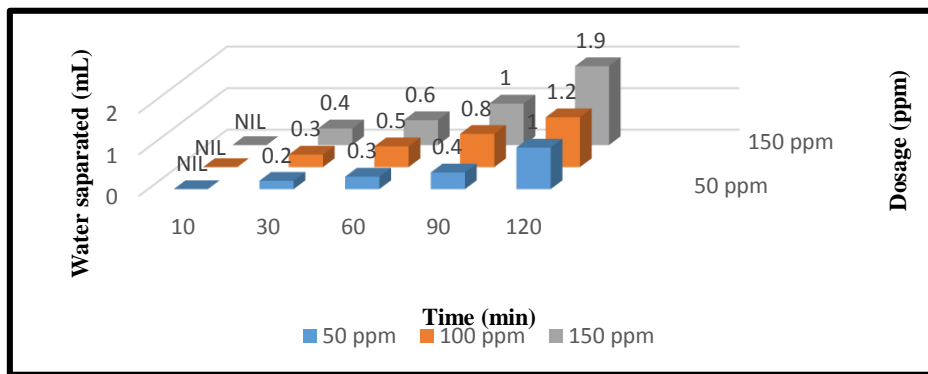
Fig. 6. Effects of the Demulsifier M1Dosage and Settling Time on separated water at 60 °C with Crude Oil.

Table 2. Separated water by using demulsifier (M2) with crude oil.

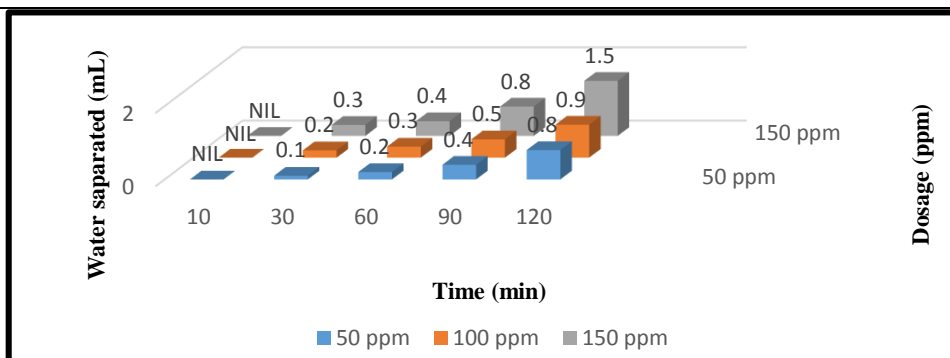| Temperature	Dosage ppm	Water Separated (mL)					E Separation (%)	Emulsion Stability (%)
		After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.		
30°C	50	Nil	0.1	0.2	0.4	0.8	30%	70%
	100	Nil	0.2	0.3	0.5	0.9	33%	67%
	150	Nil	0.3	0.4	0.8	1.5	56%	44%
60 °C	50	Nil	0.2	0.4	0.5	1	37%	63%
	100	Nil	0.4	0.7	0.9	1.4	52%	48%
	150	Nil	0.5	0.8	1.2	1.8	67%	33%

Fig. 7. Effects of the Demulsifier M2 Dosage and Settling Time on separated water at 30 °C with Crude Oil of
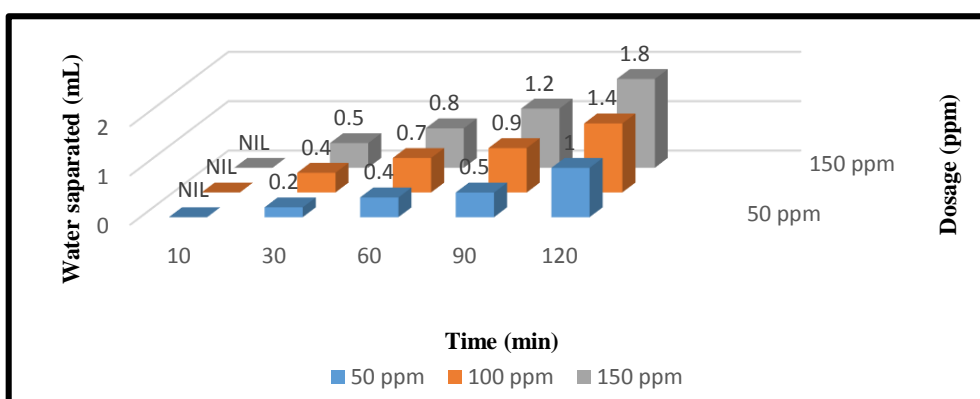

Fig. 8. Effects of the Demulsifier M2 Dosage and Settling Time on separated water at 60 °C with Crude Oil of.

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