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Synthesis of Novel Cationic Gemini surfactants and used their to Treatment W/O Emulsions which formation in heavy crude oil.

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ABSTRACT

Selected cationic Gemini surfactants were effective in separating Water – in – Oil emulsions, where cationic Gemini surfactants are C_{12}–2BU – C_{12} and C_{10}– 2BU–C_{10} that have alkyl chain length of 10 and 12. The characterization by FT – IR, ^{1}H NMR, ^{13}C NMR and mass spectra verified the structural characters of these new Gemini surfactants. The basic surface properties of these novel Gemini surfactants were investigated through measuring the relationship between the electrical conductivity and the surfactant concentration to determine critical micelles concentration CMC. Demulsification (emulsion breaking) is necessary in many practical applications as the petroleum industry and waste water 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 alkyl chain length taller was better performance on breaking emulsion than demulsifier which has alkyl chain length shorter.

Keywords: Cationic Gemini surfactants, electrical conductivity, critical micelle concentration, demulsifier, interfacial film, Water in oil emulsion.

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INTRODUCTION

Geminis are special class of surfactants where two monomeric surfactants (two hydrophilic and two hydrophobic groups) are coupled together via a spacer. Because of the unique structure, gemini surfactants have some superior properties, such as higher surface activity, lower critical micelle concentration (CMC)[1, 2] a higher efficiency in reducing the oil/water interfacial tension, unusual aggregation morphologies, and better wetting, solubilizing, foaming, and antibacterial activities [3 - 5]. The wide application of cationic surfactants in chemical industries, as well as in daily cosmetic and cleaning products, have led to their widespread occurrence in wastewater, groundwater and soils. Moreover, cationic surfactants have been proposed as additive reagents in the mitigation and remediation of organic contaminated soils [6, 7].

Water-in-oil emulsion is formed during the production of crude oil, which is often accompanied with water. The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water [8]. Under the production conditions, a proportion of water can become intimately dispersed throughout the crude oil as small droplets. The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltenes, resins, solid such as clays and waxes [9]. These components may accumulate at the water-oil interface and hinder the droplets from re-forming a separate phase. Among these components, asphaltenes are believed to be the major material involved in emulsion stabilization. Asphaltenes tend to adsorb at water-in-crude oil interfaces to form a rigid film surrounding the water droplet, thereby protecting the interfacial film from rupturing during droplet-droplet collisions [10 - 12].

In these investigations, we have found that novel quaternary ammonium Gemini surfactants with hydroxyl groups [13 - 15]. Alkyltrimethylammonium bromide is one of the types cationic surfactants that were used to determine the effect on water and oil separation [16] Herein we report the synthesis and the efficiency of breaking the emulsions of water in oil (W/O) of these Gemini surfactants.

EXPERIMENTAL

2Materials and instruments

The following materials purchased from Sigma – Aldrich company: Butylene glycol (99.5 % purity), Sodium hydrogen sulfate (98% purity), Epichlorohydrin (99.5% purity), petroleum ether dist. (ASTM D86-87) between 40 and 60°C (99% purity), ethyl acetate (99% purity), Potassium hydroxide (99 % purity), 33% aqueous dimethyl amine, chloroform (99% purity), anhydrous magnesium sulfate (99.5 % purity), methanol (99.8 % purity), 1-bromo dodecane (98 % purity), 1-bromo decane (98 % purity), absolute isopropyl alcohol (99.7 % 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 gemini surfactants on a Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Mass spectra were obtained on SHIMADZU GCMS - QP2010 Plus (EI, 70 eV). Thin layer chromatography (TLC) was conducted on aluminium 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).

Synthesis of (C$_{10}$-2BU-C$_{10}$) and (C$_{12}$-2BU-C$_{12}$)

There are three steps to get the target compounds:

Synthesis of (2BU) / 3,3'-(butane-1,4-diylbis(oxy))bis(1-chloropropan-2-ol)

To a mixture consisting of Butylene glycol (27.04 g, 0.3 mol), Sodium hydrogen sulfate NaHSO$_4$ (1.00 g, 8 mmol) and water (0.6 ml) in round bottom flask, then added Epichlorohydrin (55.50 g, 0.6 mol) drop wise at

0 °C. The mixture was stirred for 5 hours and heated to 90 - 100 °C. After that the mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 1:4, v/v) to give the target compound (BU) as transparent oil (yield 85.2 %) [17,18].

IR (KBr): 3395, 2991.7, 2880.4, 1449.1, 1341.3, 710 cm^{-1}. ^{1}H NMR (500 MHz, CDCL$_3$): δ ppm = (0.54 – 0.88) OCH$_2$ **CH$_2$CH$_2$**CH$_2$O (t, 4H, CH$_2$), (3.54 – 3.63) O**CH$_2$** CH$_2$CH$_2$**CH$_2$**O (t, 4H, CH$_2$), (3.81 – 3.89) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$** (d, 4H, CH$_2$) , (4.11 – 4.30) O(CH$_2$)$_4$OCH$_2$**CH**OH (m, 2H, CH), (3.91) O(CH$_2$)$_4$OCH$_2$CH**OH** (s, 2H, OH), (2.82 – 2.95) OCH$_2$CHOH**CH$_2$**Cl (d, 4H, CH$_2$). ^{13}C NMR (500 MHz, CDCl$_3$): δ ppm= (44.16) OCH$_2$**CH$_2$CH$_2$**CH$_2$O, (68.90) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O, (71.83) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$**, (80.41) O(CH$_2$)$_4$OCH$_2$**CH**OH, (49.11) OCH$_2$CHOH**CH$_2$**Cl. MS (EI, 70 eV) m/z (%): 275 [M]$^+$ (10.7%); 56[C$_3$H$_4$O]$^+$(100.0%); 93[C$_3$H$_6$ClO]$^+$(20.51%); 72 [C$_4$H$_8$O]$^+$ (73.4%); 44 [C$_2$H$_4$O]$^+$(41.54%); 30 [CH$_2$O]$^+$(16.9%).

Synthesis of (2BU) / 2,15- dimethyl -6,11- dioxa -2,15-diazahexadecane -4,13-diol

To a flask containing (0.67 g, 12 mmol) Potassium hydroxide was added 33% aqueous dimethyl amine (0.90 g, 0.02 mol) , then added compound (BU) (2.80 g, 0.01 mol) as drop wise with a magnetic stirrer at room temperature to produce precipitate. The mixture was filtered then the filtrate was extracted with chloroform and dried over anhydrous magnesium sulfate. After evaporation to remove solvent and the residue was purified by column chromatography on silica gel (methanol/ethyl acetate, 1:5, v/v) to give the target compound (2BU) as yellow oil (yield 65.07%).

IR (KBr): 3410.3, 2990.7, 2875.2, 1310, 1278.8, 1125.4 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ ppm = (0.57 – 0.73) OCH$_2$**CH$_2$CH$_2$**CH$_2$O (t, 4H, CH$_2$), (3.66 – 3.78) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O (t, 4H, CH$_2$), (3.90 – 4.00) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$** (d, 4H, CH$_2$) , (4.22 – 4.35) O(CH$_2$)$_4$OCH$_2$**CH**OH (m, 2H, CH), (4.09) O(CH$_2$)$_4$OCH$_2$CH**OH** (s, 2H, OH), (2.91 – 3.16) OCH$_2$CHOH**CH$_2$**N (d, 4H, CH$_2$), (2.85) CH$_2$N**(CH$_3$)$_2$** (s, 12H, CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$): δ ppm= (47.50) OCH$_2$**CH$_2$CH$_2$**CH$_2$O, (64.77) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O, (78.12) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$**, (82.63) O(CH$_2$)$_4$OCH$_2$**CH**OH, (59.16) OCH$_2$CHOH**CH$_2$**N, (50.24) CH$_2$N**(CH$_3$)$_2$**. MS (EI, 70 eV) m/z (%): 292 [M]$^+$(22.5 %); 58 [C$_3$H$_8$N]$^+$(100.0%); 118 [C$_5$H$_{12}$NO$_2$]$^+$ (30.6%); 72 [C$_4$H$_8$O]$^+$ (46.3%); 40[C$_3$H$_4$]$^+$(19.7%); 26[C$_2$H$_2$]$^+$(10.1%).

Synthesis of Gemini surfactants

(C$_{10}$-2BU-C$_{10}$) / N, N'-((butane-1,4-diylbis(oxy)) bis (2-hydroxypropane-3,1-diyl)) bis (N,N-dimethyldecan-1-aminium) dibromide

To a flask containing 1-bromodecane (1.51 g, 6.84 mmol) and absolute isopropyl alcohol (50 ml) was added compound (2BU) (1.00 g, 3.42 mmol) at room temperature. The mixture was refluxed for 1 hour. After reaction the mixture was subjected to evaporation and the residue was purified by column chromatography on silica gel (methanol/ethyl acetate, 1:5, v/v) to give the target compound (C$_{10}$-2BU-C$_{10}$) as yellow oil (83.7%). The structure and synthetic route of this surfactant is shown in Scheme (1).

IR (KBr): 3388.00, 2870.00, 2781.63, 1469.76, 1200.33, 1122.57, 720.57 cm^{-1}. ^{1}H NMR (500 MHz, CDCL$_3$): δ ppm = (0.73 – 0.90) OCH$_2$ **CH$_2$CH$_2$**CH$_2$O (t, 4H, CH$_2$); (3.70 – 3.81) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O (t, 4H, CH$_2$); (4.88 – 5.06) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$** (d, 4H, CH$_2$) ; (4.20 – 4.33) O(CH$_2$)$_4$OCH$_2$**CH**OH (m, 2H, CH); (3.95) O(CH$_2$)$_4$OCH$_2$CH**OH** (s, 2H, OH) ; (3.10 – 3.28) OCH$_2$CHOH**CH$_2$**N (d, 4H, CH$_2$); (2.93) CH$_2$N**(CH$_3$)$_2$** (s, 12H, CH$_3$); (2.55 – 2.74) N(CH$_3$)$_2$**CH$_2$** (C$_9$H$_{19}$) (t, 4H, CH$_2$); (1.21 – 1.50) N(CH$_3$)$_2$CH$_2$**CH$_2$**(C$_8$H$_{17}$) (m, 4H, CH$_2$); (0.98 – 1.18) CH$_2$CH$_2$**(CH$_2$)$_6$**CH$_2$CH$_3$ (m, 24H, CH$_2$); (1.59 – 1.85) CH$_2$(CH$_2$)$_6$**CH$_2$**CH$_3$ (m, 4H, CH$_2$); (0.53 – 0.68) CH$_2$(CH$_2$)$_6$CH$_2$**CH$_3$** (t, 6H, CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$): δ ppm= (51.68) OCH$_2$**CH$_2$CH$_2$**CH$_2$O; (64.86) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O; (87.01) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$**; (84.14) O(CH$_2$)$_4$OCH$_2$**CH**OH; (62.95) OCH$_2$CHOH**CH$_2$**N; (52.04) CH$_2$N**(CH$_3$)$_2$** ; 60.81 N(CH$_3$)$_2$**CH$_2$** (C$_9$H$_{19}$); (48.46) CH$_2$**(CH$_2$)$_7$**CH$_2$CH$_3$; (39.03) CH$_2$(CH$_2$)$_7$**CH$_2$**CH$_3$; (16.54) CH$_2$(CH$_2$)$_7$CH$_2$**CH$_3$**. MS (EI, 70 eV) m/z (%): 733 [M]$^+$(16.5 %); 58 [C$_3$H$_8$N]$^+$(100.0%); 186 [C$_{10}$H$_{18}$O$_3$]$^+$ (74.8 %); 320 [C$_{16}$H$_{36}$O$_4$N$_2$]$^+$ (50.81%); 127[C$_9$H$_{19}$]$^+$(57.2%); 28[C$_2$H$_4$]$^+$(34.1%); 18[H$_2$O]$^+$(27.1%).
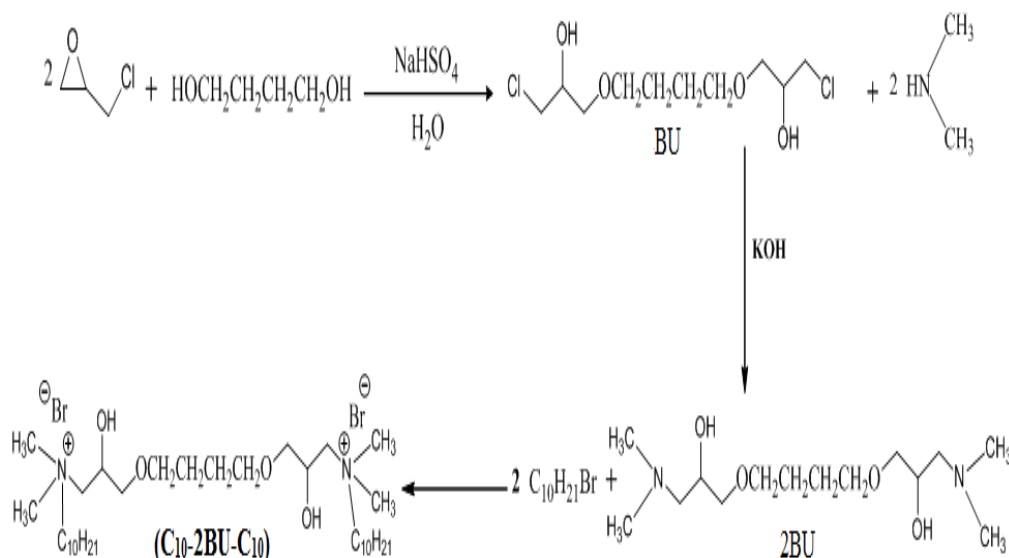
Scheme 1: Synthetic Route to Gemini surfactant (C$_{10}$-2BU-C$_{10}$)

(C$_{12}$-2BU-C$_{12}$) / N,N'-((butane-1,4-diylbis(oxy)) bis (2-hydroxypropane-3,1-diyl)) bis (N,N-dimethyldodecan-1-aminium) dibromide.

To a flask containing 1-bromododecane (1.70 g, 6.84 mmol) and absolute isopropyl alcohol (50 ml) was added compound (2BU) (1.00 g, 3.42 mmol) at room temperature. The mixture was refluxed for 1 hour. After reaction the mixture was subjected to evaporation and the residue was purified by column chromatography on silica gel (methanol/ethyl acetate, 1:5, v/v) to give the target compound (C$_{12}$-2BU-C$_{12}$) as yellow oil (yield 74.1%). The structure and synthetic route of this surfactant is shown in Scheme (2).
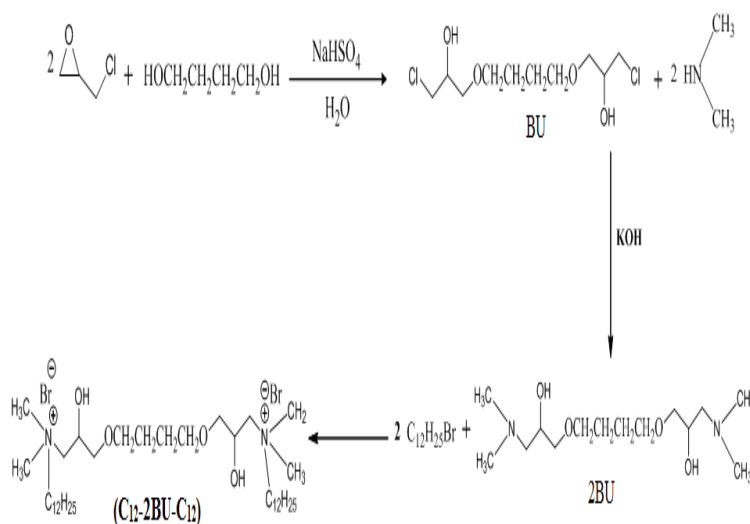
Scheme 2: Synthetic Route to Gemini surfactant (C$_{12}$-2BU-C$_{12}$)

IR (KBr): 3442.94, 2920.13, 2880.92, 1454.33, 1253.76, 1166.08, 710.08 cm^{-1}. ^{1}H NMR (500 MHz, CDCL$_{3}$): δ ppm = (0.90 − 1.12) OCH$_2$ **CH$_2$CH$_2$**CH$_2$O (t, 4H, CH$_2$); (4.15 − 4.41) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O (t, 4H, CH$_2$); (3.76 − 3.90) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$** (d, 4H, CH$_2$) ; (4.60 − 4.90) O(CH$_2$)$_4$OCH$_2$**CH**OH (m, 2H, CH); (3.65) O(CH$_2$)$_4$OCH$_2$CH**OH** (s, 2H, OH) ; (3.09 − 3.30) OCH$_2$CHOH**CH$_2$**N (d, 4H, CH$_2$); (3.00) CH$_2$N(**CH$_3$)$_2$** (s, 12H, CH$_3$); (2.60 − 2.75) N(CH$_3$)$_2$**CH$_2$** (C$_{11}$H$_{23}$) (t, 4H, CH$_2$); (2.20 − 2.45) N(CH$_3$)$_2$CH$_2$**CH$_2$**(C$_{10}$H$_{21}$) (m, 4H, CH$_2$); (1.36 − 1.56) CH$_2$CH$_2$**(CH$_2$)$_8$**CH$_2$CH$_3$ (m, 32H, CH$_2$); (1.68 − 2.05) CH$_2$(CH$_2$)$_8$**CH$_2$**CH$_3$ (m, 4H, CH$_2$); (0.56 − 0.80) CH$_2$(CH$_2$)$_8$CH$_2$**CH$_3$**

(t, 6H, CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$): δ ppm= (40.51) OCH$_2$**CH$_2$CH$_2$**CH$_2$O; (86.14) O**CH$_2$**CH$_2$CH$_2$**CH$_2$**O; (88.39) **CH$_2$**O(CH$_2$)$_4$O**CH$_2$**; (90.91) O(CH$_2$)$_4$OCH$_2$**CH**OH; (63.65) OCH$_2$CHOH**CH$_2$**N; (49.73) CH$_2$N(**CH$_3$**)$_2$; (52.03) N(CH$_3$)$_2$**CH$_2$** (C$_{11}$H$_{23}$); (31.40) CH$_2$**(CH$_2$)$_9$**CH$_2$CH$_3$; (20.77) CH$_2$(CH$_2$)$_9$**CH$_2$**CH$_3$; (14.86) CH$_2$(CH$_2$)$_9$CH$_2$**CH$_3$**. MS (EI, 70 eV) m/z (%): 789 [M]$^+$ (23.3 %); 58 [C$_3$H$_8$N]$^+$(100.0%); 204 [C$_{10}$H$_{20}$O$_4$]$^+$ (74.4 %); 475 [C$_{27}$H$_{59}$O$_4$N$_2$]$^+$ (42.1 %); 186 [C$_{10}$H$_{18}$O$_3$]$^+$(20.9%); 155 [C$_{11}$ H$_{23}$]$^+$(40.8 %); 29 [C$_2$H$_5$]$^+$ (72.5 %).

RESULTS AND DISCUSSION

Measurement of CMC Values of Surfactant Solutions by Electrical Conductivity

The critical micelle concentration (CMC) of a surfactant is an important physical parameter [19, 20], which can determine it's by the change in the electrical conductance of aqueous ionic surfactant solutions due to cationic ions and anionic ions [21, 22]. The electrical conductivity is usually influenced by solvent and temperature [23, 24] so that have been prepared a series of aqueous solutions of cationic Gemini surfactants from (1x10^{-3}) to (7x10^{-4}) then measured their conductivity at 25 $^°$C.

The values of CMC were calculated as the intersection of linear parts in the dependence conductivity versus surfactant concentration[25], and can be observed conductivity change linearly (extrusive) with the change of concentration due to the nature and concentration of counter ions in solution and the effect increases with decreasing charge density of the counter ion [26, 27].

Figure 1: CMC of (C$_{10}$-2BU-C$_{10}$) Surfactants
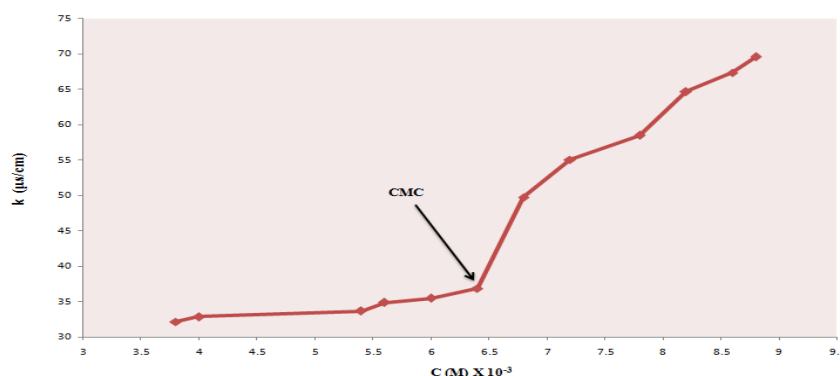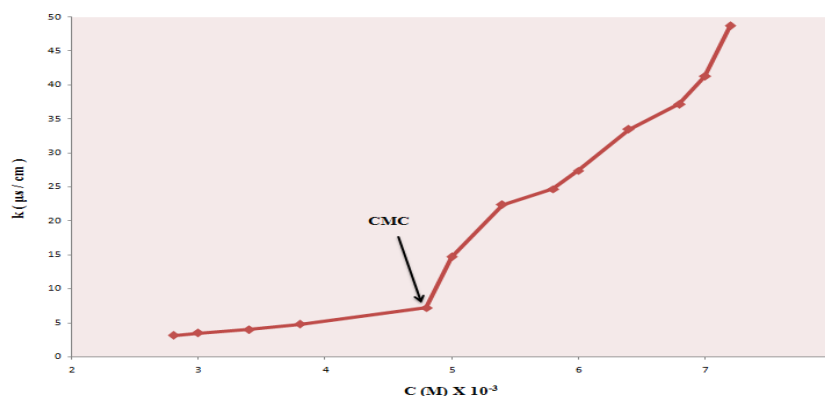

Figure 2: CMC of (C$_{12}$-2BU-C$_{12}$) Surfactants

Where noted from Figures that impairment of conductivity with reduced concentration of Gemini surfactants, can be attributed to a decline in the number of ions that contribute to the electrical conductivity, which leads to lower it, until a specific point is CMC point then be a simple change in the line as shown in the

Figures (1), (2). In addition Bis – quaternary ammonium salts from epichlorohydrin exhibit large intermolecular hydrophobic interaction that make it easy for them to form aggregates in water [28].

Through the results observed when increasing aliphatic tail length reduces the CMC value for surfactants, and the compounds with small polar heads are influenced by the length of the aliphatic tail to a much greater extent than surfactants with large non-ionic polar-regions. Where is observed that the value of CMC to $(C_{12} – 2BU – C_{12})$ (6.4×10^{-4} M) less than $(C_{10} – 2BU – C_{10})$ (4.8×10^{-3} M) [29- 31].

Study the Efficiency of Gemini Surfactants as Demulsifier by Bottle Tests

Demulsifier of the most important factors affecting the separation efficiency of water from oil and stability of emulsions through break the film which surrounded by the continuous phase, and to allow the mixed phases to be separated from each other, where the separation efficiency of emulsions depend on structure of Gemini surfactant and additives used in the composition of demulsifier [32, 33]. The separation efficiency of water from crude oil can be calculated as a function to concentration, time and temperature from equation (1) [9, 34]:

$$\% \ E_{Separation} = (V_S / V_T) \times 100 \ .... \ (1)$$

Also can be calculated emulsion stability by using equation (2) [35]:

$$\% \ Emulsion \ stability = [1 – (V_S / V_T)] \times 100 \ .... \ (2)$$

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 (15 ml) in crude oil.

The objective of a Demulsifiers "bottle test" is to investigate the performance of demulsifier in a series of tests that is designed to duplicate the conditions found in the actual production system as closely as possible. However it is not possible to simulate everything and it has been found over many years of worldwide testing that the concentration of demulsifier in the process can be different to that in the laboratory bottle test [36 - 38].

Table 1: Physicochemical Properties of the used Crude Oils

№	CHARACTERSTICS	Method	RESULT
1.	SPECIFID GRAVITY @ 60 ºF	IP160	0 .9293
2.	API GRAVITY	IP160	20.8
3.	SULPHUR CONTENT , wt. %	ASTM D-4294	3.30
4.	WATER CONTENT , vol. %	ASTM D-4006, IP-358	NIL
5.	WATER & SEDIMENT , vol. %	ASTM D-4007, IP-359	NIL
6.	SALT CONTENT , 1b/1000 brl	IP 77	38.0
7.	ASPHALTENES , wt. %	IP-143	9.6
8.	WAX CONTENT , wt. %	UOP-64	1. 97
9.	POUR POINT , ºC	ASTM D-97, IP-15	< -25
10.	KINEMATIC VISCOSITY , cSt. 1.@ 70 ºF (21.1 ºC) 2.@ 100 ºF (37.8 ºC) 3.@ 120 ºF (48.9 ºC) 4.@ 140 ºF (60.0 ºC)	ASTM D-445, IP-71	 112.0 52.50 32.47 22.50

The industrial emulsion was prepared by mixing Constant volume from synthetic - produced brine 15% (concentration 200,000 ppm) with 85 % crude oil, physicochemical properties shown in the Table (1) to become the overall percentage 100 % , which mixed by using an electric mixer can control the mixing speed (1000-2000 rpm) and duration (3 min)[19]. Emulsion was distributed in glass tubes (capacity tube 100 ml)

and placed one of them in a water bath at 50 °C and another in room temperature 25 °C for two hours, during which are read water separated (five readouts).

Through the results of laboratory testing which are shown in the Table (1), crude oil can be characterized as a heavy and sour crude oil because it has lower degrees of API gravity (20.8), higher specific gravity (0 .9293), and higher sulfur content (3.30 %). As well as heavy crude oil has high viscosity (112.0, 52.50, 32.47, 22.50) cSt. at (21.1, 37.8, 48.9, 60.0) °C respectively due to very high asphaltene content (9.6 %), but low wax content (1.97 %) leads to it is a liquid at temperature <-25 °C (pour point). Water content is (Nil) and salt content is (38.0) 1b/1000 brl. in crude oil.

Table 2. Water Separated by Using Demulsifier (2BU-C$_{10}$)

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.		
25 °C	10	Nil	Nil	Nil	Trace	0.25	1.7	98.3
	20	Nil	Nil	Trace	0.3	0.5	3.3	96.7
	30	Nil	Trace	0.3	0.8	1.5	10.0	90.0
	40	Trace	0.25	0.6	1.2	2.0	13.3	86.7
	50	0.5	1.5	3.0	4.0	4.0	26.7	73.3
50 °C	10	Nil	Nil	Trace	0.3	0.7	4.7	95.3
	20	Trace	0.25	0.6	1.0	1.4	9.3	90.7
	30	0.4	0.8	1.5	2.5	3.0	20.0	80.0
	40	1.0	1.8	3.0	5.5	5.5	36.7	63.3
	50	1.5	3.0	4.0	6.0	6.5	43.3	56.7
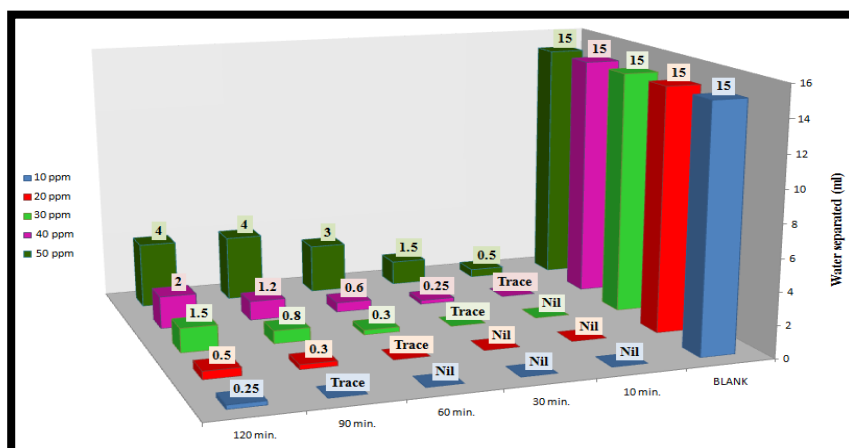
Figure 3: Effects of the Demulsifier 2BU-C$_{10}$ Dosage and Settling Time on Volume of Water which has been Separated at 25 °C
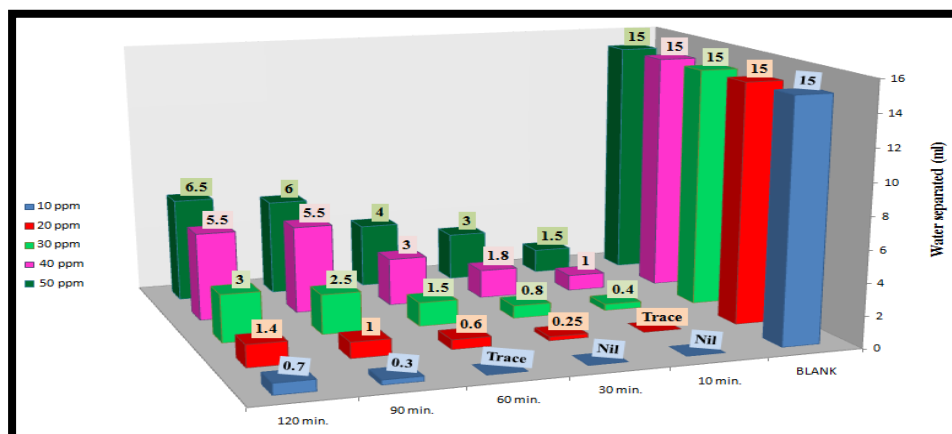
Figure 4: Effects of the Demulsifier 2BU-C$_{10}$ Dosage and Settling Time on Volume of Water which has been Separated at 50 °C

From the results obtained can be concluded that crude oils with higher densities and viscosities, and thus lower API gravities, usually contain lower levels of light cut hydrocarbon (gasoline-range hydrocarbons). Most sulfur in crude is actually in the heavy cut hydrocarbon which it has high asphaltene content, so that crude oil has high sulfur content due to has high asphaltene content. In other words, the sulfur content and the asphaltene content are inversely proportional to API value [39]. When using the demulsifier (2BU- C_{10}) that made from surfactant (C_{10}-2BU-C_{10}) to treatment W/O emulsions which are formed in crude oil, as shown in the Table (2) can be noted that at a temperature 25 °C the percentage of the best and the lowest separation efficiency (% E $_{Separation}$) were (26.7 %) in concentration 50 ppm where the volume of water separated was (4 ml), and (1.7 %) at concentration 10 ppm respectively. While at a temperature 50 °C the highest (% E $_{Separation}$) was (43.3 %) in concentration 50 ppm where the volume of water separated was (6.5 ml). and the lowest (% E $_{Separation}$) was at concentration 10 ppm (4.7 %), as shown in the Figures (3) and (4).

Also was treatment W/O emulsions that formed in crude oil by using the demulsifier (2BU-C_{12}) which contain surfactant (C_{12}-2BU-C_{12}), and from the Table (3) can be noted that at a temperature 25 °C the percentage of the best separation efficiency (% E $_{Separation}$) was (**36.7 %**) in concentration 50 ppm where the volume of water separated was (5.5 ml), and at a temperature 50 °C the (% E $_{Separation}$) was (**60.0 %**) in concentration 50 ppm where the volume of water separated was (9.0 ml). While at temperatures 25 °C and 50 °C the lowest (% E $_{Separation}$) were at concentration 10 ppm (**4.0 %**) and (**13.3 %**) respectively, as shown in the Figures (5) and (6) .

Table 3. Water Separated by Using Demulsifier (2BU-C_{12})

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.		
25 °C	10	Nil	Nil	Trace	0.3	0.6	4.0	96.0
	20	Nil	Trace	0.25	0.5	1.0	6.7	93.3
	30	Trace	0.3	0.8	1.2	2.5	16.7	83.3
	40	0.5	1.0	2.0	3.0	4.0	26.7	73.3
	50	0.8	2.5	4.0	5.0	5.5	36.7	63.3
50 °C	10	Nil	Trace	0.8	1.5	2.0	13.3	86.7
	20	0.25	0.8	2.0	3.0	4.5	30.0	70.0
	30	1.0	2.5	4.0	5.5	7.0	46.7	53.3
	40	1.5	3.0	5.0	6.5	8.5	56.7	43.3
	50	3.5	5.0	6.0	7.5	9.0	60.0	40.0
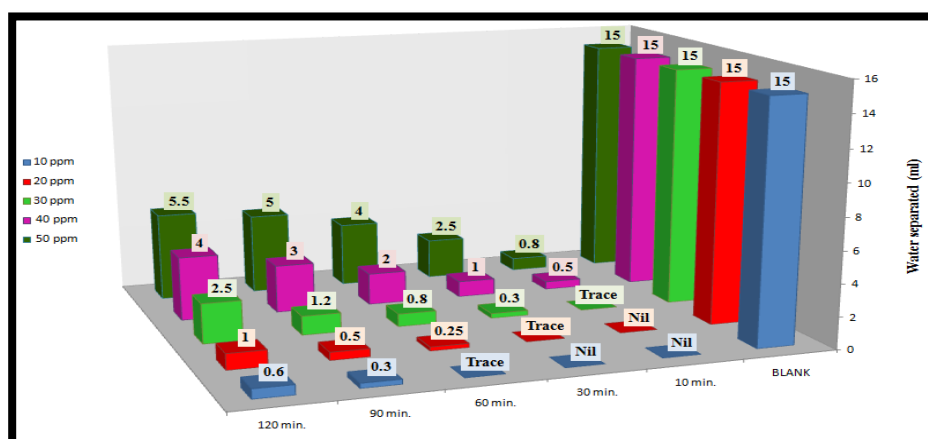
Figure 5: Effects of the Demulsifier 2BU-C_{12} Dosage and Settling Time on Volume of Water which has been Separated at 25 °C
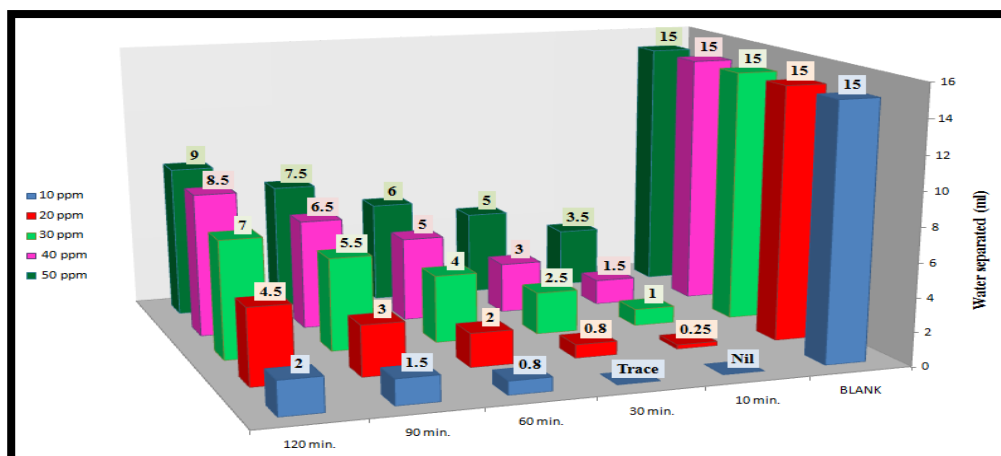
Figure 6: Effects of the Demulsifier 2BU-C$_{12}$ Dosage and Settling Time on Volume of Water which has been Separated at 50 °C

The results indicate, as shown in the Table (4.23) that the (% E $_{Separation}$) of demulsifier (2BU-C$_{12}$) at temperatures 25°C and 50 °C that there are little difference with the efficiency of the demulsifier (2BU-C$_{10}$) in both temperatures. But the demulsifier (2BU-C$_{12}$) has higher (% E $_{Separation}$) and lower (% Emulsion Stability) than (2BU-C$_{10}$), where the reason is the susceptibility of these substances to break the emulsion which was formed in crude oil and formation more stable emulsion, this is due to the nature of the compositional substance which prepared, and this substance consisting of long aliphatic chains [40] as (C$_{12}$H$_{25}$) in (2BU-C$_{12}$), and the cationic Gemini surfactant (C$_{12}$-2BU-C$_{12}$) that content the demulsifier(2BU-C$_{12}$) has CMC value (6.4 x 10^{-4}) M lower than (C$_{12}$-2BU-C$_{12}$) CMC value (4.8x10^{-3}) M. As noted at a temperature 50°C that the volume of water that has been separated more because the effect of temperature on the surface tension, which decreases with increasing temperature [41, 42]. In other words, increasing the efficiency of separation when increased concentration and temperature, as shown in the Table (4).

Therefore the separation efficiency of the demulsifiers prepared at temperatures of 25°C and 50°C will be in the following order:

(2BU – C12) > (2BU – C10)

Table 4: The Percentage of Separation Efficiency by Using Different Demulsifier to Treatment Wet Crude Oil

Temperature	Dosage ppm	% E $_{Separation}$ After 120 minutes	
		2BU-C$_{10}$	2BU-C$_{12}$
25 C°	**10**	1.7	4.0
	20	3.3	6.7
	30	10.0	16.7
	40	13.3	26.7
	50	26.7	36.7
50 C°	**10**	4.7	13.3
	20	9.3	30.0
	30	20.0	46.7
	40	36.7	56.7
	50	43.3	60.0

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 of 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 (120min).

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