

Research article

Novel Cationic Gemini surfactants: Preparation, characterization and Breaking of Water-in-Crude Oil Emulsions

Najlaa Z. Al – Ameri ^{1,2}, Mohanad J. Al- Asadi ¹

Collage of Education for pure sciences¹, University of BASRA, IRAQ.

South oil company², Ministry of oil, BASRA – IRAQ.

E-mail: alameri124@yahoo.com



This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

ABSTRACT:

A novel class of cationic Gemini surfactants $C_{14} - 2A - C_{14}$ and $C_{10} - 2B - C_{10}$ (where C_{14} and C_{10} represents the alkyl chain length of 10 and 14) synthesized and characterized by FT – IR , H^1 NMR, C^{13} NMR and mass spectra. Gemini surfactants aggregation behavior (determine critical micelles concentration CMC) were investigated by mean of electrical conductivity and obtained the surface tension at CMC point. It was found that $C_{14} - 2A - C_{14}$ and $C_{10} - 2B - C_{10}$ have superior surface activity. Cationic Gemini surfactants were used to treat the water in oil emulsions and study the effect of heat and setting time on the separation efficiency of water from crude oil. **Copyright © IJACSR, all rights reserved.**

Keywords: Cationic Gemini surfactants, electrical conductivity, critical micelle concentration, degree of micelle ionization, Water in oil emulsion.

1. Introduction:

In recent years, there is an increasing interest in novel forms of surfactants, particularly in Gemini surfactants, which consist of two conventional surfactants joined by a spacer at the head group, as they exhibit significant surface activity properties that cannot be achieved by conventional surfactants [1, 2, 3]. These

surfactants are superior to the corresponding conventional surfactants in a number of aspects such as a lower critical micelle concentration (CMC), a higher efficiency in reducing the oil/water interfacial tension, unusual aggregation morphologies, and better wetting, solubilizing, foaming, and antibacterial activities [4, 5]. These improved properties may make them very useful in many applications, such as soil remediation, enhanced oil recovery, drug entrapment and release, and the construction of high-porosity materials [6, 7]. There are two major roles of surfactants in technological applications. One is their ability of reducing surface tension, another is the spontaneous formation of aggregates to generate a wide variety of microstructures in aqueous solutions, which have been extensively explored is drug delivery [8, 9, 10]. The presence of two charged sites in a Gemini proposes stronger interaction with the neutral and oppositely charged ionic surfactants than that of the conventional surfactant combinations. However, only limited number of attempts has been made regarding mixed micellization of the Gemini and single chain surfactants [11, 12].

In these investigations, Gemini cationic surfactants were widely used in modification of montmorillonite surface. These ionic liquid-type Gemini surfactants unexceptionally are based on imidazolium unit, the typical ionic liquid core. We have found that novel quaternary ammonium Gemini surfactants with hydroxyl groups but without imidazolium also turn out to be ionic liquids [6, 9, 13]. Cationic surfactants of the type alkyltrimethylammonium bromide were used to determine the effect on water and oil separation of produced emulsions resulting from surfactant [14] and the use of surfactants in the mining industry have already been mentioned. It is in the area of crude oil recovery, however, that surfactants possibly stand to make their greatest impact in terms of natural resource exploitation[15,16,17]. As the primary extraction of crude oil continues at its hectic pace, the boom days of easy access and extraction have begun to come to an end and engineers now talk of secondary and tertiary oil recovery technology[18, 19]. As the crude oil becomes less accessible, more problems arises with regard to viscosity, pressures, temperatures, physical entrapment, and the like. While primary crude recovery presents its technological challenges, secondary and tertiary recovery processes can make them seem almost trivial [7, 19]. Herein we report the synthesis and the efficiency of breaking the emulsions of water in oil (W/O) of these Gemini surfactants.

2. Experimental

2.1. Materials and instruments

The following materials purchased from Sigma – Aldrich company: Propylene 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 tetra decane (98 % purity), Benzen (99 % purity), 1-bromo decane (98 % purity), absolute isopropyl alcohol (99.7 % purity), P – Phenylenediamine (99.5 % purity), Triethyl amine (99.5 % purity), Hydrochloric acid (37 %), silica gel high-purity grade 40 (35-70 mesh). Twice distilled water was used in the preparation of all solutions.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM 500 spectrometer. CDCl₃ was used as solvent and chemical shifts recorded were internally referenced to TMS (0 ppm). IR spectra were obtained 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 silica gel uniplates, and Surface tension of the surfactant solution was measured with a premium tensiometer– K100 (KRÜSS GmbH, Germany). The CMC values of the surfactant solution were determined from Electrical conductivity with a WTW Inolab cond 740 conductivity meter (Germany).

2.2. Synthesis of Cationic Gemini surfactants

2.2.1. Synthesis of Gemini surfactants (C₁₄-2A-C₁₄)

There are three steps to get the target compound. The first synthesis of compound (A) /3,3'-(propane-1,3-diylbis(oxy)) bis(1-chloropropan-2-ol).

To a mixture consisting of Propylene glycol (22.8 g, 0.3 mol), Sodium hydrogen sulfate NaHSO₄ (1 g, 8 mmol), water (0.6 mL), added Epichlorohydrin (55.5 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 (A) as transparent oil (yield 83.6 %) [20, 21].

IR (KBr): 3405, 2998, 2875, 1454.9, 1332, 715 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ Ppm = (1.64 – 1.9) OCH₂CH₂CH₂O (m, 2H, CH₂), (3.36 – 3.48) OCH₂CH₂CH₂O (t, 4H, CH₂), (3.55 – 3.67) CH₂O(CH₂)₃CH₂ (d, 4H, CH₂), (3.86 – 4.02) O(CH₂)₃OCH₂CHOH (m, 2H, CH), (4.22) O(CH₂)₃OCH₂CHOH (s, 2H, OH), (3.68 – 3.76) OCH₂CHOHCH₂Cl (d, 4H, CH₂). ¹³C NMR (500 MHz, CDCl₃): δ Ppm = 62.8 (OCH₂CH₂CH₂O), 83.4 (OCH₂CH₂CH₂O), 85.62 (CH₂O(CH₂)₃CH₂), 88.31 (O(CH₂)₃OCH₂CHOH), 47.56 (OCH₂CHOHCH₂Cl). MS (EI, 70 eV) m/z (%): 261 [M]⁺ (4%); 166 [C₆H₁₁ClO₃]⁺ (50.4%); 137 [C₅H₁₀ClO₂]⁺ (76.2%); 93[C₃H₆ClO]⁺ (30.6%); 59[C₃H₇O]⁺ (100%); 43 [C₂H₃O]⁺ (18.5%); 108[C₄H₉OCl]⁺ (28 %).

The second step synthesis of compound (2A) / 2,14-dimethyl-6,10-dioxa-2,14-diazapentadecane-4,12-diol.

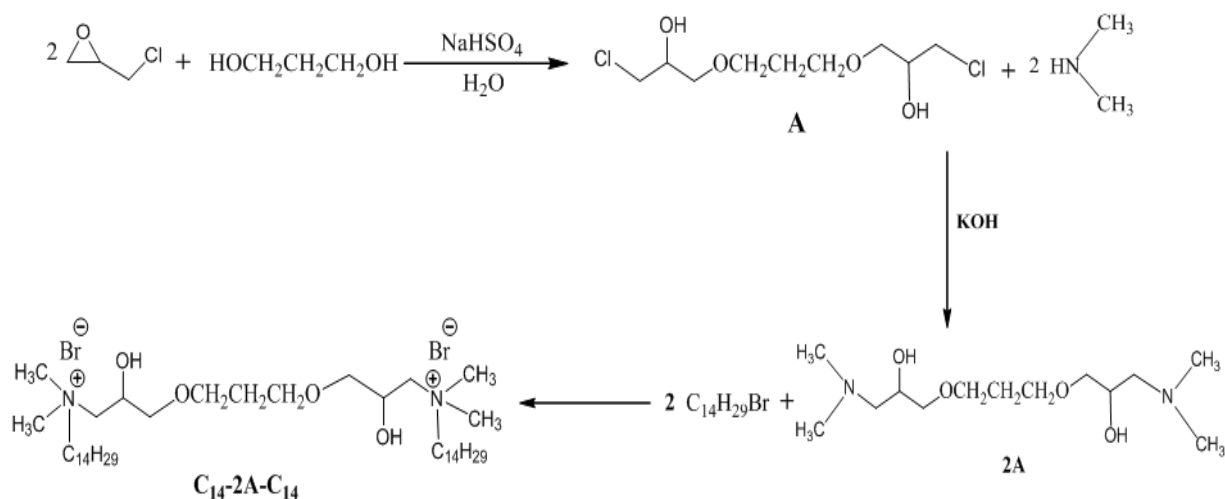
To a flask containing (0.67 g, 12 mmol) Potassium hydroxide was added 33% aqueous dimethyl amine (0.9 g, 0.02 mol), then added compound A (2.8 g, 0.01 mol) as drop wise with a magnetic stirrer at room temperature to produce precipitate. The mixture was filtered then the filtrate was extracted with chloroform 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 (2A) as yellow oil (yield 70.14%).

IR (KBr): 3430, 2958.20, 2865.23, 1450.5, 1340, 1205, 1103.9 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ Ppm = (1.70 – 1.83) OCH₂CH₂CH₂O (m, 2H, CH₂), (3.22 – 3.36) OCH₂CH₂CH₂O (t, 4H, CH₂), (3.48 – 3.51) CH₂O(CH₂)₃CH₂ (d, 4H, CH₂), (3.76 – 3.95) O(CH₂)₃OCH₂CHOH (m, 2H, CH), (4.12) O(CH₂)₃OCH₂CHOH (s, 2H, OH), (3.55 – 3.68) OCH₂CHOHCH₂N (d, 4H, CH₂), (2.73) CH₂N(CH₃)₂ (s, 12H, CH₃). ¹³C NMR (500 MHz, CDCl₃): δ Ppm = 62.1 (OCH₂CH₂CH₂O), 84.5 (OCH₂CH₂CH₂O), 87.29 (CH₂O(CH₂)₃CH₂), 89.71 (O(CH₂)₃OCH₂CHOH), 63.2 (OCH₂CHOHCH₂N), 54.87 (CH₂N(CH₃)₂). MS (EI, 70 eV) m/z (%): 278[M]⁺ (31 %); 176 [C₈H₁₈NO₃]⁺ (12.1%); 86 [C₅H₁₂N]⁺ (21.8%); 44[C₂H₄O]⁺ (54.9%); 58 [C₃H₈N]⁺ (100%); 60[C₃H₈O]⁺ (75.8%); 118[C₅H₁₀O₃]⁺ (48.3%).

The last step synthesis of N,N'-((propane-1,3-diylbis(oxy))bis(2-hydroxypropane-3,1-diyl)) bis (N,N-dimethyltetradecan -1- aminium) dibromide

To a flask containing 1-bromo tetra decane (2.00 g, 7.19 mmol) and absolute isopropyl alcohol (50 mL) was added compound (2A) (1.0 g, 3.6 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 (C₁₄-2A-C₁₄) as yellow oil (yield 76.9 %). The structure and synthetic route of this surfactant is shown in Scheme 1.

IR (KBr): 3450.69, 2967.33, 2875.23, 1454.33, 1350.13, 1253.73, 1107.23 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ Ppm = (1.9 – 2.17) OCH₂CH₂CH₂O (m, 2H, CH₂); (4.2– 4.3) OCH₂CH₂CH₂O (t, 4H, CH₂); (4.02 – 4.15) CH₂O(CH₂)₃OCH₂ (d, 4H, CH₂); (4.4 – 4.62) O(CH₂)₃OCH₂CHOH (m, 2H, CH); (3.9) O(CH₂)₃OCH₂CHOH (s, 2H, OH); (3.2 – 3.29) OCH₂CHOHCH₂N (d, 4H, CH₂); (3.09) CH₂N(CH₃)₂ (s, 12H, CH₃); (3.3 – 3.49) N(CH₃)₂CH₂ (C₁₃H₂₇) (t, 4H, CH₂); (1.59 – 1.81) N(CH₃)₂CH₂CH₂ (C₁₂H₂₅) (m, 4H, CH₂); (1.18 – 1.49) CH₂CH₂(CH₂)₁₀CH₂CH₃ (m, 40H, CH₂); (0.82 – 1.03) CH₂(CH₂)₁₀CH₂CH₃ (m, 4H, CH₂); (0.5 – 0.74) CH₂(CH₂)₁₀CH₂CH₃ (t, 6H, CH₃). ¹³C NMR (500 MHz, CDCl₃): δ Ppm = (60.29) OCH₂CH₂CH₂O; (87.14) OCH₂CH₂CH₂O; (88.39) CH₂O(CH₂)₃OCH₂; (91.83) O(CH₂)₃OCH₂CHOH; (63.37) OCH₂CHOHCH₂N; (51.60) CH₂N(CH₃)₂; 52.16 N(CH₃)₂CH₂ (C₁₃H₂₇); (50.57) CH₂(CH₂)₁₁CH₂CH₃; (35.81) CH₂(CH₂)₁₁CH₂CH₃; (14.12) CH₂(CH₂)₁₁CH₂CH₃. MS (EI, 70 eV) m/z (%): 831.8 [M]⁺(22.1 %); 172 [C₉H₁₆O₃]⁺ (58.7 %); 306 [C₁₅H₃₄O₄N₂]⁺ (60.94%); 190[C₉H₁₈O₄]⁺(38.4%); 58 [C₃H₈N]⁺(100%); 28[C₂H₄]⁺(62.2%); 18[H₂O]⁺(55.6%).



Scheme 1. Synthetic route to Gemini surfactant C₁₄-2A-C₁₄

2.2.2. Synthesis of Gemini surfactants Synthesis of compound (C₁₀-2B-C₁₀)

There are three steps to get the target compound . The first step Synthesis of compound (B) / 3,3'-(1,4-phenylenebis(azanediy))bis(1-chloropropan-2-ol).

The mixture of P – Phenylenediamine (32.4 g, 0.3 mol) , Triethyl amine (1.01 g, 0.01 mol), Potassium hydroxide (33.6 g, 0.6 mol) and 25 ml water was stirred vigorously then added Epichlorohydrin (55.5 g, 0.6 mol) as drop wise with stirring for 20 hours at 25–30 °C to produce precipitate after that the mixture was filtered then added dilute hydrochloric acid (25 ml, 0.024 M) as drop wise on it. The mixture was performed in refluxing and stirring for 3 hours. The reaction mixture was extracted with Ethyl acetate. The organic layer was dried (MgSO_4) and filtered. Ethyl acetate and excess of Epichlorohydrin were removed under vacuum and the residue was purified by column chromatography on silica gel (ethyl acetate / benzene, 1: 2, v/v) to give the target compound (B) as Browne oil (yield 71%)[20, 22].

IR (KBr): 3452.22, 3310.54, 3011.14, 2993.04, 2820.6, 1610.28, 1530.05, 1448.74 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ Ppm = (6.00 – 6.21) CH aromatic (m, 4H, CH), (4.9) Ph-NH- CH_2 (s, 2H, NH), (2.83 – 2.91) NHCH₂CHOH (d, 4H, CH_2) , (4.32 – 4.61) NHCH₂CHOH (m, 2H, CH), (4.2) NHCH₂CHOH (s, 2H, OH), (3.28 – 3.34) NCH₂CHOHCH₂Cl (d, 4H, CH_2). ^{13}C NMR (500 MHz, CDCl_3): δ Ppm = 119.62 (CH aromatic), 134.72 (ph- N), 64.41 (NHCH₂CHOH), 82.13 (NHCH₂CHOH), 58.68 (NCH₂CHOHCH₂Cl) . MS (EI, 70 eV) m/z (%): 293 $[\text{M}]^+$ (10.56 %); 93 $[\text{C}_3\text{H}_6\text{ClO}]^+$ (70.3 %); 84 $[\text{C}_5\text{H}_{10}\text{N}]^+$ (24.8 %); 66 $[\text{C}_5\text{H}_6]^+$ (100%); 50 $[\text{CH}_3\text{Cl}]^+$ (15.1 %); 28 $[\text{C}_2\text{H}_4]^+$ (63.4 %).

The second step Synthesis of compound (2B) / 3,3'-(1,4-phenylenebis(azanediy))bis(1-(dimethylamino)propan-2-ol).

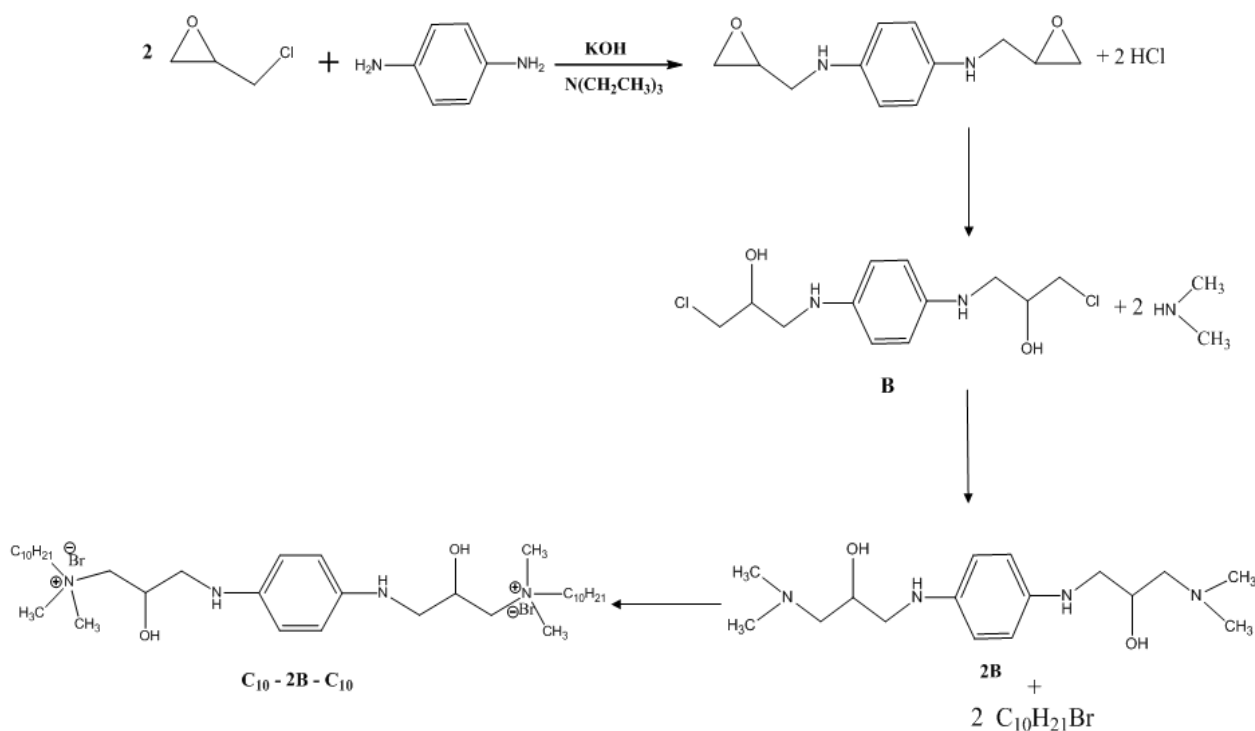
To a flask containing (0.67 g, 12 mmol) Potassium hydroxide was added 33% aqueous dimethyl amine (0.9 g, 0.02 mol) , then added compound B (2.93 g, 0.01 mol) as drop wise with stirred at room temperature to produce precipitate. The mixture was filtered then the filtrate was extracted with chloroform and dried over anhydrous magnesium sulfate. After evaporation to remove solvent and the residue was purified by column chromatography on silica gel (ethyl acetate / benzene, 1: 2, v/v) to give the target compound (2B) as Browne oil (yield 49.29%).

IR (KBr): 3453.22, 3324.12, 3009.4, 2994.71, 2825.82, 1604.59, 1535.1, 1440 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ Ppm = (6.11 – 6.33) CH aromatic (m, 4H, CH), (4.84) Ph-NH- CH_2 (s, 2H, NH), (2.7 – 2.81) NHCH₂CHOH (d, 4H, CH_2) , (4.1 – 4.52) NHCH₂CHOH (m, 2H, CH), (4.03) NHCH₂CHOH (s, 2H, OH), (2.94 – 3.06) NCH₂CHOHCH₂N (d, 4H, CH_2); (2.88) $\text{CH}_2\text{N}(\text{CH}_3)_2$ (s, 12H, CH_3) . ^{13}C NMR (500 MHz, CDCl_3): δ Ppm = 114.88 (CH aromatic), 135.34 (ph- N), 65.12 (NHCH₂CHOH), 82.25 (NHCH₂CHOH), 63.47 (NCH₂CHOHCH₂N); 51.85 ($\text{CH}_2\text{N}(\text{CH}_3)_2$) . MS (EI, 70 eV) m/z (%): 310 $[\text{M}]^+$ (22. 6 %); 90 $[\text{C}_4\text{H}_{12}\text{NO}]^+$ (29.1 %); 106 $[\text{C}_6\text{H}_6\text{N}_2]^+$ (13.9 %); 66 $[\text{C}_5\text{H}_6]^+$ (100%); 58 $[\text{C}_3\text{H}_8\text{N}]^+$ (82.4 %); 28 $[\text{C}_2\text{H}_4]^+$ (66.7 %).

The last step synthesis of N,N'-((1,4-phenylenebis(azanediy))bis(2-hydroxypropane-3,1-diyl)) bis (N,N-dimethyldecan-1-aminium) dibromide.

To a flask containing 1-bromo decane (4.42 g, 0.02 mol) and absolute isopropyl alcohol (50 mL) was added compound 2B (3.1 g, 0.01 mol) 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 (ethyl acetate / benzene, 1:3, v/v) to give the target compound (C_{10} -2B- C_{10}) as Browne oil (yield 70.8 %). The structure and synthetic route of this surfactant is shown in Scheme 2.

IR (KBr): 3458.69, 3300.41, 3010.54, 2905.93, 2889.23, 1600.92, 1541.73, 1410.23, 1360.75, 1275.33, 1215.10 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ Ppm = (6.2 – 6.42) CH aromatic (m, 4H, CH), (5.5) Ph-**NH**-CH₂ (s, 2H, NH), (3.31 – 3.4) NH**CH₂**CHOH (d, 4H, CH₂), (4.6 – 4.9) NHCH₂**CHOH** (m, 2H, CH), (4.33) NHCH₂**CHOH** (s, 2H, OH), (3.16 – 3.27) NCH₂CHOH**CH₂**N (d, 4H, CH₂); (2.98) CH₂N(**CH₃**)₂ (s, 12H, CH₃); (2.6 – 2.8) N(CH₃)₂**CH₂** (C₉H₁₉) (t, 4H, CH₂); (2.12 – 2.25) N(CH₃)₂CH₂**CH₂**(C₈H₁₇) (m, 4H, CH₂); (1.88 – 2.03) CH₂CH₂(**CH₂**)₆CH₂CH₃ (m, 24H, CH₂); (1.45 – 1.71) CH₂(CH₂)₆**CH₂**CH₃ (m, 4H, CH₂); (1.02 – 1.2) CH₂(CH₂)₆CH₂**CH₃** (t, 6H, CH₃) .. ^{13}C NMR (500 MHz, CDCl_3): δ Ppm = 113.14 (CH aromatic), 131.95 (ph-N), 62.95 (NH**CH₂**CHOH), 86.14 (NHCH₂**CHOH**), 60.81 (NCH₂CHOH**CH₂**N); 52.03 (CH₂N (**CH₃**)₂); 60.12 (N(CH₃)₂**CH₂** (C₉H₁₉)); 40.51 (CH₂CH₂(**CH₂**)₇CH₂CH₃); 34.02 (CH₂(CH₂)₇**CH₂**CH₃); 14.96 (CH₂(CH₂)₇CH₂**CH₃**). MS (EI, 70 eV) m/z (%): 751.8 [M]⁺ (25 %); 592 [C₃₆H₇₂N₄O₂]⁺ (76.7 %); 338 [C₁₈H₃₄N₄O₂]⁺ (14.4 %); 66 [C₅H₆]⁺ (100%); 58 [C₃H₈N]⁺ (87.2 %); 102[C₅H₁₂NO]⁺ (34.4 %); 84[C₅H₁₀N]⁺ (47.1 %).



3. Results and Discussion

3.1. Measurement of CMC Values of Surfactant Solutions

This method can only be applied to measure the CMC of ionic surfactants. The change in the electrical conductance of aqueous ionic surfactant solutions due to Cationic ions and Anionic ions. The electrical conductivity is usually influenced by solvent and temperature [23, 24]. The conductivity measurements were carried out in a jacketed beaker thermo stated at 25 °C by circulating water and preparation a series of aqueous solutions of cationic Gemini surfactants.

The values of critical micelle concentration were calculated as the intersection of linear parts in the dependence conductivity versus surfactant concentration.

The critical micelle concentration (CMC) of a surfactant is an important physical parameter [25]. Through the results observed when increasing aliphatic tail length reduces the CMC value for surfactants, 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. The ionic quaternary compounds $C_{14}\text{-2A-C}_{14}$ and $C_{10}\text{-2B-C}_{10}$ tested show the CMC values at $(1.7 \times 10^{-4} \text{ M})$ (Fig. 1) and $(4.2 \times 10^{-3} \text{ M})$ (Fig. 2) respectively. When comparing the two values, CMC decrease with tail carbon length regardless of the type of Spacer.

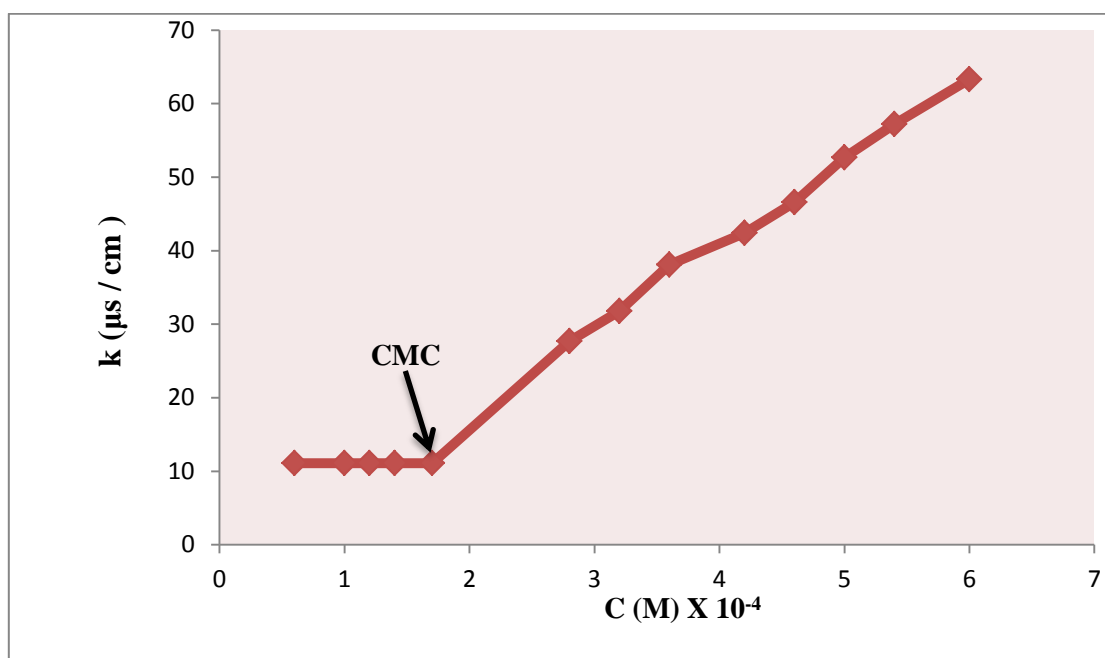


Figure 1. CMC of cationic dimeric surfactants $C_{14}\text{-2A-C}_{14}$

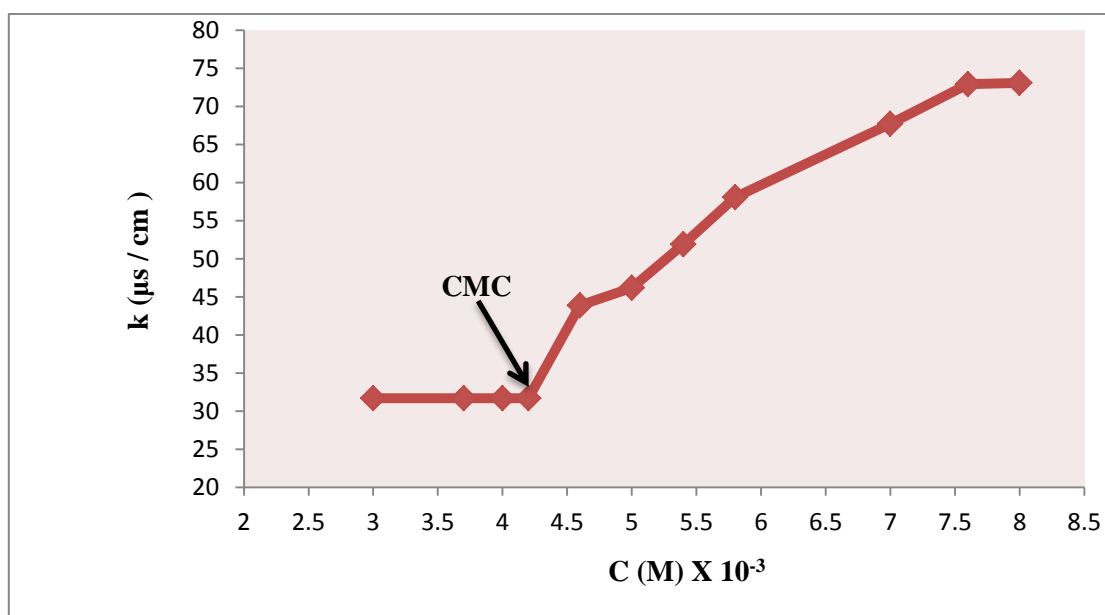


Figure 2. CMC of cationic dimeric surfactants $C_{10}\text{-2B-C}_{10}$

Bis – quaternary ammonium salts from epichlorohydrin exhibit large intermolecular hydrophobic interaction that make it easy for them to form aggregates in water. Compounds C₁₀-2B-C₁₀ and C₁₄-2A-C₁₄ show maximum ability to lower surface tension at the cmc point γ_{cmc} . Their γ_{cmc} values increased slightly with increased alkyl chain length (36.2, 39.4) mN m⁻¹ respectively.

3.2. Emulsion Preparation and Bottle Tests:

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 [26, 27, 28].

The industrial emulsion was prepared by mixing Constant volume from synthetic - produced brine 15% (concentration 200,000 ppm) with 85 % crude oil (Table 1.) to become the overall percentage 100 % , which mixed by using an electric mixer can control the speed of rotation and a specific time period. Emulsion was Distributed in glass tubes (capacity tube 100 cm³) 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) after the end of two hours takes a liquid from the bottoms of the bottles using a syringe, which represents the oil to obtain the amount of water remaining in it by (Dean & Stark).

To study the effectiveness of Surfactants in the treatment of W/O emulsions by using crude oil have 2.1 % Asphaltenes content and 25.4 API gravity (Table 1.). Also study the phase behavior to determine the percentage of water separated and observation the effect of temperatures on the volume of water separated.

The results of this study indicated that Demulsifier C₁₄-2A-C₁₄ was found to be effective in reducing the water content to 86.7 % in 50 ppm at room temperature (25 C°) and the separation efficiency of water at 50 C° was 93.3% in 40 and 50 ppm (Table 2.), (Fig 3. a, b.) show the effects of the C₁₄-2A-C₁₄ dosage and settling time. While the separation efficiency of water to Demulsifier C₁₀-2B-C₁₀ at room temperature (25 C°) was 46.7 % and at 50 C° separated water was 9 ml this means the efficiency of water separation was 60 % (Table 3.) also (Fig 4. a, b.) show the effects of the C₁₀-2B-C₁₀ dosage and settling time.

Table 1:Physicochemical properties of the used crude oils

No	CHARACTERSTICS	Method	CRUDE OIL
1.	SPECIFID GRAVITY @ 60 °F	IP160	0.9017
2.	API GRAVITY	IP160	25.4
3.	SULPHUR CONTENT, wt. %	ASTM D-4294	4.09
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	Nil
7.	ASPHALTENES, % wt.	IP-143	2.1

8.	WAX CONTENT , wt. %	UOP-64	3.5
9.	POUR POINT , °C	ASTM D-97 , IP-15	- 21
10.	KINEMATIC VISCOSITY , cSt.	ASTM D-445 , IP-71	38.0
	1.@ 70 °F (21.1 °C)		
	2.@ 100 °F (37.8 °C)		
	3.@ 120 °F (48.9 °C)		
	4.@ 140 °F (60.0 °C)		19.10
			13.21
			9.742

Table 2: The volume of water separated when used C₁₄ - 2A - C₁₄ with crude oil

Temperature	Dosage PPM	water separated (ml)					water remaining (ml)	The percentage of separation %
		After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.		
R.T. (25 C°) CRUDE 1	10	Trace	1.0	3.0	5.0	7.0	8.0	46.6
	20	0.8	1.5	4.5	7.0	9.5	5.5	63.3
	30	1.2	2.5	6.0	9.0	11.0	4.0	73.3
	40	3.0	5.0	8.0	11.0	12.0	3.0	80
	50	6.0	8.5	11.0	12.0	13.0	2.0	86.7
50 C° CRUDE 1	10	0.25	3.0	5.0	8.5	10.0	5.0	66.7
	20	2.0	4.0	7.0	10.0	12.0	3.0	80
	30	3.0	6.0	9.0	11.0	13.0	2.0	86.7
	40	5.0	8.0	10.0	12.0	14.0	1.0	93.3
	50	7.0	11.0	13.0	14.0	14.0	1.0	93.3

Table 3: The volume of water separated when used C₁₀ - 2B - C₁₀ with crude oil

Temperature	Dosage PPM	water separated (ml)					water remaining (ml)	The percentage of separation %
		After 10 min.	After 30 min.	After 60 min.	After 90 min.	After 120 min.		
R.T. (25 C°) CRUDE 1	10	Nil	Nil	Trace	0.3	0.6	14.4	4.0
	20	Nil	Trace	0.5	0.8	1.0	14.0	6.7
	30	Trace	0.5	1.0	1.5	2.5	12.5	16.7
	40	0.3	1.4	2.5	3.5	5.0	10.0	33.3
	50	1.0	2.0	3.5	5.0	7.0	8.0	46.7
50 C° CRUDE 1	10	Nil	Trace	0.25	0.8	1.2	13.8	8.0
	20	0.4	1.0	1.5	2.5	3.0	12.0	20.0
	30	1.0	2.0	4.0	5.0	6.0	9.0	40.0
	40	2.5	4.0	5.5	7.0	8.0	7.0	53.3
	50	4.5	7.0	8.0	8.0	9.0	6.0	60.0

From values of CMC and study the efficiency of separation was observed the surfactant C_{14} -2A- C_{14} has a higher efficiency of separation from C_{10} -2B- C_{10} , the reason is that the surfactant C_{14} -2A- C_{14} has lower CMC and higher surface tension than C_{10} -2B- C_{10} .

Temperature plays an active role in increasing the efficiency of separation and increasing the speed of separation. When comparing the volumes of water separated between room temperature and at 50 C° can be observed that the volume of water at high temperature will be larger at lower concentration to the same surfactant than at room temperature (Fig 3. a, b.) and (Fig 4. a, b.). This is due to the low viscosity of crude oil at higher temperatures (Table 1.), which facilitates the movement of water droplets in crude oil and this movement is irregular, which increases the chance of a collision with some drops and leads to break the emulsion film.

As for the effect of setting time on the separation water, where the more setting time will be increase in the volume of water separated, but when there are two factors of temperature and concentration the result will be the separation is better and less setting time. (Fig 3. a, b.) and (Fig 4. a, b.).

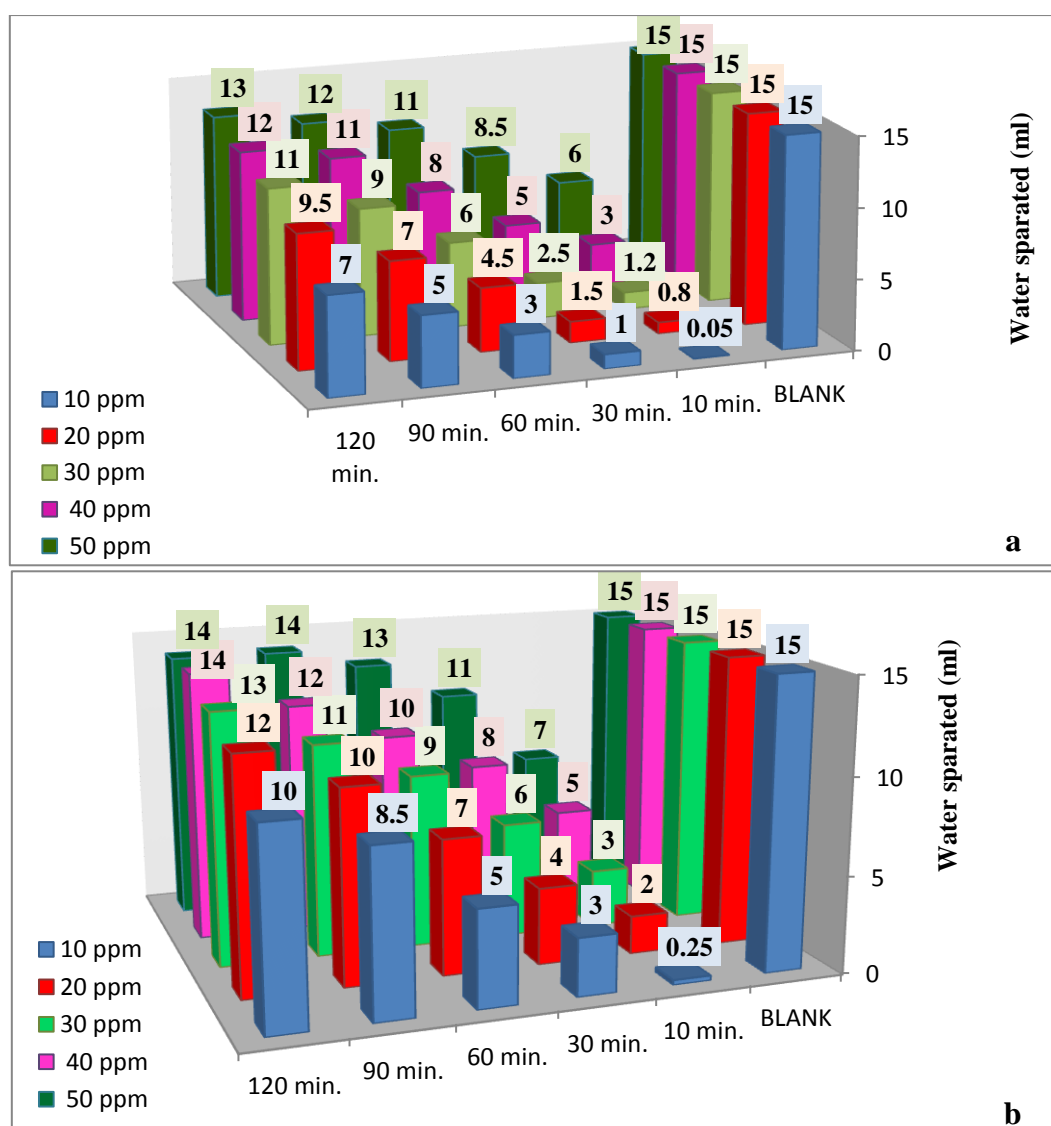


Figure 3. Effects of the C_{14} -2A- C_{14} dosage and settling time for emulsions with 15% water cut: a. at room temperature, b. at 50° C

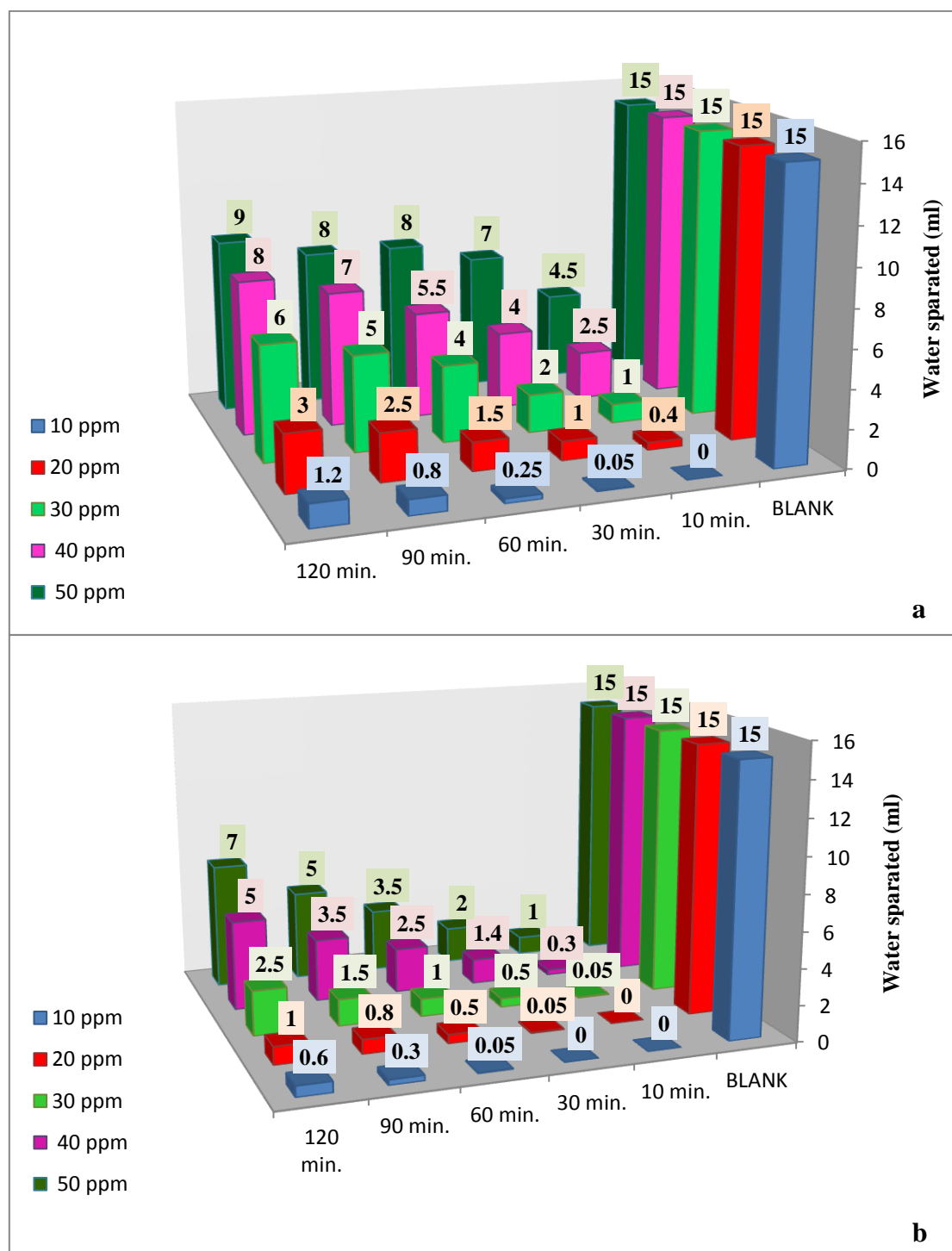


Figure 4. Effects of the C₁₀-2B-C₁₀ dosage and settling time for emulsions with 15% water cut at room temperature: a. at room temperature, b. at 50° C

References

- [1] Limei Zhou, Hua Chen, Xiaohui Jiang, Fang Lu, Yafen Zhou, Wenmin Yin, Xiaoyang Ji, Modification of montmorillonite surfaces using a novel class of cationic gemini surfactants, *J. Journal of Colloid and Interface Science* 332 (2009) 16–21.

[2] Hongqi Li, Chaochao Yu, Rui Chen, Juan Li, Jinxing Li , Novel ionic liquid-type Gemini surfactants: Synthesis, surface property and antimicrobial activity, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 395 (2012) 116– 124.

[3] Dipti Shukla , V.K. Tyagi, Cationic Gemini surfactants : A review , *J. Oleo Sci.*, Vol. 55, No.8, (2006) 381-390.

[4] G. Roshan Deen, L.H. Gan, Y.Y. Gan , A new cationic surfactant N,N'-dimethyl-N-acryloyloxyundecyl piperazinium bromide and its PH-sensitive gels by microemulsion polymerization, *J. Polymer* 45 (2004) 5483–5490.

[5] Drew Myers, *Surfactant science and technology* , Third edition ,2006.

[6] Fang Yang ,Gang Li , Nian Xu • Rong Liu ,Song-Mei Zhang , Zeng-Jiang Wu, Synthesis and Critical Micelle Concentration of a Series of Gemini Alkylphenol Polyoxyethylene Nonionic Surfactants , *J. Surfact Deterg* (2011) 14:339–345.

[7] Laurier L. Schramm , *Surfactants : Fundamentals and Applications in the petroleum industry* , first published 2000.

[8] Bo Cai, Xuefeng Li, Yi Yang, Jinfeng Dong, Surface properties of Gemini surfactants with pyrrolidinium head groups, *J. Colloid and Interface Science* 370 (2012) 111–116.

[9] Jia Wei, Guohe Huang, Hui Yu, Chunjiang An, Efficiency of single and mixed Gemini/conventional micelles on solubilization of phenanthrene, *J. Chemical Engineering Journal* 168 (2011) 201–207.

[10] Richard J. Farn, *Chemistry and Technology of Surfactants*, published 2006.

[11] Mohmad Shafi Sheikh, Kabir-ud-Din, Aijaz Ahmad Dar, Synergistic interaction of Gemini surfactant pentanediyl-1,5-bis(dimethylcetylammmonium bromide) with conventional (ionic and nonionic) surfactants and its impact on the solubilization ,*J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 378 (2011) 60–66.

[12] Qi Zhang, Zhinong Gao, Feng Xu, Shuxin Tai, Effect of hydrocarbon structure of the headgroup on the thermodynamic properties of micellization of cationic gemini surfactants: An electrical conductivity study, *J. Colloid and Interface Science* 371 (2012) 73–81.

[13] Qi Zhang, Zhinong Gao, Feng Xu, Xia Zou , Adsorption and corrosion inhibitive properties of gemini surfactants in the series of hexanediyl-1,6-bis-(diethyl alkyl ammonium bromide) on aluminium in hydrochloric acid solution, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 380 (2011) 191–200.

[14] De-Yu Zhu, Fa Cheng, Yu Chen, Shi-Chun Jiang, Preparation, characterization and properties of anionic gemini surfactants with long rigid or semi-rigid spacers, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 397 (2012) 1– 7.

[15] Juan Carlos Pereira, Jose Delgado Linares, Cesar Scorzza, Miguel Rond_on, Sandra Rodríguez, and Jean-Louis Salager, Breaking of Water-in-Crude Oil Emulsions. 4. Estimation of the Demulsifier Surfactant Performance To Destabilize the Asphaltenes Effect, *J. Energy & Fuels* ,December 5, 2010.

[16] Alexandre Goldszal and Maurice Bourrel, Demulsification of Crude Oil Emulsions: Correlation to Microemulsion Phase Behavior, *J. Ind. Eng. Chem. Res.* 2000, 39, 2746-2751.

[17] George J. Hirasaki, Clarence A. Miller, Olina G. Raney, Michael K. Poindexter, Duy T. Nguyen, and John Hera, Separation of Produced Emulsions from Surfactant Enhanced Oil Recovery Processes, *J. Energy Fuels*, DOI:10.1021/ef101087u, October 20, 2010.

[18] Inge Harald Auflem, Influence of Asphaltene Aggregation and pressure on crude oil emulsion stability, Thesis submitted in partial fulfillment of the requirements for the degree of Doktor, Norwegian university of science and technology, June 2002.

[19] A.M. Al-Sabagh, Nehal S. Ahmed, Amal M. Nassar, M.M. Gabr, Synthesis and evaluation of some polymeric surfactants for treating crude oil emulsions Part I: treatment of sandy soil polluted with crude oil by monomeric and polymeric surfactants, *J. Colloids and Surfaces A: Physicochem. Eng. Aspects* 216 (2003) 9 /19.

[20] D. L. Rahmankulof, B. K. Kemcanof, N. A. Lokmeonof, U. K. Dmumreef, R. R. Chaneshef, Epichlorohydrin, synthesis procedure, physical and chemical properties, production technology, Moscow chemistry 2003.

[21] G. A. Akmedova, New Oligomer surfactants from ethylene glycol and epichlorohydrin, *J. Applied chemistry* .2008.T.81.

[22] Rimgaile Degutyte, Jolanta Stumbraite and Vytautas Getautis, Synthesis of a bifunctional ,2,3,4-tetrahydroquinoline derivative:4,4'-(1,4-phenylene) di(1,2,3,4-tetrahydrobenzo[f]quinolin-2-ol), *J. ARKIVOC* 2009 (vii) 26-32.

[23] Ana Dominguez, Aurora Fernandez, Noemi Gonzalez, Emilia Iglesias and Luis Montenegro, Determination of Critical Micelle Concentration of Some Surfactants by Three Techniques, *J. Chemical Education*, Vol. 74 No. 10 October 1997.

[24] Ana Kroflic, Bojan Sarac and Marija Bester-Rogac, What Affects the Degree of Micelle Ionization: Conductivity Study of Alkyltrimethylammonium Chlorides, *J. Acta Chim. Slov.* 2012, 59, 564–570.

[25] Richard J. Farn, *Chemistry and Technology of Surfactants*, 2006.

[26] C. Ijogbemeye Oseghale, Akpabio E. and Udotong, Breaking of Oil -Water Emulsion for the Improvement of Oil Recovery Operations in the Niger Delta Oilfields. *J. Engineering and Technology* Volume 2 No. 11, November, 2012.

[27] Shweta D. Mehta, MAKING AND BREAKING OF WATER IN CRUDE OIL EMULSIONS, A Thesis Submitted to the Office of Graduate Studies of Texas A&M University in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE, 2005.

[28] M. Nuraini, H. N. Abdurahman and A. M. S. Kholijah, Effect of chemical breaking agents on water-in-crude oil emulsion system, *J. Chemical and Environmental Engineering*, August 2011, Volume 2, No.4.