Synthesis of Non Ionic Gemini surfactants and used As Demulsifier to Treatment Water in Crude Oil (W/O) Emulsions

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Abstract— Three new non ionic Gemini surfactants with different spacer (number carbon atoms = 2 – 4), but have alkyl chain length of 16 carbon atoms. The new compounds were synthesized and characterized by FT/IR, mass spectroscopy and 1H-NMR spectroscopy. The basic surface properties of these 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. The demulsification performances of these demulsifiers were investigated by conventional graduated bottle test. The results show that the demulsification efficiency is dependent on critical micelles concentration CMC value of these demulsifiers. It was also correlated to the interfacial activity and the dilational elasticity at the water-oil interface. The lower CMC value of demulsifiers, the better the demulsification efficiency is.

Index Terms — non ionic Gemini surfactants, electrical conductivity, critical micelle concentration, Water in oil emulsion.

I. INTRODUCTION

The surfactants play critical roles in all industry, 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]. It is well known that crude oil plays an important role in providing the energy supply of the world among various sources of energy [6]. Through numerous studies on the stability of water-in oil emulsion, more light has been shed on the mechanism of emulsion stabilization in the petroleum field. Many researchers now attribute the stability of emulsion to the viscoelastic interfacial film made up of surface active molecules such as asphaltenes, resins, and other organic and inorganic particles [7]. The degree to which solids increases emulsion stability depends on several factors such as particle size, shape and morphology, density, concentration and

surface coverage, and wettability [8],[9], [10], [11], [12], [13].

Emulsion stabilized by fine solids and asphaltenes were most stable at a 2:1 fraction area ratio of asphaltene to solids. There is a strong correlation between asphaltene content and emulsion tightness [14]. The presence of wax in addition to asphaltene and resins are known to promote the stabilization of water-in-oil emulsion. Asphaltenes are flat sheets of condensed polyaromatcic hydrocarbons linked together by sulfide, ether, and aliphatic chain groups. The edges of the sheets are alkyl chains. The polar parts of the asphaltene molecules interact with each others forming aggregates or micelles. As such, these micelles are very much polar. Resins are less polar and made up of smaller molecules with one end being hydrophilic made up of functional groups and the other end hydrophobic made up of alkyl chains. In crude oils,the resins are attached to the asphaltene micelles at the polar end and the non polar end of the resin interact with crude oil. The resins solvate the asphaltene aggregates and keep them in colloidal suspension in the oil [15].

II. EXPERIMENTAL

### A. Materials and Instruments

The following materials purchased from different companies: Butylene glycol (99.5 % purity), Propylene glycol (99.5 % purity), Ethylene glycol (99.5 % purity), Cetyl alcohol (95% purity), Epichlorohydrin (99.0% purity), Toluene (99% purity), Sulfuric acid, Sodium hydroxide (99 % purity), Ethanol (99.8 % purity), Twice distilled water was used in the preparation of all solutions.

The characterization by ^{1}H NMR was recorded on a Bruker AM 300 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 Shimadzu IR. Anffinity-1. Mass spectra were obtained on Agilent mass spectrometer 5975 quadro pole analyser (70 ev). The CMC values of the surfactant solution were determined from Electrical conductivity with a Jenway PCM3 conductivity meter.

B. Synthesis of (A₁), (A₂) and (A₃)

There are two steps to get the target compounds:

1. Synthesis of (A)
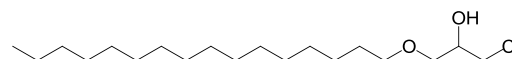
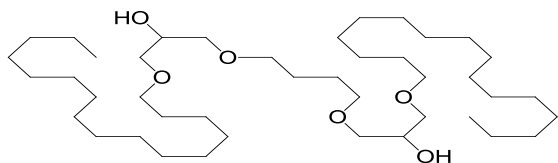1-chloro-3-(hexadecyloxy)propan-2-ol

To a mixture consisting of Epichlorohydrin (0.9 g, 0.01 mol), Cetyl alcohol (2.42 g, 0.01 mol), and Toluene as solvent with Sulfuric acid (0.3 ml) as catalyst in round bottom flask. The mixture was stirred for 4 -6 hours and heated to 110 °C.
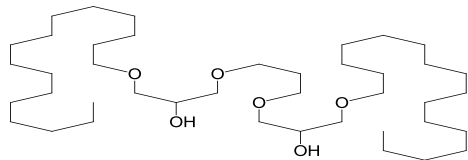
2. Synthesis of (A$_1$)

17,21,26,30-tetraoxahexatetracontane-19,28-diol

To a flask containing compound A (7.38 g, 0.022 mol) and absolute Ethanol (50 ml) was added Butylene glycol (0.9 ml, 0.01 mol) and used Sodium hydroxide as catalyst. The mixture was refluxed to 80 °C for 10 - 11 hours. After reaction the mixture was purified by recrystallization through mixture of solvent acetone: water (1:5) to give the target compound A$_1$ as a white solid crystals in 70 % yield, m.p. 56- 59 °C, FT – IR (KBr): 3300, 2954, 1132, 720. ^{1}HNMR (CDCl$_3$) δ = 0.9 (t, 6H, CH$_3$), 1.2-1.3(m,48,CH$_2$), 1.58(m,4H,CH$_2$), 1.72(m,8H,CH$_2$), 3.43(t,4H,OCH$_2$), 3.53(d,m,8H,OCH$_2$), 3.72 (m,2H,CH-OH), 3.54(d,2H,OH). MS (EI, 70 eV) m/z (%): 687 [C$_{42}$H$_{86}$O$_6$]$^{+\cdot}$ (1.41%), 225 [C$_{16}$H$_{33}$]$^+$ (66.03%), 113 [C$_8$H$_{17}$]$^+$ (81.1%), 85 [C$_8$H$_{17}$]$^+$ (100%). The structure and synthetic route of this surfactant is shown in Scheme (1).
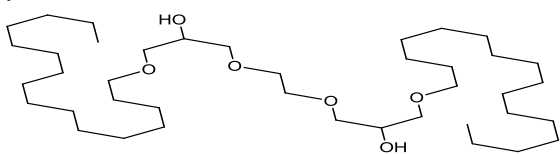
3. Synthesis of (A$_2$)

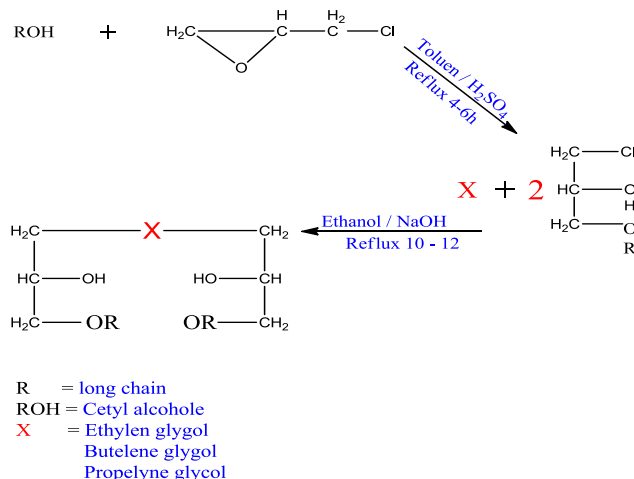17,21,25,29-tetraoxapentatetracontane-19,27-diol

To a flask containing compound A (7.38 g, 0.022 mol) and absolute Ethanol (50 ml) was added Propylene glycol (0.76 ml, 0.01 mol) and used Sodium hydroxide as catalyst. The mixture was refluxed to 80 °C for 10 - 12 hours. After reaction the mixture was purified by recrystallization through mixture of solvent acetone: water (1:5) to give the target compound A$_2$ as a white solid crystals in 65 % yield, m.p. 59-62 °C, FT – IR (KBr): 3329, 2954, 1132, 720. ^{1}HNMR (CDCl$_3$) δ = 0.88(t, 6H, CH$_3$), 1.2-1.3 (m,48,CH$_2$), 1.56 (m,8H,CH$_2$), 3.3 (t,8H,OCH$_2$), 3.4 (d,m,8H,OCH$_2$), 3.7 (m,2H,CH-OH), 3.5(d,2H,OH) . MS (EI, 70 eV) m/z (%): 672 [C$_{41}$H$_{84}$O$_6$]$^{+\cdot}$ (0.25%), 297 [C$_{19}$H$_{37}$O$_2$]$^+$ (2.38%), 57 [C$_4$H$_9$]$^+$ (98%), 97 [C$_7$H$_{13}$]$^+$ (100%). The structure and synthetic route of this surfactant is shown in Scheme (1).

4. Synthesis of (A$_3$)

17,21,24,28-tetraoxatetratetracontane-19,26-diol

To a flask containing compound A (7.38 g, 0.022 mol) and absolute Ethanol (50 ml) was added Ethylene glycol (0.62 ml, 0.01 mol) and used Sodium hydroxide as catalyst. The mixture was refluxed to 80 °C for 10 - 12 hours. After reaction the mixture was purified by recrystallization through mixture of solvent acetone: water (1:5) to give the target compound A$_3$ as a white solid crystals in 45 % yield, m.p. 55- 58 °C, FT – IR (KBr): 3327, 2954, 1132, 719. ^{1}HNMR (CDCl$_3$) δ = 0.9 (t, 6H, CH$_3$), 1.22-1.3(m,48,CH$_2$), 1.56 (m,4H,CH$_2$), 1.71(m,4H,CH$_2$), 3.2 (t,4H,OCH$_2$), 3.4 (t, 4H,OCH$_2$), 3.72 (m,2H,CH-OH), 3.54 (d,2H,OH). MS (EI, 70 eV) m/z (%): 659 [C$_{40}$H$_{82}$O$_6$]$^{+\cdot}$ (0.01%), 467 [C$_{29}$H$_{55}$O$_4$]$^+$ (39.5%), 113 [C$_7$H$_{13}$O]$^+$ (51.8%), 97 [C$_7$H$_{13}$]$^+$ (100%). The structure and synthetic route of this surfactant is shown in Scheme (1).

R = long chain
ROH = Cetyl alcohole
X = Ethylen glygol
        Butelene glygol
        Propeleyne glycol

Scheme 1. Synthetic Route to Gemini surfactant

III. RESULTS AND DISCUSSION

A. Measurement of CMC Values 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 surfactant solutions [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 Gemini surfactants 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 concentrations [25], and can be observed conductivity change linearly (extrusive) with the change of concentration due to the nature and concentration of solution [26], [27]. Where noted from Figures (1), (2) and (3) that impairment of conductivity with reduced concentration of Gemini surfactants, can be attributed to a decline in the electrical conductivity, until a specific point is CMC point. In addition Gemini surfactants from epichlorohydrin exhibit large intermolecular hydrophobic interaction that make it easy for them to form aggregates in water [28].

Through the results as shown in table (1) observed when increasing aliphatic spacer length reduces the CMC value for surfactants [29], [30], [31].

Table 1. The CMC Values to the Prepared Gemini Surfactants

CHARACTERSTICS	METHOD	RESULT
SPECIFID GRAVITY @ 60 °F	IP160	0 .9293
API GRAVITY	IP160	20.8
SULPHUR CONTENT, WT. %	ASTM D-4294	3.30
WATER CONTENT, VOL. %	ASTM D-4006, IP-358	NIL
ASPHALTENES, WT. %	IP-143	9.6
KINEMATIC VISCOSITY , cSt. 1.@ 70 °F (21.1 °C) 2.@ 100 °F (37.8 °C) 3.@ 120 °F (48.9 °C) 4.@ 140 °F (60.0 °C)	ASTM D-445, IP-71	112.0 52.50 32.47 22.50

Compound	CMC (M)
A_1	3×10^{-4}
A_2	3.5×10^{-4}
A_3	4×10^{-4}
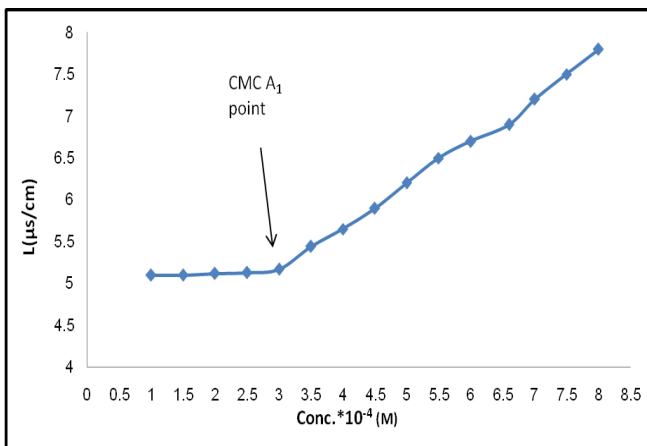
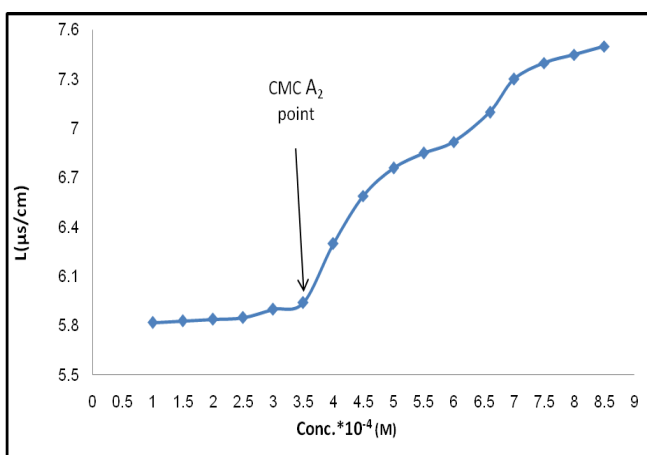**1. CMC of (A_1) Surfactant**

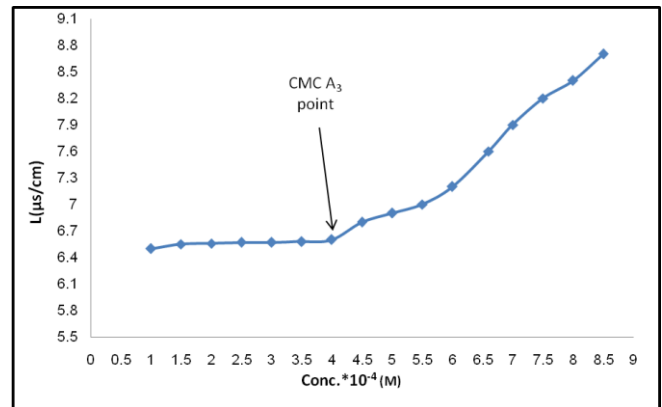**Figure 2. CMC of (A_2) Surfactant**

Figure 3. CMC of (A_3) Surfactant

B. 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. The separation efficiency of water from crude oil can be calculated as a function to concentration, time and temperature from equation (1) [32].

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

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.

Through the results of laboratory testing which are shown in the Table (2), crude oil can be characterized as a heavy and sour crude oil because it has API (20.8), and higher sulfur content (3.30 %).

Table 2.Physicochemical Properties of the used Crude Oil

When using the demulsifiers that made from surfactants (A_1, A_2, A_3) at different concentrations (10, 30, 40, 50) ppm as shown in the figures (4, 5, 6, 7) respectively, to treatment W/O emulsions which are formed in crude oil.
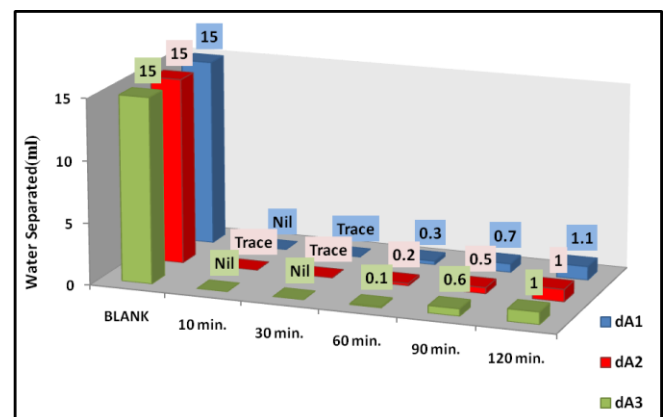

Figure 4. Effects of 10 ppm from Demulsifiers and Settling Time on separated water at 45 °C
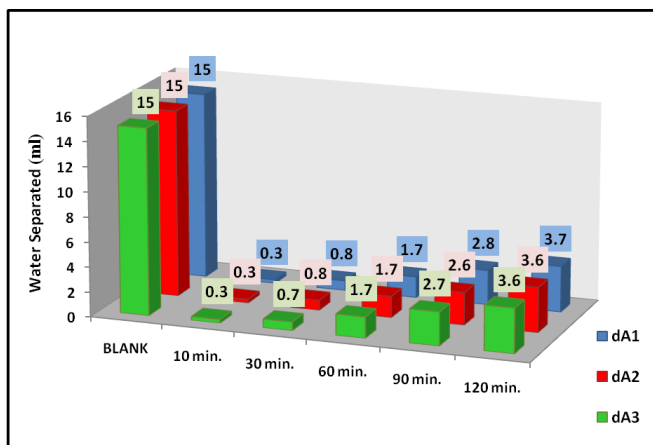
Figure 5. Effects of 30 ppm from Demulsifiers and Settling Time on separated water at 45 °C
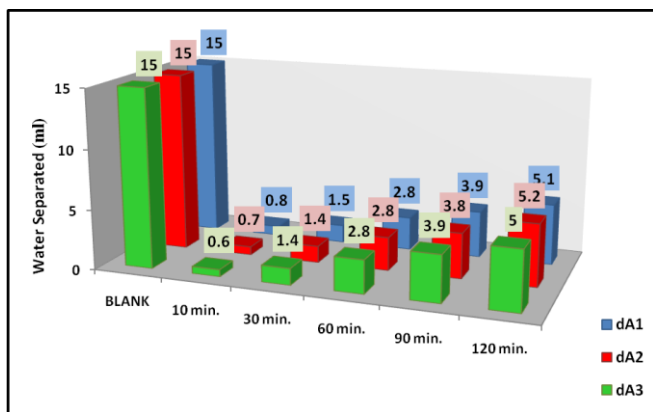

Figure 6. Effects of 40 ppm from Demulsifiers and Settling Time on separated water at 45 °C
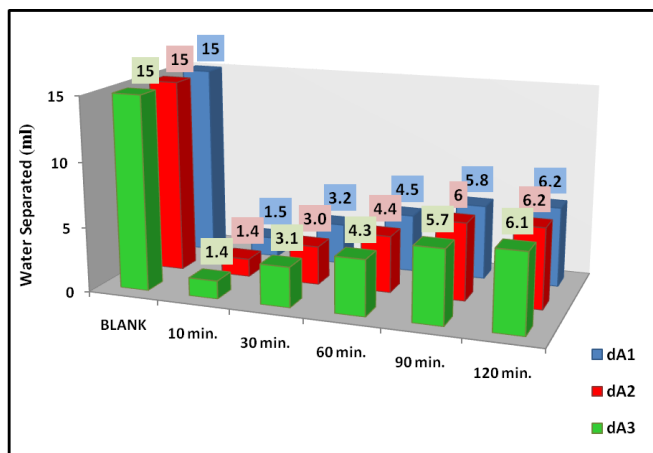

Figure 7. Effects of 50 ppm from Demulsifiers and Settling Time on separated water at 45 °C

The results indicate, there are little difference in the (% E $_{Separation}$) for all prepared demulsifiers due to all of them have approximately same CMC value , can be noted that the separation efficiency (% E $_{Separation}$) of the prepared demulsifiers at temperatures 45°C will be in the following order:

$$A_1 > A_2 > A_3$$

IV. CONCLUSION

Generally, emulsion breaking occurred by supplied demulsifiers, where water separation efficiency increases with increasing dosage 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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