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Synthesis and evaluation of novel cationic gemini surfactants based on *Guava* crude fat as petroleum-collecting and dispersing agents

Mohammed Abo-Riya *, Ahmed H. Tantawy *, Wagdy El-Dougdoug

Chemistry Department, Faculty of science, Benha University, Benha, Egypt

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ABSTRACT

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Keywords: Cationic gemini surfactants *Guava* crude fat surface properties petroleum-collecting and dispersing indices Cationic gemini surfactants based on *Guava* fat mixed fatty alcohols and isolated fatty alcohols C_8 , C_{12} , C_{16} , C_{18} were synthesized. The surface properties and thermodynamic parameters of micellization process, of the new cationic gemini surfactants have been investigated. Furthermore, the petroleum-collecting and dispersing indices of obtained surfactants, in waters of varying salinity have been studied. The results revealed that the tendency of these surfactants toward adsorption process was more than its tendency micellization and show high petroleum-collecting and dispersing properties.

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1. Introduction

The products based on vegetable oil have widespread uses in industry as they have much preference on petroleum products, owing to they are derived from renewable resources, nontoxic, easily biodegradable, inexpensive, and environmentally friendly [1–3]. Fatty acids of vegetable oils are produced by hydrolysis of the triglycerides, followed by elimination of glycerol moiety.

Gemini surfactants are one of the oil based products which consists of two amphiphilic moieties, usually fatty chain, attached to each other by flexible or rigid spacer. It was noted that gemini surfactants can show preferable properties than the commonplace surfactants [4–6]. Recently, some gemini surfactants were synthesized, and a formidable number of reports on their unusual physicochemical properties has been published [7].

Pollution of water by petroleum oil is a great problem facing our ailing environment. This problem has significant impact on the marine environment and also on both birds, and animals. Sources of such pollution include production operations and oil exploration, natural seeps, tanker accidents, industrial discharge, atmospheric input, and urban run-off [8].

Surfactants are widely used for collecting and dispersing the thin films of petroleum on water surface [9–12]. Many types of surfactants were synthesized and their usage as petroleum-collecting and dispersing were studied. Such types include non-ionic surfactants

* Corresponding authors.

E-mail addresses: MOHAMED.ABORYA@fsc.bu.edu.eg (M. Abo-Riya),

AHMED.TANTAWY@fsc.bu.edu.eg (A.H. Tantawy).

which allow a good efficiency of removal of oil leaks from the water surface [13–16]. Ionic surfactants containing hydroxyl groups have a great potential to collect and disperse the fluffy petroleum films from the water reservoirs surface [17,18]. Moreover, quaternary ammonium salts or complexes based on fatty acids and nitrogen-containing compounds have a high activity in collecting and dispersing the spilled crude oil [19–25].

In this work, we synthesized a new type of cationic gemini surfactants from non-edible oil as quaternary ammonium salt. Their surface activity and their collecting and dispersing capacities were evaluated for use in collecting and dispersing the petroleum films from water surface.

2. Experimental

2.1. Materials

Guava crud material was obtained from Kaha Company for food products and juices, Egypt, Octadecyl, hexadecyl, tetradecyl, dodecyl, decyl and octyl alcohols, chloroacetic acid and *N*,*N*,*N*',*N*'tetramethylethylenediamine were obtained by Aldrich Chemical Company (Germany).

2.2. Instrumentation

Gas liquid chromatography (GLC) of *Guava* methyl ester was done by Perkin Elmer Auto System XL gas chromatograph by using flame ionization Detector (FID) with fused silica capillary column ZB-5 (60 m * 0.32 I, d). Helium flow rate was 1mL / min. The peaks were identified

Table 1

Fatty acids composition of Gawafa fat and chemical characteristics of Gawafa fat.

Fatty acid composition of	Gawfa fat	Chemical characteristics of Gawfa fat				
Fatty acid	Peak area %					
Saturated Fatty acids:						
Octanoic (C _{8:0})	12.51	Acid value	23.45			
Decanoic (C _{10:0})	01.89	Iodine value	10.89			
Dodecanoic (C _{12:0})	26.54	Saponification value	197.40			
Tetradecanoic (C _{14:0})	03.33	Unsaponifiable matter	002.03			
Hexadecanoic (C _{16.0})	19.99					
Octadecanoic (C _{18.0})	31.03					
Unsaturated Fatty acids:						
Octadecenoic $(C_{18:1})$	04.54					

by comparing it with chromatograms of standard fatty acid methyl esters (sigma, USA) in National Research Centre, Dakki, Cairo, Egypt.

The infrared spectra of the prepared surfactants were run on FT-IR spectra recorded in KBr on a thermo nicolet iS10 FTIR spectrophotometer. The ¹H-NMR spectra were generated with 400 MHz signal and 4,000 gauss magnetic field in deuterated (DMSO) and /or in chloroform (CDCl₃) as a solvent and tetramethylsilane (TMS) as an internal reference. The surface tension values of surfactants solutions determined

by a Kruss K6 tensiometer. The synthesis of the target gemini surfactants is shown in Fig. 4.

2.3. Synthesis of quaternary ammonium gemini surfactants:

2.3.1. Extraction of Oil

The dried and cleaned seeds were grinding. Using non polar such as *n*-hexanes the oil was extracted and dried using anhydrous sodium sulfate. Using rotary evaporator, the solvent was separated to offer the oil sample.

2.3.2. Composition of Fatty acids of Guava fat and its specification

Fatty acids as methyl esters were analyzed [26] via GLC and the composition and chemical characteristics of Guava fat, such as iodine, acid and saponification values, and unsaponifiable matter, were determined according to AOCS Methods [27] and are given in Table 1. The obtained results were agreement with previous studies by El-Dougdoug et al. [28].

2.3.3. Reduction of fatty acids

Fatty alcohols of *Guava* seeds fat were obtained by reduction of the corresponding methyl ester mixture via lithium aluminum hydride (LAH) [29].



Fig. 1. (a) IR (b) ¹H-NMR spectra of Octadecyl-2-chloroacetate CH₃(CH₂)₁₆CH₂-OCOCH₂Cl(I_c)

2.3.4. Synthesis of 2-chloroacetate derivatives.

Fatty alcohols, namely, octanol, dodecanol, hexadecanol, octadecanol and mixed *Gawfa* fatty alcohols (I_{a-e}) (0.1 mol) and chloroacteic acid (0.1 mol, 9.45 gm) esterified separately in the presence of 0.01% *p*-toluene sulphonic acid as a catalyst and toluene as solvent, till the calculated amount of water (0.1 mol, 1.8 mL) was separated [30]. Using vacuum rotary evaporator to remove the solvent and the excess residual materials were distilled off. All the synthesized esters (I_{a-e}) have the same structure formula but different in the alkyl chain length and were characterized using IR, ¹H-NMR and ¹³C-NMR analysis.

2.3.4.1. Octyl-2-chloroacetate (I_a) CH₃(CH₂)₆CH₂-OCOCH₂Cl. Colorless, viscous liquid, yield = 89%. The IR spectrum of octyl-2-chloroacetate (I_a) revealed that, characteristic bands at 2953, 2922 and 2853 cm⁻¹ (v_{C-H} aliphatic fatty chain), 1740 cm⁻¹ (v_{C-0} of ester); 1155 cm⁻¹ (v_{C-0}). On the other hand, ¹H NMR of the same compound (I_a); gave signals at δ (ppm): 0.85 (t, 3H, terminal **CH**₃), 1.26 (s, 10H, (**CH**₂)₅-), 1.65 (m, 2H,CH₂CH₂CH₂-O), 4.04 (s, 2H, **CH**₂-Cl) and 4.18 (t, 2H, **CH**₂-O).

2.3.4.2. Dodecyl-2-chloroacetate $(I_b)CH_3(CH_2)_{10}CH_2$ -OCOCH₂Cl. Yellow color, viscous liquid, yield = 87%. IR spectrum of compound (I_b) showed stretching bands at 2953, 2922, and 2853 cm⁻¹ (ν_{C-H} , aliphatic fatty



Fig. 2. (a) IR (b) ¹H-NMR and (c) ¹³C-NMR spectra of 1,2-ethane bis (dimethyl 2-(dodecyloxy)-2- oxoethyl ammonium chloride(CGS12)

chain), 1745 cm⁻¹ ($\nu_{C=0}$ of ester), 1160 cm⁻¹ (ν_{C-0}). The ¹H NMR spectrum of compound (I_b); showed δ (ppm): 0.85 (t, 3H, terminal <u>CH₂-),</u> 1.30 (s, 18H, (<u>CH₂)</u>-), 1.66 (m, 2H, <u>CH₂-CH₂-O), 4.07 (s, 2H, <u>CH₂-Cl),</u> 4.20 (t, 2H, CH₂-O).</u>

2.3.4.3. Hexadecyl-2-chloroacetate (I_c) CH₃(CH₂)₁₄CH₂-OCOCH₂Cl. White color, solid, mp = 45 °C, Yield = 85 %. IR showed bands at 2953, 2920, and 2849 cm⁻¹ (ν_{C-H} , aliphatic fatty chain), 1748 cm⁻¹ ($\nu_{C=0}$ of ester), and 1212cm⁻¹ (ν_{C-0}).¹H NMR δ (ppm): 0.89 (t, 3H, terminal<u>CH₃-</u>), 1.28 (s, 26H, (CH₂)₁₃-), 1.68 (m, 2H, <u>CH₂CH₂-O), 4.06 (s, 2H, CH₂-Cl), 4.20 (t, 2H, CH₂-O).</u>

2.3.4.4. Octadecyl-2-chloroacetate (I_d) $CH_3(CH_2)_{16}CH_2$ -OCOCH₂Cl. White color, solid, mp = 47 °C, Yield = 84 %. IR showed bands at 2954, 2921, and 2851 cm⁻¹ (ν_{C-H} , aliphatic fatty chain), 1749 cm⁻¹ ($\nu_{C=0}$ of ester), and 1213cm⁻¹ (ν_{C-0}) (Fig. 1a; **supporting data**). ¹H NMR δ (ppm): 0.89 (t, 3H, terminal<u>CH₃-</u>), 1.28 (s, 30H, (<u>CH₂)₁₅-</u>), 1.68 (m, 2H, <u>CH₂</u>CH₂-O), 4.06 (s, 2H, <u>CH₂-</u>Cl), 4.20 (t, 2H, <u>CH₂-</u>O) (Fig. 1b; **supporting data**).

2.3.5. Synthesis of Novel Cationic Gemini Surfactants (CGS8, CGS12, CGS16, CGS18 and CGS_{Guava})

Cationic gemini surfactants from precursors CGS8, 12, 16, 18 were synthesized according to the literature [31]. 2-chloroacetate derivatives (18 mmol) is added to *N,N,N',N'*-tetramethylethylenediamine (9 mmol, 1.35mL) dissolved in 35 mL of diethyl ether with stirring at room temperature to afford dimeric surfactants. The reaction mixture was filtered and the product was washed by diethyl ether. The yield range is from 85 to 93 %. The structures of the obtained surfactants were proven by IR, ¹H and ¹³C NMR spectra. Detailed spectral data are given below:

2.3.5.1. <u>CGS8</u>:1, 2-ethane bis (dimethyl2 -(octyloxy)-2-oxoethyl ammonium chloride). White color, viscous liquid, yield = 93%. IR spectrum of compound revealed that, stretching bands at 2955, 2924, and 2853 cm⁻¹ (ν_{C-H} , aliphatic fatty chain), 1740 cm⁻¹ ($\nu_{C=0}$ of ester), 1155 cm⁻¹ (ν_{C-O}). ¹H NMR δ (ppm): 0.86 (t, 6H, 2 [**CH**₃-CH₂-]), 1.28 (s, 16 H, 2 [**(CH**₂)₄-]), 1.69 (p, 4H, 2 [**CH**₂CH₂CH₂-O]), 2.53 (s, 4H, 2 [CH₂CH₂CO]), 3.72 (s, 12H, 4 [**CH**₃-N⁺]), 4.21 (t, 4H, N⁺-**CH**₂-**CH**₂-N⁺), 4.80 (t, 4H, 2 [**CH**₂-O]), 4.93 (s, 4H, 2 [O = C-**CH**₂-N⁺]). ¹³C NMR δ_C (ppm, DMSO): 15.32 (2 [**-CH**₃ alkyl chain]), 23.43 (2 [**CH**₂-CH₃]), 25.72 (2 [**CH**₂-CH₂-O]), 30.62-34.18 (-CH₂- alkyl chain of fatty alcohol), 44.29 (4 [**CH**₃-N⁺]), 51.74 (⁺N-**CH**₂-**CH**₂N⁺), 59.87 (2 [-**CH**₂-C = O]), 66.11 (2 [-**CH**₂-O]), 166.43 (2 [-CH₂-**C**=**O**]).

2.3.5.2. <u>CGS12</u>: 1,2-ethane bis (dimethyl 2-(dodecyloxy)-2-oxoethyl ammonium chloride). Yellowish white color, viscous liquid, yield = 92%. IR: 2953, 2924, and 2854 cm⁻¹ (C–H, aliphatic fatty chain), 1741 cm⁻¹ ($\nu_{C=0}$ of ester), and 1180 cm⁻¹ ($\nu_{C=0}$) (Fig. 2a; **supporting data**). ¹H



Fig. 3. (a)¹H-NMR and (b) ¹³C-NMR spectra of 1,2-ethane bis (dimethyl 2-(octadecyloxy)-2- oxoethyl ammonium chloride (CGS18)

Table 2		
The General	characterization	of waters

Water type	Density	pН	Cations		Anions			
			Sodium	Calcium	Potassium	Magnesium	Chloride	Sulfate
Fresh water Sea water	1.000 g/cm ³ 7.5 g/cm ³	6.93 3.1g/kg	6.93 mg/l 0.31g/kg	0.8 mg/l 0.11g/kg	0.31 mg/l 0.65g/kg	0.24 mg/l 4.88g/kg	0.06 mg/l 2.78g/kg	1.3 mg/l 2.98 g/kg

 $\begin{aligned} & \mathsf{NMR}\,\delta\,(\mathsf{ppm}){:}\,0.87\,(\mathsf{t},\mathsf{6H},2\,[\mathbf{\underline{CH}_3}{-}\mathsf{CH}_2{-}]),\,1.26\,(\mathsf{S},32\,\mathsf{H},2\,[(\mathbf{\underline{CH}_2})_8{-}]),\,1.67\\ & (\mathsf{m},\mathsf{4H},2\,[\mathbf{\underline{CH}_2}\mathsf{CH}_2\mathsf{CH}_2\mathsf{-O}]),\,2.53\,(\mathsf{s},\mathsf{4H},2\,[\mathsf{CH}_2\mathbf{\underline{CH}_2}\mathsf{CH}_2{-}\mathsf{O}]),\,3.72\,(\mathsf{s},12\mathsf{H},\\ & 4\,[\mathbf{\underline{CH}_3}{-}\mathsf{N}^+]),\,4.17\,(\mathsf{t},\mathsf{4H},\mathsf{N}^+{-}\mathbf{\underline{CH}_2}{-}\mathbf{CH}_2{-}\mathsf{N}^+),\,4.81\,(\mathsf{t},\mathsf{4H},2\,[\mathbf{\underline{CH}_2}{-}\mathsf{O}]),\,4.91\\ & (\mathsf{s},\mathsf{4H},2\,[\mathsf{O}\!=\!\mathsf{C}\!{-}\mathbf{\underline{CH}_2}\!{-}\mathsf{N}^+])\,(\mathsf{Fig},2\mathsf{b};\mathsf{supporting\,data}).\ ^{13}\mathsf{C}\,\mathsf{NMR}\,\delta_{\mathsf{C}}\,(\mathsf{ppm},\\ \end{aligned}$

 $\begin{array}{l} DMSO): 14.21 \ (\ 2 \ [-CH_3 \ alkyl \ chain \]), 22.43 \ (2 \ [CH_2-CH_3]), 25.22 \ (2 \ [CH_2-CH_2-O]), 28.11-34.34 \ (-CH_2- \ alkyl \ chain \ of \ fatty \ alcohol), 43.31 \ (4 \ [CH_3-N^+]), 51.76 \ (^+N-\underline{CH_2-CH_2}N^+), 60.39 \ (2 \ [-CH_2-C=O]), 66.25 \ (2 \ [-CH_2-O]), 166.23 \ (2 \ [-CH_2-C=O]) \ (Fig. \ 2c; \ supporting \ data). \end{array}$



Fig. 4. Scheme 1. Synthetic route of Novel Cationic Gemini Surfactants.

2.3.5.3. <u>CGS16</u>: 1,2-ethane bis (dimethyl 2-(hexadecyloxy)-2-oxoethyl ammonium chloride). Yellowish white color, viscous liquid, yield =92%. IR: 2953, 2924, and 2854cm⁻¹(C-H, aliphatic fatty chain), 1741cm⁻¹ ($\nu_{C=0}$ of ester), and 1180cm⁻¹(ν_{C-0}). ¹H NMR δ (ppm): 0.87 (t, 6H, 2 [**CH**₃-CH₂-]), 1.26 (s, 48 H, 2 [(**CH**₂)₁₂-]), 1.67 (p, 4H, 2 [**CH**₂CH₂CH₂-O]), 2.53 (s, 4H, 2 [CH₂CH₂CH₂-O]), 3.7 2 (s, 12H, 4 [**CH**₃-N⁺]), 4.17 (t, 4H, N⁺-**CH**₂-**CH**₂-N⁺), 4.81 (t, 4H, 2 [**CH**₂-O]), 4.91 (s, 4H, 2 [O = C-**CH**₂-N⁺]). ¹³C NMR δ_{C} (ppm, DMSO):14.21 (2 [-**CH**₃ alkyl chain]), 22.43 (2 [**CH**₂-CH₃]), 25.22 (2 [**CH**₂-CH₂-O]), 28.11-34.34 (-CH₂- alkyl chain of fatty alcohol), 43.31 (4 [**CH**₃-N⁺]), 51.76 (⁺N-**CH**₂-**CH**₂N⁺), 60.39 (2 [-**CH**₂-C=O]), 66.25 (2 [-**CH**₂-O]), 166.23 (2 [-**CH**₂-**C**=**O**]).

2.3.5.4. <u>CGS18</u>: 1,2-ethane bis (dimethyl 2-(octadecyloxy)-2-oxoethyl ammonium chloride). White color, solid, mp = 90 °C yield = 89%. IR: 2953, 2921, and 2851 cm⁻¹ (C–H, aliphatic fatty chain), 1749 cm⁻¹ ($\nu_{C=0}$ of ester), and 1213 cm⁻¹ (ν_{C-0}). ¹H-NMR δ ppm: 0.87 (t, 6H, 2 [CH₃-CH₂-]), 1.25 (s, 56 H, 2 [(CH₂)₁₄-]), 1.64 (p, 4H, 2 [CH₂CH₂CH₂-O]), 2.24 (s, 4H, 2 [CH₂CH₂-O]), 3.72 (s, 12H, 4 [CH₃-N⁺]), 4.07 (t, 4H,N⁺-CH₂-CH₂-N⁺), 4.21 (t, 4H, 2 [CH₂-O]), 4.80 (s, 4H, 2 [O=C-CH₂-N⁺]), (Fig. 3a; supporting data). ¹³C-NMR δ_{C} (ppm, DMSO): 14.22 (2 [-CH₃ alkyl chain]), 22.43 (2 [CH₂-CH₃]), 25.22 (2 [CH₂-CH₂-O]), 29-32.68 (-CH₂- alkyl chain of fatty alcohol), 43.78 (4 [CH₃-N⁺]), 52.58 (⁺N-CH₂-CH₂N⁺), 61.54 (2 [-CH₂-C=O]), 66.11 (2 [-CH₂-O]), 165.22 (2 [-CH₂-C=O]) (Fig. 3b; supporting data).

2.4. Surface properties

2.4.1. Surface and Interfacial Tension Measurements

Surface tension values were measured by Krüss (Model K 6) tensiometer with a platinum–iridium ring [32]. Distilled water with 72 dyne/cm surface tension at 25 °C used to prepare 0.1 % weight solution. The values of surface tension were determined at least four times and the average value was taken.

Interfacial tension was measured for surfactant–oil system at 25 °C with a 0.1 % surfactant solution. The value, at which the ring was separated at the interfacial surface between the two layers, was measured as interfacial tension. The interfacial tension between the distilled water and the paraffin oil used is 56.2 dyne/cm.

2.4.2. Krafft point

The temperature at which 0.1 % surfactants solution becomes clear by heating is gauge the aqueous solubility. The Krafft points of gemini surfactants were measured by gradually heating of the surfactant solution until it became clear [33].

2.4.3. Emulsion stability

Powerful stirring of a 10 mmole solution (10.0 mL) and 10 mL of light paraffin oil at 25 °C and measuring the time desired for separate aqueous phase (9.0 mL). This time was determined as the emulsion stability [34].

2.4.4. Foam Height

A 100 ml of the surfactant solution (0.1 wt %) was strongly shaken for 10 seconds in a 500 mL graduated cylinder at 25 °C. The foam height was measured (in mL) as the foam height initially produced. [35].

Table 3						
Surface	properties	of (Cationic	Gemini	surfactants	s.

2.4.5. Stability to hydrolysis

In a thermostat at 40 $^{\circ}$ C, 10 mL (10 mmole) surfactant with 10 mL of 0.05 N NaOH or 2 N sulfuric acid was poured. The stability to hydrolysis was indicates by the time of sample solution takes to be clouded [36].

2.5. The petroleum-collecting and dispersing properties

Petroleum-collecting and dispersing capacities of the gemini surfactants from *Guava* crude fat in the solid state and in the 5% wt. water solution have been studied on the Red sea crude oil (density and kinematic viscosity at 20°C are respectively 0.84 g/cm³ and 0.13 cm²/s) from the oil fields in the south sina (Egypt). The synthesized surfactant (0.02 g) or its solution was added to the surface of distilled, fresh and the red Sea water (Table 2) (separately) in Petri dishes with a thin film (thickness 0.16–0.17 mm) of this petroleum. The petroleum collecting coefficient (K) are calculated from the formula $K = S_o/S$, where S_o is an area of the surface of initial petroleum film and S is an area of the surface cleaning degree (k_d) is found at fixed times of measurements. K_d is calculated as the ratio of the surface area of the oil at the peripheral part of the dish and the surface area of the initial oil slick [20].

3. Results and discussion:

3.1. Synthesis

Guava seeds are considered as remnants of guava juice industries and it had no economic value. Fatty substances in the seeds were extracted by using *n*-hexanes and examined to determine the fatty acid compositions and its chemical characteristics. The fatty acid composition was determined by using GLC as fatty acid methyl ester, from the data obtained we can clearly see that the most fatty acids are saturated acids, about 95 %, for that reason it called *Guava* fat. The mixed fatty acids were separated from its fat by the alkali hydrolysis, and then converted to methyl ester. The corresponding alcohols were obtained by the hydrogenation of these fatty acids methyl ester.

Cationic gemini surfactants were synthesized from different fatty alcohols as shown in Fig. 4. The fatty alcohols (C_8 , C_{12} , C_{16} , C_{18} and mixed *Guava* fatty alcohols) were esterification with 2-chloroacetic acid, respectively. The quaternization process of these esters was done by reaction with *N*,*N*,*N*',*N*'-tetramethylethylenediamine to give the quaternary salts. All the synthesized cationic gemini surfactants (CGS8, 12, 16 and 18) have been elucidated using spectroscopic tools as shown above.

Moreover, the physical characterization and the petroleumcollecting and dispersing of cationic gemini surfactants, with different number of methylene groups, were investigated and listed in Tables 3, 4 and 5. Also the effect of the structure on surface-active parameters was studied.

3.2. Surface Properties

Surface-active properties measurements of the synthesized cationic gemini surfactants were made to evaluate the surface activity of surfactants and the corresponding data are listed in Tables 3 and 4. It indicates

Compound No.	I.F.T 0.1% (dyne/cm)	Kraft p. 0.1% 0C	Emu. stab. 10 mmole min : Sec.	Foam h. 0.1% (mm)	Stab. to hyd. acid Hrs.: min.	Stab. to hyd. Base min : Sec.
CGS8	8	<0	4:10	360	6:31	00:45
CGS12	11	<0	7:55	290	8:15	02:34
CGS16	12	<0	10:43	210	12:30	04:30
CGS18	13	<0	11:26	150	More than one day	04:32
GS _{mix}	9	<0	4:53	320	More than one day	10:13

Table 4
Some surface-active parameters of the synthesized cationic surfactant

Compounds	CMCx10 ⁻⁵ (Mol/l)	$\gamma_{\text{CMC}}(mN/m)$	$\Pi_{\text{CMC}} (\text{mN/m})$	$\Gamma_{\rm max} \times 10^{10} (m mol \ cm^{-2})$	$A_{\min} (nm^2)$	ΔG_{mic}^{o} (kJ mol ⁻¹)	ΔG_{ads}^0 (kJ mol ⁻¹)
CGS8	1.0	43	29	3.06	0.54	-28.524	-37.950
CGS12	0.16	35	37	3.20	0.52	-33.064	-44.65
CGS16	3.16	47	25	2.60	0.64	-25.673	-35.309
CGS18	6.3	49	23	1.95	0.85	-23.964	-35.738

that the surface and interfacial tension of water are reduced by addition the cationic gemini surfactants, this is because the migration of the surfactants molecules to the surface due to a hydrophobicity of two fatty chain lengths in the gemini surfactants molecules. The critical micelle concentration (CMC) is an important value in the solution parameters; it can be specified from the slopes of surface tension versus the natural logarithm of concentration plots, in which the suddenly change in the was taken as the CMC (see Fig. 5). From Table 4, all the examined cationic gemini surfactants have lower CMC values. The CMC values decrease with increasing the alkyl chain length for CGS8 and CGS12 as expected, it can be interpreted as an increase of the hydrophobic chain the molecules easily migrate to the surface and the micelle formed at low concentration. On the contrary, the CMC values increase by increasing the alkyl chain length for CGS16 and CGS18; this may be attributed to the large size of the molecule makes it movement more difficult and hardly migrate to the surface.

The π_{cmc} is the effectiveness of surface tension reduction or the surface pressure was determined from the plots of surface tension with logarithm of concentration, π_{cmc} is defined as (Eq. (1)):

$$\pi_{\rm cmc} = \gamma_0 - \gamma_{\rm cmc} \tag{1}$$

Where γ_0 is the surface tension of pure solvent and $\gamma_{\rm cmc}$ is the surface tension of solution at cmc. The maximum reduction in surface tension has been determined by $\pi_{\rm cmc}$ and as a result $\pi_{\rm cmc}$ makes the effectiveness of the amphiphile direct to lower the surface tension of the water [37]. The surfactants synthesized in present work (CGS8, CGS12, CGS16 and CGS18) have been studied and show a greater ability to reduce surface tension of water; especially CGS12 has a greater efficiency in decrease surface tension. However, $\gamma_{\rm cmc}$ increases and $\pi_{\rm cmc}$ decreases with increases the length of chain except CGS12 which is in agreement with the earlier report except CGS12 [38].

The maximum surface excess quantity (Γ_{max}) at the air/water interface can be studied from the following Gibbs adsorption isotherm [39].

$$\Gamma_{max} = -(d\gamma/d \ \log C)_T / 2.303 nRT \tag{2}$$

where, R is the gas constant (equal to 8.314 J mol⁻¹K⁻¹); T is the absolute temperature; $d\gamma/d\log C$ is the slop below the cmc in the surface tension plots, *n* is a constant and depends on the number of surfactant molecules adsorbed at the interface (assumed as 4 in our calculation). Also the minimum area occupied by surfactant molecule at interface (A_{min}, in nm²) has been computed by following relation (Eq. (3)), [40].

$$A_{\min} = 10^{14} / \Gamma_{\max} N_A \tag{3}$$

Where N_A is Avogadro's constant (6.022×10^{23} mol⁻¹), A_{min} . Table 4 reflects the packing density of surfactant monomer at the air–water solution which is related to surface activities of the cationic gemini surfactants. The Γ_{max} value decreases while the A_{min} value increases with the raising the methylene groups in chain length except CGS8 suggesting that the surfactant with lower hydrophobicity has higher packing densities at air/water interface. Similar trends were also observed for other cationic gemini surfactants where it was mentioned that the lower alkyl chain can be vertical to the surface and not liable to fold at the air/water interface, while the higher surfactant molecules show folding [41]. Also the adsorption and micellization parameters of the prepared surfactants were studied using Gibb's adsorption equations [32,42]:

$$\Delta G_{mic}^{o} = 2.303 RT \log CMC \tag{4}$$

$$\Delta G_{ads}^o = \Delta G_{mic}^o - (0.06023\pi_{CMC}A_{\min}) \tag{5}$$

Whereas (ΔG_{ads}^0) is adsorption free energy and (ΔG_{mic}^0) is micellization free energy. The adsorption free energy (ΔG_{ads}^0) is the energy of transfer of 1 mol of gemini surfactant solution to the interface, and the

Table 5

Petroleum-collecting and petroleum dispersing properties of some novel Gemini surfactants based on Gawafa crude fat

Type of Gemini surfactants	Undiluted product					5% wt. water solution						
	Distilled water		Fresh water		Sea water	Sea water		Distilled water		er	Sea water	
	τ(h)	K (k _d)	τ(h)	K (k _d)	τ(h)	K (k _d)	τ(h)	K (k _d)	τ(h)	K (k _d)	τ(h)	K (k _d)
CGS _{mix}	0	80.7%	0	92.2%	0	91%	0	41%	0	74%	0	92%
	5-166	92.2%	7	94.3%	5-55	95.2%	7-55	94%	7	90.1%	7	93.9%
	-	-	31-100	96.5%	166	1.7	166	90%	10-70	95.9%	31-70	95.1%
CGS ₁₈	0	4.8	0	98.1%	0-10	93.1%	0	3.5	0-1	3.7	0-7	90%
	7-55	95.9%	7-100	95.5%	23-166	95.3%	5-166	97.2%	5-166	97%	20	92.3%
	60-166	97.2%	-	-	-	-	-	-	-	-	30-166	97.1%
CGS ₁₆	0	4.8	0	95.1%	0-10	93.1%	0	3.5	0-1	3.7	0-7	90%
	7-55	92.9%	7-100	95.5%	23-166	95.3%	5-166	95.8%	5-166	95%	20	92.3%
	60-166	95.2%	-	-	-	-	-	-	-	-	30-166	95.1%
CGS ₁₂	0	3.1	0	10	0-10	93.2%	0-10	92.3%	0	6.65	0	90.2%
	5	6.65	5-100	95.6%	15-100	95.4%	15-55	93.1%	5-55	96.6%	5-15	93.4%
	10	93.2%	-	-	-	-	70-166	95.2%	60-166	15.4	20-166	95.2%
	15-155	95.3%	-	-	-	-	-	-	-	-	-	-
CGS ₈	0	82%	0	94%	0-1	93.1%	0-1.5	84.2%	0-25	95%	0	92.7%
	5-50	95.3%	5-49	94.2%	5-45	94.3%	15-20	94.9%	30-120	97%	5-166	93.8%
	75-155	88%	68-100	95.1%	55-70	80.5%	25-49	93%	-	-	-	-
	-	-	-	-	80-166	50%	60-100	92%	-	-	-	-



Fig. 5. Variation of surface tension with log cationic Gemini surfactants concentration in aqueous solution at 298 K

free energy of micellization (ΔG_{mic}^{o}) is the work required for the micellization [43]. When (ΔG_{mic}^{o}) and (ΔG_{ads}^{0}) is permanently negative the surfactants molecules tend to adsorb at the interface and form micelles in solution [44]. The (ΔG_{mic}^{o}) and (ΔG_{ads}^{0}) values of the surfactants are showed in Table 4. It is noted that the (ΔG_{mic}^{o}) and (ΔG_{ads}^{0}) always have negative values, leading to the two processes are spontaneously. Also, it was noticed that the adsorption energies are higher negative than (ΔG_{mic}^{o}) , reference to that the surfactants tend to be absorbed at the interface more than micellization in the solution.

3.3. Krafft point

The Krafft point's results of the surfactants are found in Table 3. The Krafft points of all cationic gemini surfactants within this study have been determined and found to be less than 0 °C. This gives it the ability to be used at low temperatures.

3.4. Emulsion stability

The emulsifying ability of the cationic gemini surfactants is display in Table 3. It shows that all studied surfactants have good emulsifying power. In addition to that the time it takes to separate the oil and aqueous phases increase as the fatty chain increase as expected [45].

3.5. Foam Height

The foaming power of surfactants is an important phenomenon while it determines in which types of applications it can be used. The foam height data are listed in Table 3; it showed that all surfactants have a high foaming height. Moreover, the values of foam height in general decrease by increasing the length of fatty chain.

3.6. Stability to hydrolysis

All the synthesized cationic gemini surfactants have been exposed to acidic and basic mediums to study its hydrolysis. While all the prepared surfactants have ester linkage which is easily hydrolysis in basic medium, for that all compounds have a lower stability in a basic medium, as shown in Table 3. On the other hand, all the surfactants examined under this study exhibited good stability in an acidic medium. It is also show that the increase in lengths of fatty chain leads to more stability to hydrolysis in both acidic and basic media.

3.7. Petroleum-collecting and dispersing properties of novel Gemini surfactants

The surfactants were added in undiluted form and as 5% wt. water solutions. Fig. 6a, b and c show the petroleum-collecting and dispersing abilities of the gemini surfactants. Fig. 6a and b show the petroleum oil film before and after the addition of reagent. While Fig. 6c show two different dispersion shapes of petroleum oil after addition of reagent. The data were reported in Table 5 and it is clear that all synthesized gemini surfactants in diluted and undiluted form offer better petroleumdispersing action. Additionally, CGS18 and CGS16 gave high petroleumdispersing properties in diluted and undiluted forms than the other surfactants, whereas K_d is ranging from 93.1 to 97.2%, $\tau = 166$ h (in distilled, fresh and sea waters), moreover the diluted form show a very high petroleum-dispersing effect than in undiluted form (in diluted form $K_d = 97.2$ and 95.8%, $\tau = 166$ h in distilled water, $K_d = 97$ and 95% , $\tau\!=\!166$ h in the fresh water, $K_d=$ 97.1 and 95.1% , $\tau=\!166$ h in the sea water). Interestingly, CGS12 exhibits high petro-dispersing properties in the first days (K_d = 96.6%, τ = 55 h) as diluted form in fresh water more than distilled and sea water and the effect converted to petroleum-collecting effect after two days ($K_{max} = 15.4 \tau = 60-166 h$). While the undiluted form CGS12 showed high petroleum-dispersing effect in all types of water (in distilled water $K_d = 95.3\%$, $\tau = 155$ h, fresh water K_d = 95.6%, τ = 100 h, sea water K_d = 95.4%, τ = 100 h). CGS8 gave high petroleum-dispersing effect in fresh water both in diluted and undiluted form, and was stable for long time, while it has a moderate effect in diluted form in both distilled and sea water. Also CGS_{Guava} in diluted and undiluted form in distilled, fresh and sea waters gave highly effect if it compared with the last two surfactants (CGS8 and CGS12) and the effect is stable for long time as observed in the Table 5. From all the results obtained, it is noted that the strength of petroleumdispersing properties depends on the hydrophobic part whereas the effect increases with hydrophobic part increases. Finally, all of the prepared gemini surfactants gave a good petroleum-dispersing effect and it can be used as petroleum-dispersing agents especially CGS18, CGS16, CGS12 and CGS_{Guava}.



Fig. 6. Shape of petroleum film at water surface before addition of reagent (a), different collection shapes after addition of reagent (b), different dispersion shapes after addition of reagent (dispersion of petroleum) (c).

The synthesized cationic gemini surfactants have better petroleumdispersing properties comparing with the corresponding conventional surfactants studied before [23–25].

4. Conclusion

Novel cationic gemini surfactants from *Guava* crude fat were synthesized and its structures were elucidated using spectroscopic tools such as IR, ¹H and ¹³C NMR spectra. The synthesized cationic gemini surfactants offered high surface activity and have tendency to adsorbed at the interface more than the micellization in the bulk of their solutions. It has been found that found that the surface activity was affected by the change in the length of the hydrophobic part present in these cationic gemini surfactants. On the other hand, most of the synthesized surfactants show high petroleum-collecting and dispersing properties especially CGS18, CGS16 and CGS12. It is remarkable that CGS_{*Guava*} gave highly petroleum-dispersing effect. We conclude that all synthesized surfactants can be used as petroleum-collecting and dispersing agents.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2016.05.083.

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