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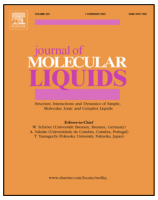

Novel synthesized amide-incorporating copolymeric surfactants based on natural wastes as petro-dispersing agents: Design, synthesis, and characterizations

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ABSTRACT

New cationic copolymeric surfactants were synthesized based on the fatty acid obtained from Juagafa seed wastes, which gave an appropriate yield of lauric acid, which upon esterification and reduction processes was converted to lauryl alcohol. Through the reaction of lauryl alcohol with methacrylic acid (MAA) in the presence of *N,N′*-dicyclohexylcarbadiimide (DCC), lauryl methacrylate (LMA, as a starting monomer) was obtained. A series of copolymerization feeds between lauryl methacrylate and methacrylic acid in different molar ratios initiated by benzoyl peroxide (BP) were carried out. Also, the obtained data from ^{1}H NMR for the different molar ratios of the poly(LMA-co-MAA) were utilized to estimate the monomer reactivity ratio. The synthesized poly(LMA-co-MAA) with different molar ratio was modified by direct amidation with *N,N′*-dimethyl-1,3-propanediamine. The amidated copolymers **(PA1-5)** were quaternized with methyl and ethyl iodides to obtain the corresponding cationic copolymeric surfactants (**PSM** and **PSE**). The chemical structures of the prepared compounds were confirmed by FT-IR and ^{1}H NMR analysis. The critical micelle concentrations of the prepared cationic copolymeric surfactants were investigated. Also, the studies of petroleum-collecting and dispersing properties showed that copolymeric surfactants (**PSE**) have promised effects than **PSM** ones, especially in sea water and diluted form, and the best molar ratio that gave excellent dispersion of petroleum is **PSM-3** and **PSE-3**.

1. Introduction

Surfactants made from natural building blocks rather than petroleum compounds have gotten a lot of press in recent years [1–3]. Furthermore, vegetable oils, which are triglycerides produced from plants, have been widely employed to incorporate hydrophobic fatty acyl groups into surfactants [4–6]. The surfactants prepared from vegetable oils showed different properties [7]. Also, anionic surfactants generated from animal fat and vegetable oil have been used in water treatment to remove some contaminants, including dyes in the presence of calcium ions, from which sodium soap creates another insoluble surfactant [8].

The polymeric surfactant is becoming increasingly important in current industry and scientific research. However, at today's universities, the introduction of polymeric surfactants is still insufficient [9]. The combination between the polymeric material and the surface-active agents can happen through two concepts. The first step is the preparation of the polymer, then the surfactant molecule binds strongly with the polymer molecule in the second step, in which the polymer becomes very hydrophilic [10]. Polymeric surfactants are macromolecules that include both hydrophobic and hydrophilic groups. As a result they are frequently referred to as amphiphilic polymers, which have characteristic with molecular weights greater than thousands [11–14]. The presence of two moieties (hydrophilic and hydrophobic) in one molecule can be identified as a crucial property which is responsible for their unique behaviors in solution [15]. This gives polymeric surfactant several applications and is considered as very good choice for enhanced oil recovery in addition to vital role in different applications such as pharmaceutical, the industry of detergents as well as microemulsion designing. Also, polymeric surfactants are often used to treat wastewater because they have a high surface activity and can thicken and strengthen fluids [15–17].

In recent years, a lot of attentions have been directed to the manufacture of polymeric materials from renewable resources. Also, the use of vegetable oils in the manufacture of polymeric materials and chemical industries represents one of the important processes currently. This is due to the vegetable oils representing the largest renewable platform due to their availability, low cost,

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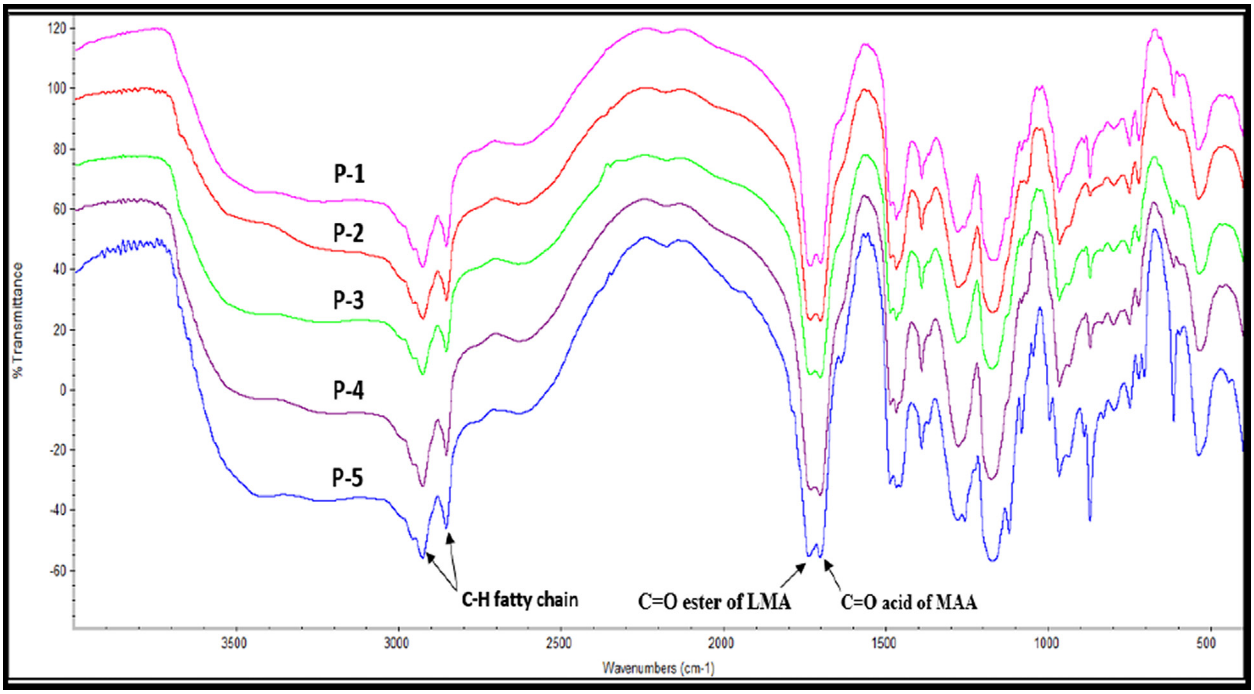

Fig. 1. FT-IR spectra of poly (LMA-co-MAA) with different ratios.

biodegradable and finally considered environmentally friendly (i.e., low ecotoxicity and low toxicity toward humans) [18]. Based on the use of alginic acid with alkyl chains like octyl, dodecyl, and hexadecyl, many activated cationic polymeric surfactants and antimicrobial agents were synthesized with good properties such as their foam power and emulsion stability, in addition to their good activity against some bacteria and fungi. Also, its performance as a mixed type inhibitor on mild steel corrosion [19]. Cationic surfactants, particularly quaternary ammonium compounds, have the most potent antimicrobial activity. They have been employed to stop the spread of several bacterial types [19–21]. The detergency, emulsification, and foaming qualities of polymeric surfactants can vary greatly depending on their chemical features. The molecule's surface-active qualities have been influenced on the water-loving groups' characteristics and positions, a number of hydrophobic groups and their arrangement [22–24]. The cationic groups along the polymer surfactant backbone lead to a significant increase in viscosity and offer control over colloidal stability [15].

Sharma et al studied the synthesis of a bio-based polymeric surfactant based on the collection of waste cooking oil (WCO) from a local restaurant, which having environmentally beneficial through the recycling of WCO to obtain the starting material used in the manufacture of polymeric surfactant [25]. Also, Zhang et al, reported a previous study for the usage of WCO for the synthesis of bio-based zwitterionic surfactants [26]. Grape seed oil was extracted by El-Dougdoug et al, through efficient procedures and used to prepare amphoteric surfactants that exhibited antimicrobial and antifungal properties. Furthermore, as emulsifier properties [27]. Also, El-Dougdoug et al synthesized sulfonated acrylate esters surfactants based on fatty alcohols as renewable raw materials isolated from Al-Ceder oil [28]. Due to the renewable and environmentally friendly nature of bio-based surfactants, the attention of both scientific and industrial communities has been attracted [29–34]. Also, some of the seed oils extracted from the plants, such as cotton oil, peanut oil, palm fruit oil, soybean oil, sun flower oil, pomegranate peel oil, rice brane oil, are natural sources whose extracted oil has shown promising results in several fields as in stabilizing emulsion, health beneficial effects, antiatherogenic, anticancer, antihypertensive, and used for modern medicine instead of traditional purposes, and some of them are used in food industry as anticorrosive and natural antioxidant in bioactive film or coating for various food applications [35–44].

This research aims to exploit Juagafa seed wastes, which cause a complicated problem inside factories and have little commercial value by extracting vegetable oil. After several processes for vegetable oils, a lauryl alcohol was obtained and then used to produce lauryl methacrylate as a monomer. The synthesis of copolymers of lauryl methacrylate and methacrylic acid by free radical copolymerization with different molar ratios was studied, then the synthesized copolymer was converted to a new type of cationic polymeric surfactant via efficient procedure, which may be utilized in the petroleum field. The structures of synthesized compounds were confirmed by FT-IR and ^{1}H NMR analyses.

2. Materials and experimental technique

2.1. Materials

Juagafa seeds waste was obtained from kaha company for food products and juice, Egypt. Methacrylic acid (MAA) and *N,N′*-dimethyl-1,3 propane diamine, were obtained from sigma-aldrich. *N,N′*-dicyclohexyl-carbadiimide (DCC), benzoyl peroxide (BP) was used after crystallization in methanol/chloroform. Methyl iodide and Ethyl iodide obtained from Fisher, UK. 1,4-Dioxane, Tetrahydrofuran (THF), lithium aluminum hydride (LAH), Diethyl ether, Dichloromethane (DCM), n-hexane were obtained from PLOBA. Potassium hydroxide, Methanol, Ethanol, Ethyl acetate, Sodium carbonate, Sulfuric acid, Hydrochloric acid were purchased from AL-Nasr chemical company.

2.2. Experimental technique

2.2.1. Extraction of fatty matter from Juagafa seeds

The extraction process of fatty acids from Juagafa seeds has been described in detail in our previous reported work [45]. The

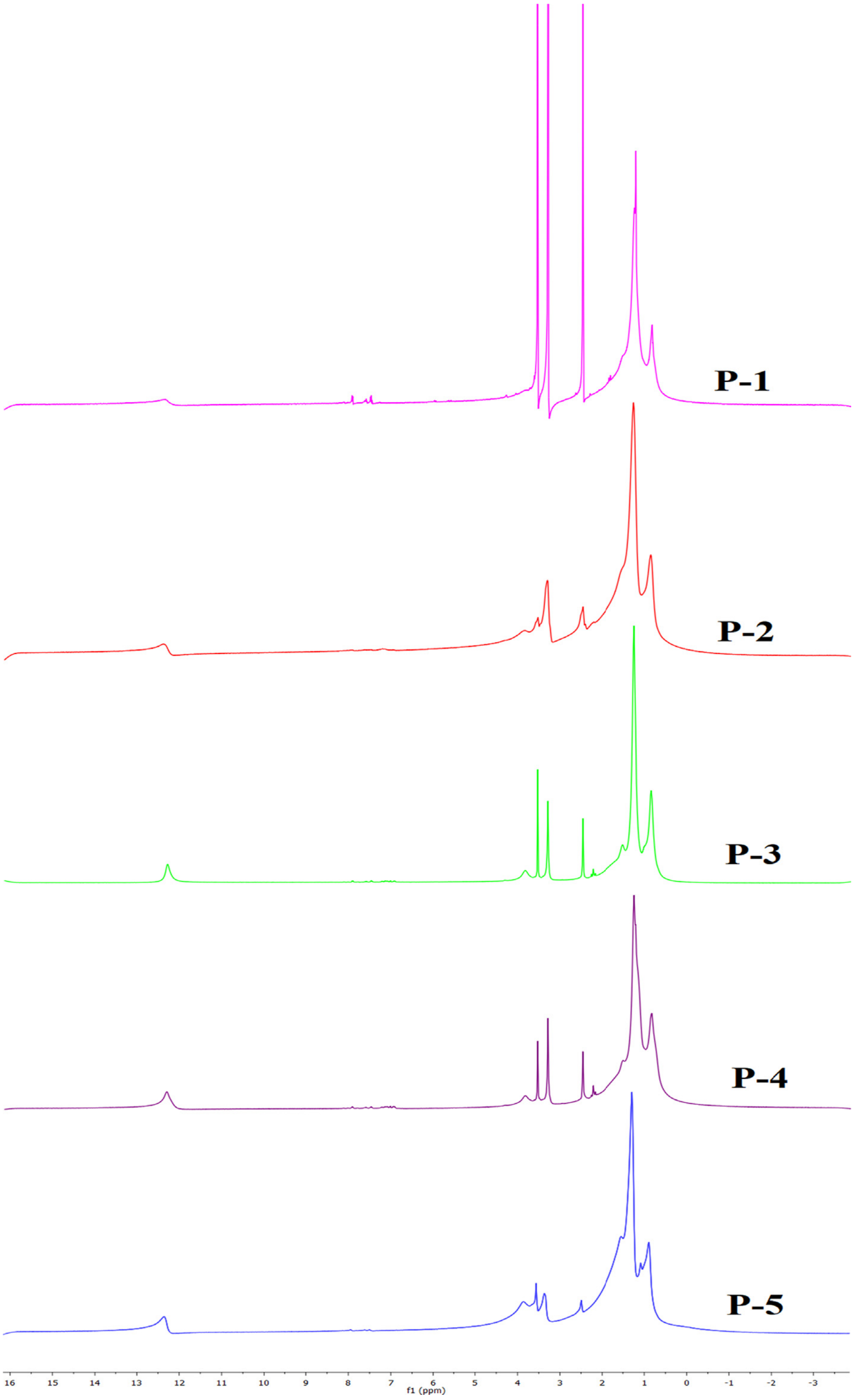

Fig. 2. ^{1}H NMR spectra of poly (LMA-co-MAA) with different ratios.

obtained fatty acids were refluxed in the presence of a methylating agent (methanol with concentrated sulfuric acid) in dry toluene. This reaction is placed in a round bottom flask and refluxed for 4 hrs until the mixture becomes a clear homogenous solution. The latter was washed by sodium carbonate to neutralize the excess of concentrated sulfuric acid, washed with distilled water, dried over sodium sulfate anhydrous, filtrate and removed the solvent to afford a mixed fatty ester of Juagafa oil as a pale yellow viscous oily product.

2.2.2. Reduction of fatty acids methyl esters and synthesis of lauryl methacrylate

According to the previous reported work, the reduction of lauric acid ester by lithium aluminum hydride (LAH) was done to produce the target lauryl alcohol [45]. In an ice bath system, dropwise of a solution of lauryl alcohol (10 mmol) dissolved in dry DCM was added to a solution of DCC (11 mmol) and methacrylic acid (10 mmol) in DCM (20 mL) with continuous stirring for 10 mins. The reaction was stirred for 4 hrs at room temperature. After this

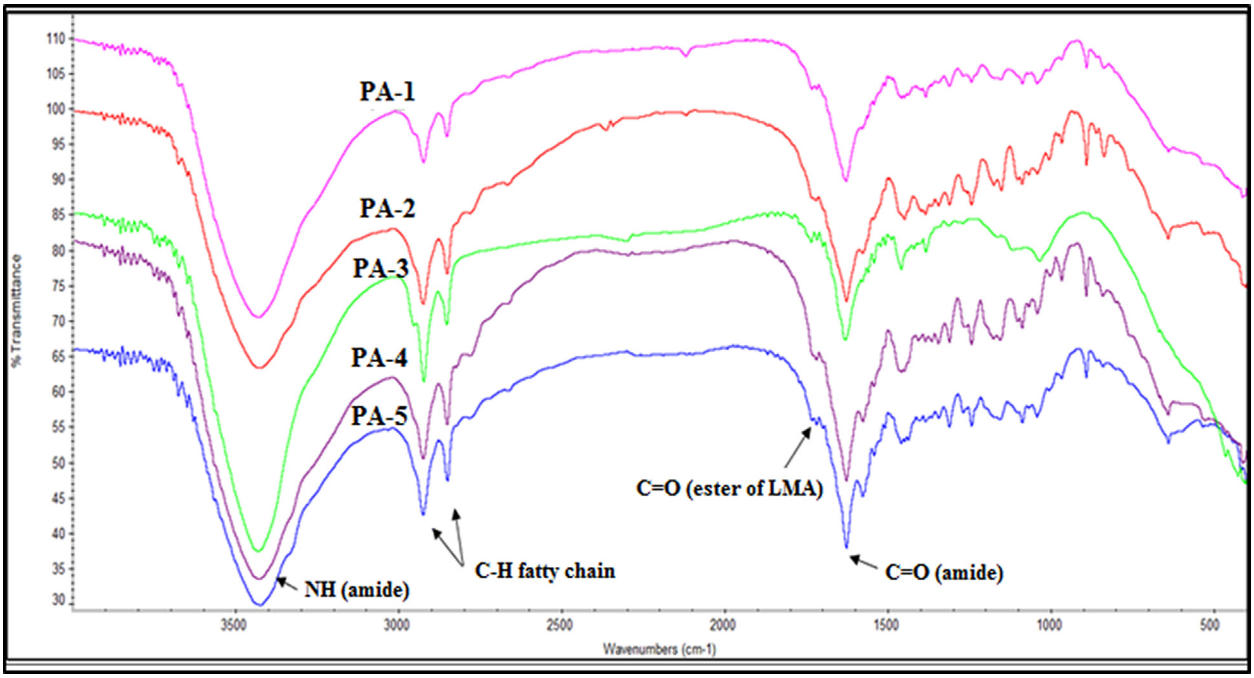

Fig. 3. FT-IR spectra of amidated poly (LMA-co-MAA) (**PA1-5**) with different ratios.

time, the reaction was filtrated to remove dicyclohexyl urea, the filtrate was concentrated under vacuum, and the LMA product was purified using silica gel as an adsorbent (eluent: DCM) in column chromatography to yield lauryl methacrylate [46]**.**

2.2.3. Copolymerization of lauryl methacrylate (LMA) and methacrylic acid (MAA)

Based on a reported procedure [46]**,** a copolymerization between lauryl methacrylate and methacrylic acid was carried out in phenol tube using benzoyl peroxide as initiator and dry 1,4-dioxane as a solvent. This mixture was heated at (70–80 °C) in water bath until the viscous liquid was obtained. The copolymer precipitates by addition of distilled water, and then it was washed several times with distilled water and diethyl ether. This copolymerization was carried out with different molar ratios to obtain copolymers (**P1-P5**) The purified copolymers were dried, grinded and characterized by FT-IR and ^{1}H NMR.

All the FT-IR spectra of poly(LMA-co-MAA) with different molar ratio (Fig. 1) showed that bands at 2926.97 and 2855.14 cm^{-1} were attributed for C-H of fatty aliphatic chain, 1702 cm^{-1} corresponding to carbonyl group of acid, 1736 cm^{-1} for carbonyl group of ester, 1171 cm^{-1} for C-O and broad band from 2800 to 3500 cm^{-1} for OH group of acid. On the other hand, all the ^{1}H NMR spectra of the copolymers (Fig. 2); ^{1}H NMR (400 MHz, DMSO d_6) showed signals at δ (ppm):0.89 ppm (t, 3H, terminal **–CH_3** for fatty chain), 1.24 ppm (m, 20H, **$(CH_2)_{10}$** for fatty chain), 1.54 ppm (s, 6H, **acrylate** group), 2.21 ppm (s, 4H, **$(CH_2)_2$** polymerized), 3.86 ppm (t, 2H, **CH_2-O** for methylene group in ester), 12.35 ppm (s, H, –**COOH** of acid).

2.2.4. Amidation of poly (LMA-co-MAA) (PA1-5)

According to the procedure [47]**,** the poly(LMA-co-MAA) was amidated with *N,N*'-dimethyl-1,3-propane diamine. This reaction is placed in round bottom flask and refluxed for 48 hr at 60 °C with continuous stirring. The modified copolymer was precipitated in diethyl ether. After this, the amidated copolymers of poly(LMA-co-MAA) were washed with diethyl ether several times and dried at room temperature. All the above processes were carried out with the copolymer having different molar ratios. The obtained modified copolymers (**PA1-5)** were confirmed by FT-IR and ^{1}H NMR.

The obtained FT-IR spectra of the modified copolymers of poly (LMA-co-MAA) (**PA1-5)** (Fig. 3) showed that bands at 2929.10 and 2851.57 cm^{-1} attributed for C-H of fatty aliphatic chain, 1721 cm^{-1} corresponding to carbonyl group of ester, 1244 cm-1 for C-O, 1626.90 cm^{-1} for carbonyl group of amide. The broad band in the region of 2800–3500 cm^{-1} for υO-H of acid is disappeared, this is due to the appearing of 3327.94 cm^{-1} for single υN-H of primary amide. On the other hand, all ^{1}H NMR spectra of the modified copolymers (**PA1-5)** (Fig. 4) showed signals at δ (ppm): ^{1}H NMR (400 MHz, DMSO d_6); 1.03 ppm (t, 3H, terminal –CH_3 for fatty chain), 1.7 ppm (m, 2H, middle CH_2 in amine, 1.26 ppm (m, 20H, $(CH_2)_{10}$ for fatty chain), 1.26 ppm (s, 6H, $2CH_3$ of acrylate group), 1.78 ppm (s, 4H, $2CH_2$ -C polymerized), 2.14 ppm (s, 6H, $2CH_3$ terminal in $2CH_3$-N (R), 2.25 ppm (t, 2H, CH_2-N$(CH_3)_2$), 3.2 ppm (t, 2H, CH_2-NH), 3.94 ppm (t, 2H, O-CH_2). Also, the disappearance of peak at 12.35 ppm (s, H, –COOH of acid), is due to the appearing of 8.25 ppm (s, H, N-H of amide)**.**

2.2.5. Quaternization of the modified copolymers of poly(LMA-co-MAA)

In a closed system, the modified copolymer is converted to a cationic copolymeric surfactant by reacting the modified copolymer in the absence of solvent with an excess amount of alkyl halide (methyl and ethyl iodide). The mixtures were heated at (70–80 °C) for 96 hr with stirring. The as-prepared products (**PSM-PSE**) were purified via washing with diethyl ether three times to separate all unreacted substances. The structures of as-prepared copolymeric surfactants (**PSM, PSE**) were confirmed by FT-IR spectrum that revealed strong absorption bands of the 1,3- dialkylammonium cation [48] at 1461, 1252 and 1160 cm^{-1}. The strong a broad peak at 3440 cm^{-1} is returned to the absorbed water molecules in the investigated compound, showing the strongly hygroscopic nature of synthesized molecules as shown in Fig. 5**A, B.** Also, ^{1}H NMR spectra of the as-prepared copolymeric surfactants as **PSM-5** and

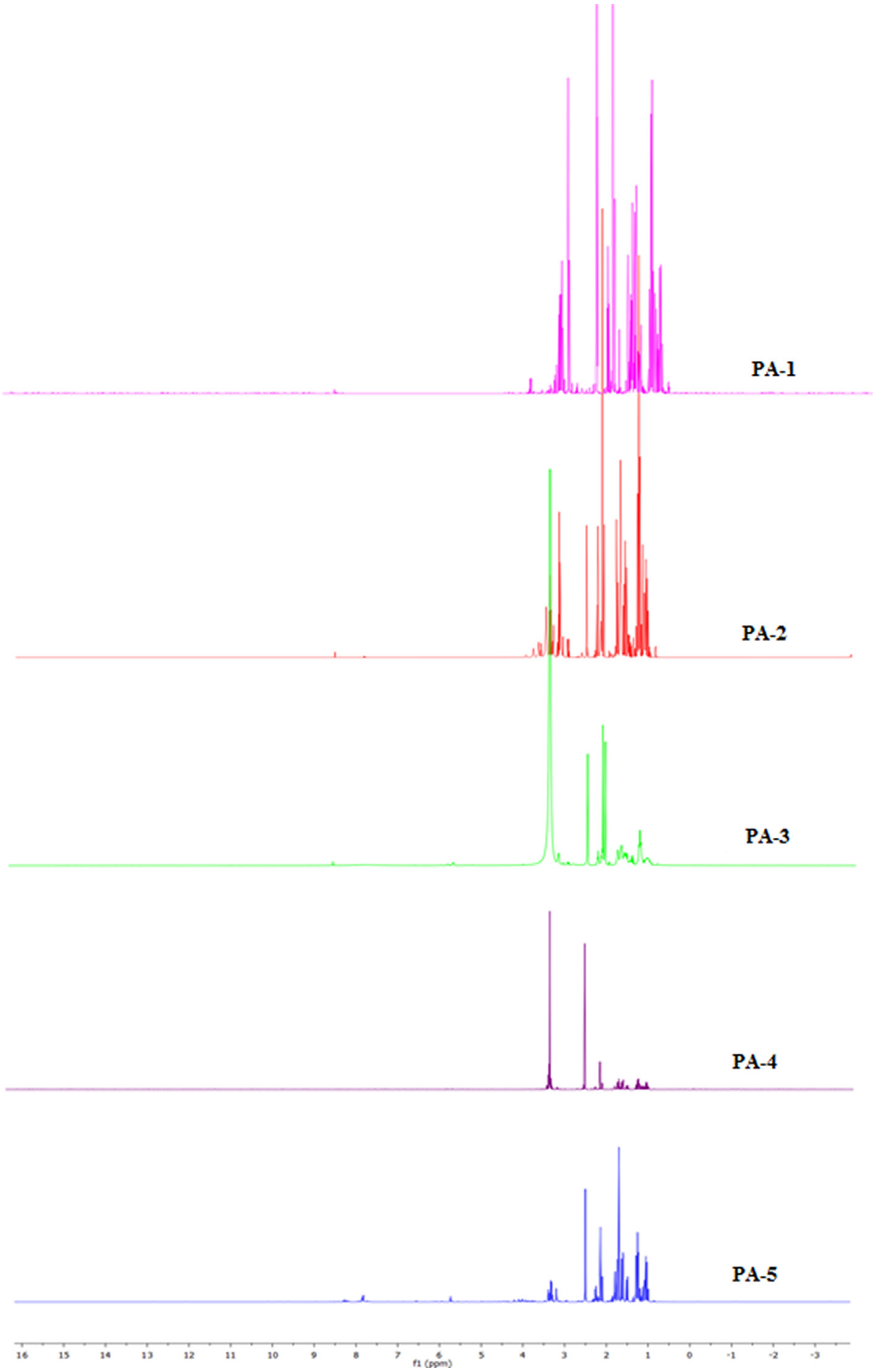

Fig. 4. ^{1}H NMR spectra of amidated poly (LMA-co-MAA) (**PA1-5**) with different ratios.

PSE-5 was carried out. Whereas, the ^{1}H NMR (400 MHz, D_2O) of **PSM-5** showed a new band at 3.22 ppm (S, 3H, N^{+}–CH_3) (**Figure S5**, **A**). As well as, the ^{1}H NMR (400 MHz, D_2O) of **PSE-5** showed new bands at 1.21 ppm (m, 3H, N^{+}–$CH_2\underline{\mathbf{CH_3}}$), 3.42 ppm (m, 2H, N^{+}–$\underline{\mathbf{CH_2}}$-$CH_3$), (**Figure S5**, B).

2.3. Surface-active properties

2.3.1. Surface tension and electrical conductivity measurements

The surface tension values of freshly prepared solutions of the synthesized copolymeric surfactants were determined at 25 °C via a Kruss-K6 tensiometer. Whereas, at the ancient temperature, copolymeric surfactant solutions were kept for one day to achieve a balance. Before each measurement, the use of distilled water several times was done to clean the platinum ring and remove the residual sediment on the surface. Three readings values were recorded for each sample to verify repeatability and to generate an average value.

Also, a conductivity meter “model type AD3000; EC/TDS and temperature meter” at 25 °C was used to measure the values of electrical conductivity of the generated copolymeric surfactant solutions. Before the measurements, all prepared copolymeric surfactants solutions were carried out with ultrapure water keeping for at least one day and each electrical conductivity value is an

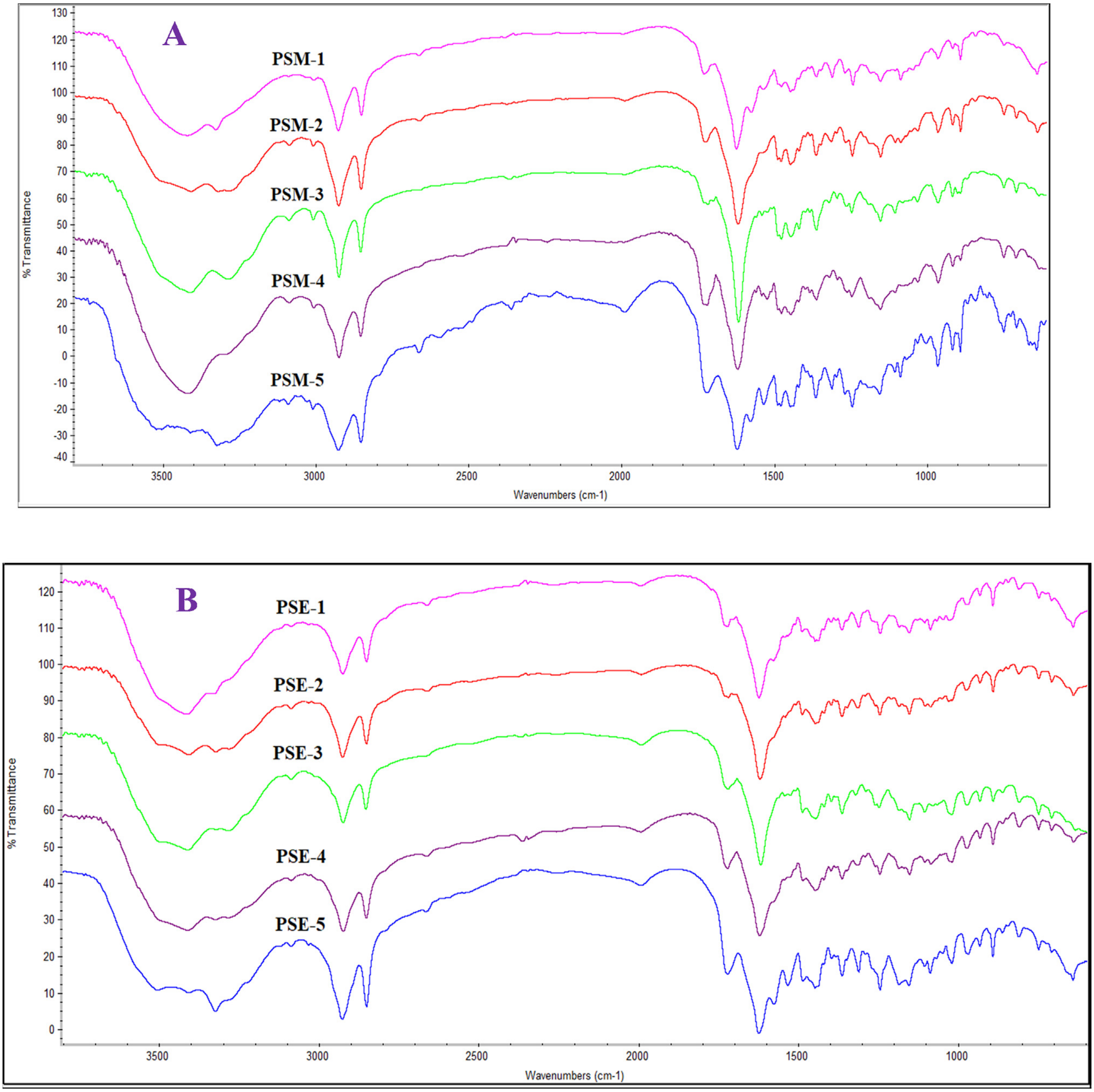

Fig. 5. FT-IR spectra of a) **PSM-1**: **PSM-5** and b) **PSE-1**: **PSE-5.**

average value of three measurements to decrease data errors as reported in our previous work [49].

2.3.2. Foaming power and emulsifying stability

Based on previous reported procedures [46], the foaming power and the stability of the foam of the as-prepared copolymeric surfactant solution was determined. Also, the strength of as-prepared copolymeric surfactants to form a stable emulsion (emulsion stability) was represented by the time required to separate 6 mL of the pure synthesized surfactant solution from the paraffin oil phase.

2.3.3. Petroleum-collecting and petroleum-dispersing capacities

Copolymeric surfactants (in the pure state and in the 2.5 wt% aq solution form) were studied for their collecting/ dispersing actions toward petroleum thin slicks. The crude oil from the South Sinai (Egypt) oil fields was utilized ("kinematic viscosity and density" at 20 °C are 0.13 cm^2/s and 0.84 g/cm^3, respectively). Calculation was done using the method described in the literature [50,51]. The pure state of prepared copolymeric surfactant (0.01 g) or its aqueous solution (2.5%) was taken to add to a petroleum thin film (thickness ≈ 0.15 mm) of the petroleum crude oil on the tested waters' surface (distilled, fresh (river), and red sea) in Petri dishes. Through the relationship $K = S_o/S$, petro-collecting factor (K) was calculated, whereas S_o is the surface area of the petroleum thin film at the beginning of the test, S denotes the surface area of the petroleum spot formed under the action of the prepared surfactant. During the observations, the surface area of the spot was measured periodically, K-values were computed for these specific time intervals (τ). Petro-dispersing ability (K_D) was calculated by the degree of cleaning of polluted water surface from petroleum which was calculated as a percentage of clean water surface areas and the initial area of the petroleum film.

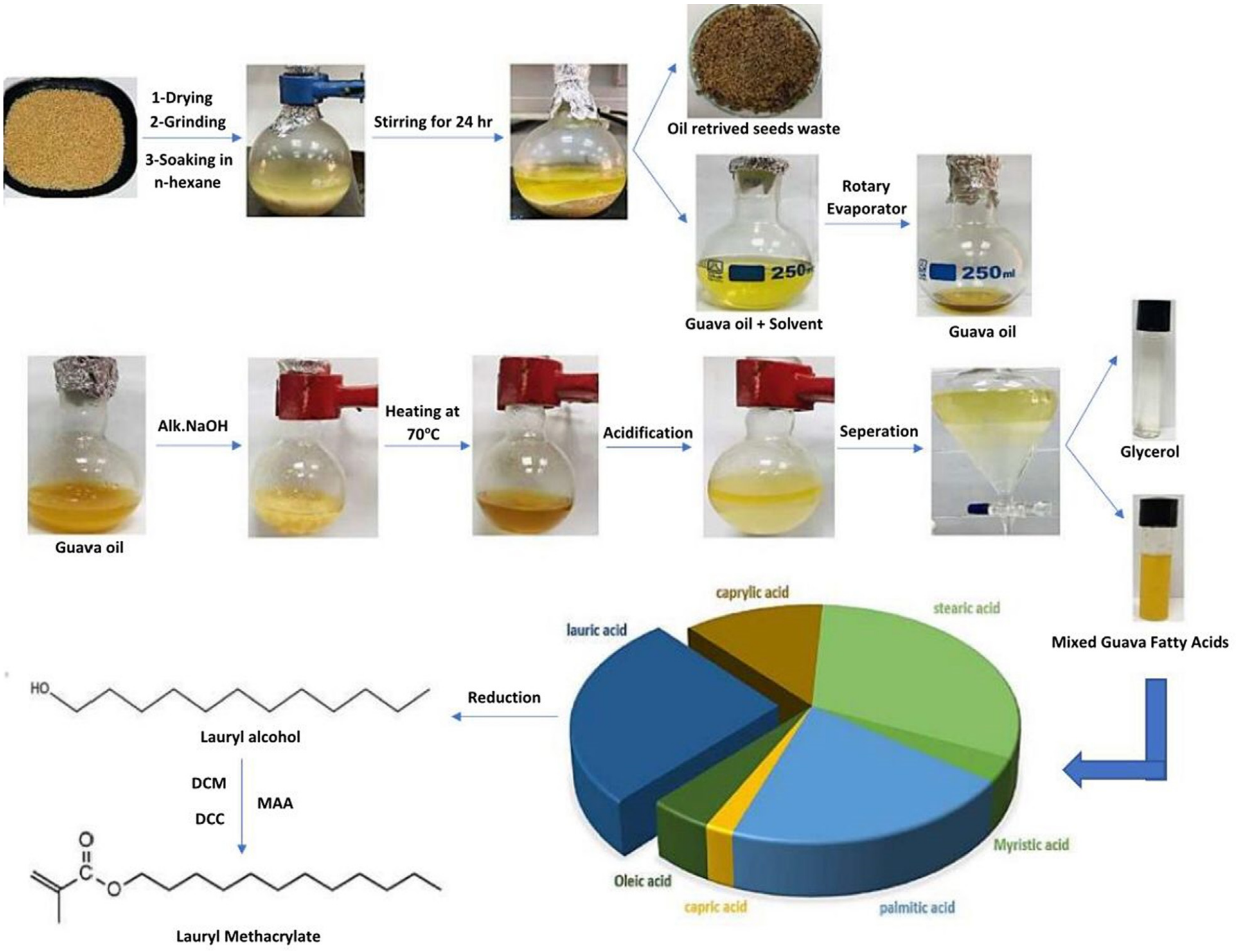

Fig. 6. Synthetic route for the preparation of lauryl methacrylate.

2.4. Characterization technique

The synthesized compounds were assured by run on FT-IR spectra recorded in KBr on a thermo Nicolet IS10 FT-IR spectrophotometer. Also, Nuclear magnetic resonance spectroscopy (^{1}H NMR) was carried out by Bruker Avance 400 MHz signal and 4000 gauss magnetic field (Switzerland) in DMSO as solvent and using tetra methyl silane (TMS) as an internal reference.

3. Result and discussion

3.1. Synthesis

As noted in **scheme 1**, new series of cationic copolymeric surfactants were synthesized based on the following steps. Initially, the separation of lauric acid from guava seeds, followed by the esterification and reduction processes to form lauryl alcohol. Secondly, lauryl alcohol was reacted with **MAA** in the presence of DCC to obtain lauryl methacrylate as a starting monomer for the polymerization process as shown in Fig. 6 and Fig. 7. At different series of molar ratios, copolymerization between lauryl methacrylate (LMA) and methacrylic acid was carried out to generate copolymeric compounds (**P1-P5**) and their structures were elucidated. In the next step, the synthesized **poly(LMA-co-MAA)** with different molar ratios were amidated with *N,N*′-dimethyl-1,3- propane diamine according to the method described in [47] to form the corresponding amide compound (**PA1-5)**. The quaternization process of the obtained modified copolymers of poly (LMA-co-MAA) (**PA1-5)** was done by reaction with alkyl halides (methyl iodide, ethyl iodide) to give new cationic copolymeric surfactants (**PSM, PSE**). The structures of synthesized compounds were elucidated via various spectroscopic tools.

3.2. Molar reactivity ratio

The compositions of the prepared copolymers were estimated by ^{1}H NMR spectroscopic data as the method described previously [52–54]**.** In this study, ^{1}H NMR spectroscopy was employed to quantitatively analyze for these copolymers. To calculate the relative moles of each monomer, the resonance area that represents the monomer component must be calculated, followed by subtracting any interferences and then dividing that area by the number of protons per monomer component. The results are shown in Table 1**.**

Both methods of the Fineman-Ross (FR) [55] and the Kelen Tüdös (KT) [56] were applied to study the reactivity ratios between LMA with MAA in the copolymerization process. The equation of FR is showed as followed:

$$F\,(f-1)/f = (F^2/f)\, r_1 - r_2$$

where, F and f represent the molar ratios of the monomers in the feed and in the copolymer, respectively. By plotting F(f-1)/f vs. F^2/f, straight line was obtained, which r_1 and r_2 were obtained from the slope and the intercept, respectively.

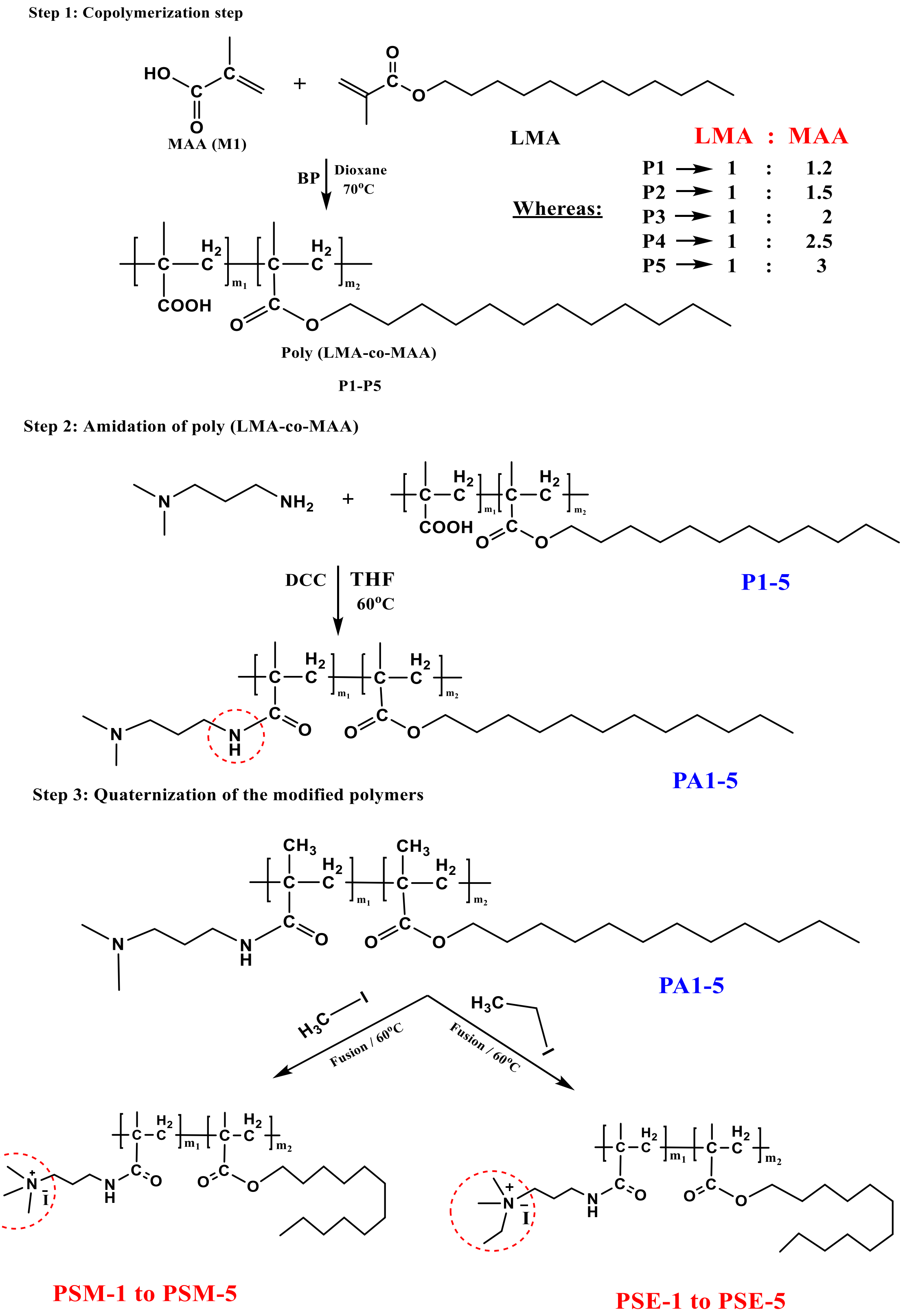

Fig. 7. General scheme for synthetic procedure of copolymeric surfactants.

Table 1
Analytical data for copolymerization of LMA with MAA with different ratios by using ^{1}H NMR.

Compound No.	Feed composition, F	Copolymer composition, f
P-1	1.21	0.64
P-2	1.50	0.76
P-3	2.07	0.94
P-4	2.51	1.11
P-5	2.95	1.18

F = M1/M2 in the feed composition.
f = m1/m2 in the copolymer composition.

KT equation includes an arbitrary constant with the goal of equally separating the data while also allowing all points to have the same statistical weight, and is written as:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

where

$$\eta = (F^2/f)/(F^2/f + \alpha),\ \xi = F^2/(\alpha f + F^2)$$

$$\alpha = F_{\min} * \frac{F_{\max}}{(f_{\min} * f_{\max})^{1/2}}$$

Using both FR and KT methods, the monomer reactivity ratios were estimated using the monomer fractions in the feed as well as the composition of the copolymers as already stated in (Table 1), Fineman–Ross (Fig. 8**A**) showed that $r_1 = 0.2268 \pm 0.02$ and $r_2 = 1.1594 \pm 0.11$, while Kelen–Tüdös reported $r_1 = 0.2346 \pm 0.05$, $r_2 = 1.1937 \pm 0.25$ (Fig. 8**B**). The r_1r_2 value for LMA-co-MAA equals 0.28, which implies that the monomer units in a copolymer should be distributed randomly. Also, the composition curve for the copolymerization of LMA with MAA was showed in Fig. 8**C**.

3.3. Critical micelle concentration

Surface tension is the most important feature among the surface-active indices of copolymeric surfactant solutions. **Figures S1 and S2** depicted the relationship between surface tension (γ) and concentration of the as-prepared copolymeric surfactant at 25 °C. These figures show that the initial elevation of the concentration results in a sudden drop in the surface tension value of the surfactant solution. However, a slow decrease in the γ values occurred at the break point, referring to the accumulation process of surfactant molecules to generate aggregates. The value of the as-prepared copolymeric surfactant concentration at the breakpoint is noted as the CMC of the synthesized copolymeric surfactants. The recorded values of CMC of the as-prepared copolymeric surfactants are noted in Fig. 9. As shown in Fig. 9, the most significant values for copolymeric surfactants are 0.024, 0.052, and 0.059% for **PSM-1, PSM-4** and **PSE-4**, respectively.

Figure S3 and S4 display the relationship between the concentration of the as-prepared copolymeric surfactant solutions and the electrical conductivity (K). In each plot, the intersection at the point CMC was acquired from two lines with various slopes. The calculated CMC values from the figures were registered and drawn as shown in Fig. 9**.** Finally, as noted in Fig. 9**,** it was seen that the CMC values generated from "surface tension" measurements approach those acquired from "electrical conductivity" measurements.

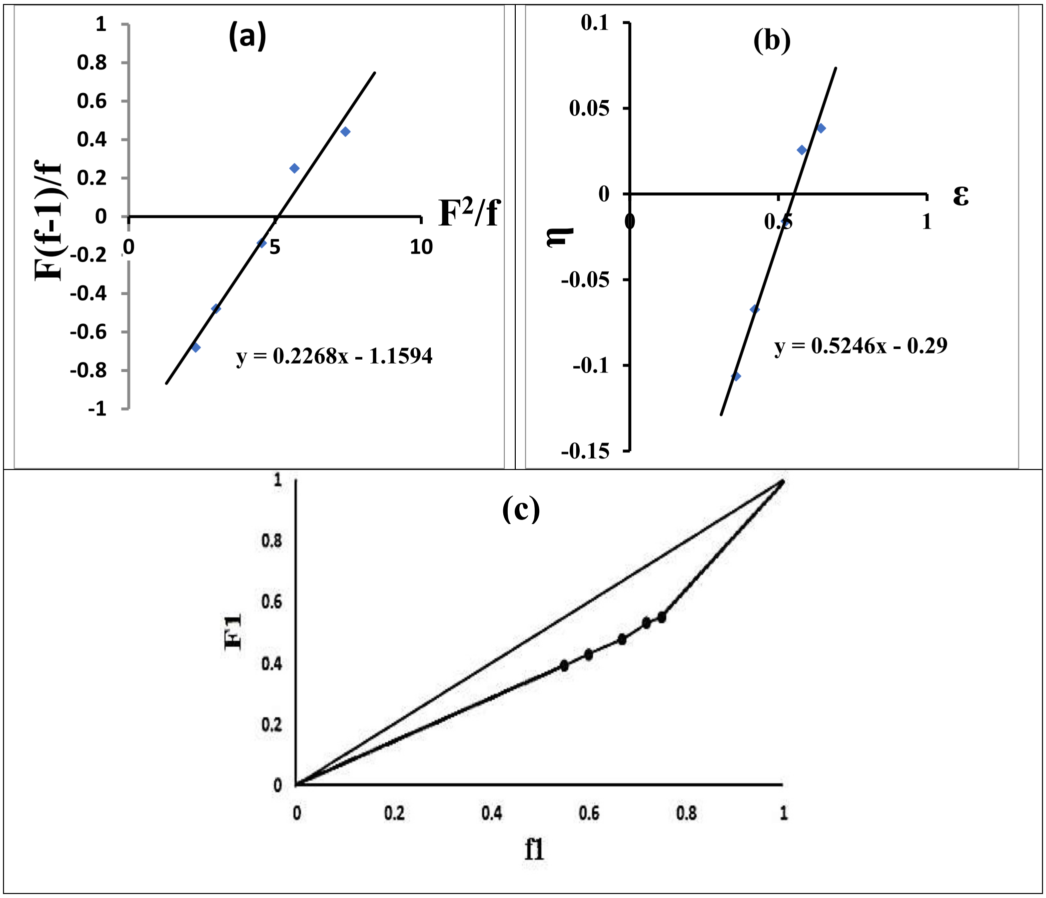

Fig. 8. (a) Finemen-Ross plot, (b) Kelen-Tüdös plot for copolymerization and (c) Composition curves for copolymerization of LMA with MAA.

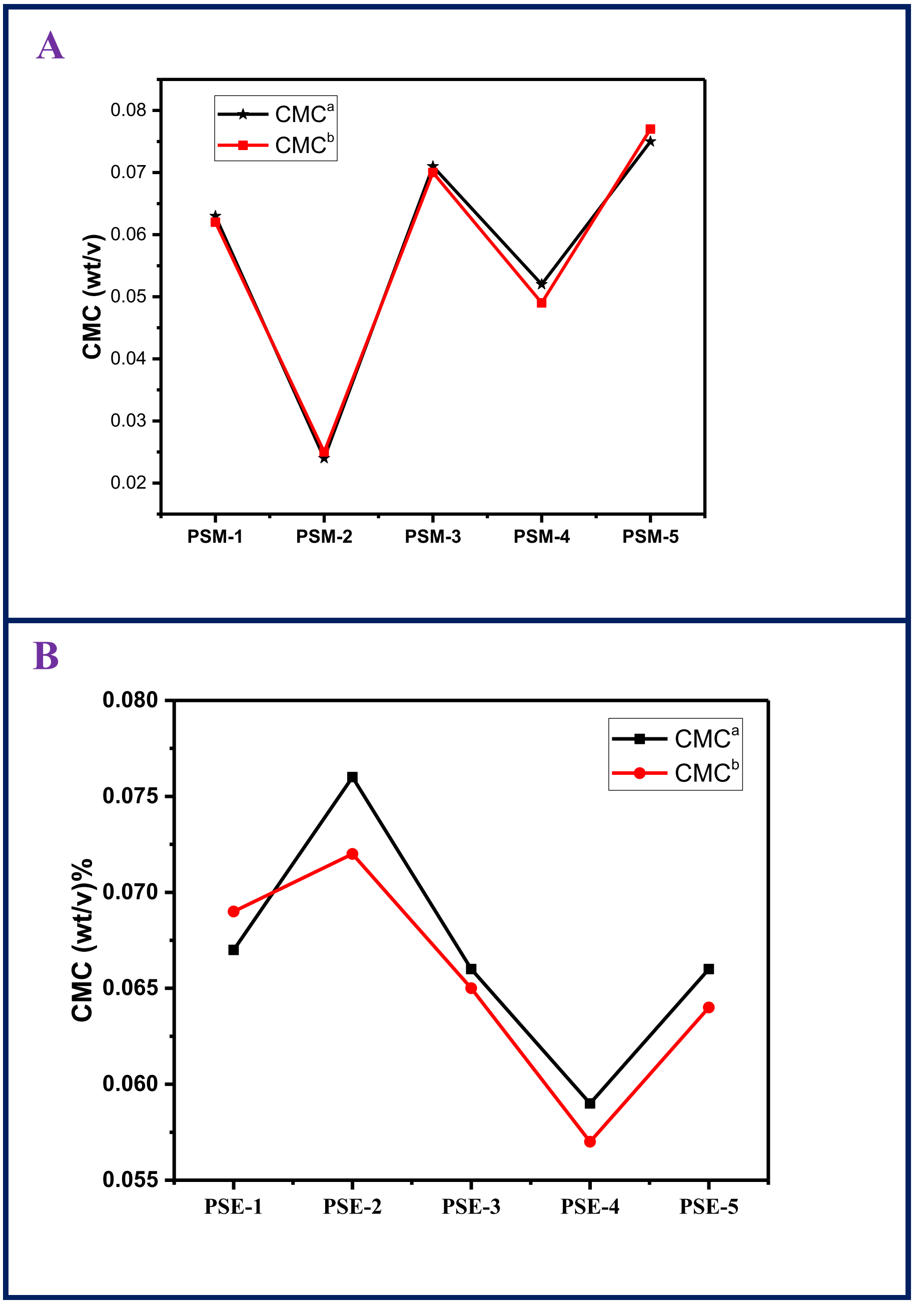

Fig. 9. CMC Values versus molar ratios of synthesized polymeric surfactants, **a) PSM-1** to **PSM-5**; **b) PSE-1** to **PSE-5**. (CMC^a by surface tension; CMC^b by electrical conductivity).

3.4. Emulsifying power

The tendency of the copolymeric surfactant solutions to produce oil/water or water/oil emulsions reflects the tendency of as-prepared surfactant molecules to locate on the border surfaces between the diverse phases. Thus, the active particles of the most absorbing surface at the interface are the most powerful emulsion factors. The efficiency of the emulsion in this study was measured as the required time for removing 6 mL of fresh water from the emulsion that consists of the surface solution (0.5 % wt) and paraffin oil (4 mL). The stability of the emulsion is shown by how long it takes to separate the desired amount of water from the emulsified system, and vice versa.

According to Fig. 10, the greater the emulsion stability value, the longer **PSM-4** and **PSM-5** need to remove a required volume of H_2O than the other as-prepared compounds, the preferable stability of the O/W emulsions can be. Interestingly, it is noticed in Fig. 10 that the emulsion stability values increase by increasing the molar ratio of the targeted copolymeric surfactants up to **PSM-4** and **PSE-3**, where the values begin to decrease in the remaining molar ratios. The technology of “emulsion formation” is the most significant in various applications, particularly paints, drug formulations, and cosmetics.

3.5. Foaming properties

Foaming properties are utilized to control the commercial application capacity of the as-prepared copolymeric surfactants. The as-prepared compounds showed relatively elevated foaming heights. The copolymeric surfactant solutions exhibited high foam-

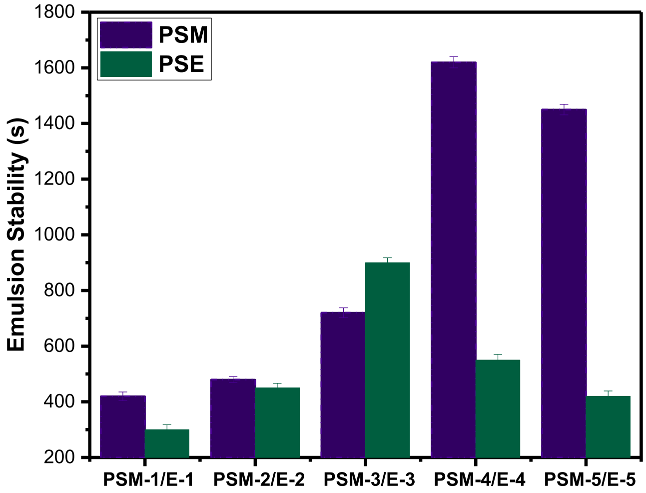

Fig. 10. Emulsion stability and polymeric surfactant solutions (Molar ratios).

ing volumes varying from 150 to 200 mL for **PSM-1 to PSM-5** and were the best foaming agents and foam stabilizers among all the as-prepared copolymeric surfactants as shown in Fig. 11 **and Table S1**. The as-prepared surfactant solutions exhibited moderate foaming volumes varying from 75 to 150 mL for **PSE-1 to PSE-5** as shown in Fig. 11**.** For copolymeric surfactants, the adsorption process of surfactant molecules on the interface is a diffusion-controlled process with low times, small adsorption, and without interaction among the adsorbent and adsorbent macromolecules. Furthermore, the presence of charged substituents groups or higher hydrophilic can increase this absorption via raising the area per molecule and forming a lower cohesive force on the surface. Consequently, PSM compounds exhibit better foam-producing ability and foam stability, and PME behaves conversely.

3.6. Petro-collecting / petro-dispersing capacities of the as-prepared copolymeric surfactants.

Water surface pollution by oil slicks was carried out through accidents of oil pipelines, oil-carrying tankers, and oil leaks during the drilling period [57]**.** Various mechanical methods are used to remove thick oil slicks, but after the removing procedures, the thin petroleum films are still on the water surface. These thin petroleum films are very dangerous from an environmental point of view as they lead to the deterioration of the oxygen uptake by the water and the penetration of sunlight into the depth of the water, which leads to a negative effect on the life activity of marine flora and fauna. The most convenient method of removing thin petroleum films is the application of petro-collecting and dispersing agents [58]**.**

Under laboratory conditions, studies of the petro-collecting and dispersing indices of the as-prepared copolymeric surfactants were done using pure state solids and 2.5% wt. aqueous solutions of the copolymeric surfactants on the example of thin (thickness 0.17 mm) film of red sea crude oil on the surface of three different waters including the distilled, fresh, and sea. The recorded results of the petro-dispersing and petro-collecting properties of the as-prepared copolymeric surfactants are listed in Table 2. Notably, all synthetic copolymeric surfactants were unstable in solid form to improve petro-dispersing and collecting capacities.

The results showed that in waters of a different mineralization degree, most of the synthesized copolymeric surfactants under investigation exhibit lower petroleum effects in a solid-state form compared to in the diluted form. In contrastly, it is noticeable that on the surface of the sea water, **PSE-2** and **PSE-1** gave good petroleum effects in undiluted form, whereas k_D = 72.12%, τ = 30–96 h; k_D = 73.44%, τ = 30–96 h, respectively. By the action of the 2.5% aqueous solution of **PSE-1** and **PSE-3**, the collection of petroleum occurred in distilled water, whereas K_{max} = 12.01, τ = 30–96 h; K_{max} = 9.32, τ = 5–96 h, respectively. In the fresh water, **PSE-3** and **PSE-4** showed excellent petroleum-dispersing action in diluted form, whereas k_D = 96.65%, τ = 60–96 h; k_D = 83.21%, τ = 60–96 h, respectively. Also, in the case of 2.5% aqueous solution of **PSE-2** and **PSE-5**, a good dispersing of petroleum is observed in fresh water whereas k_D = 80.21%, τ = 60–96 h; k_D = 79.89%, τ = 60–96 h, respectively but **PSE-1** compound exhibit a moderate petroleum-dispersing effect (k_D = 73.66%, τ = 60–96 h). On the whole, in sea water, the aqueous solution of synthesized copolymeric surfactants **PSE-3, PSE-2, PSM-3** and **PSE-1** are strong petro-dispersing agents, whereas k_D = 96.11%, τ = 30–96 h; k_D = 91.22%, τ = 30–96 h, k_D = 85.75%, τ = 30–96 h, k_D = 85.22%, τ = 30–96 h, respectively. But **PSM-2** aqueous solution gave a good dispersing of petroleum film in sea water (k_D = 70.56%, τ = 30–96 h) and a moderate dispersing of petroleum of **PSM-1** and **PSM-4** are observed, whereas k_D = 51.34%, τ = 70–96 h; k_D = 50.11%, τ = 5–96 h, respectively.

Regarding the petroleum-structure capacity relationship, synthesized copolymeric surfactants with the ethyl substituted group exhibited the highest petroleum-dispersing capacities compared to the methyl-substituted group, especially in seawater and in the case of 2.5% aqueous solution. Interestingly, as observed in Fig. 12, the dispersing of petroleum slicks is increased in seawater as the molar ratio increases, and this is observed especially in seawater and in diluted form. Then the dispersing effect reaches a maximum value in the case of **PSM-3** and **PSE-3** and the effect starts to decrease in the case of **PSM-4** and **PSM-5, PSE-4** and **PSE-5.** This may be due to increasing the molar ratio, leads to increasing the polar hydrophilic groups compared to the hydrophobic part. The solubility increases until it reaches a certain degree at which the effect begins to decrease. Finally, the results can be summarized in two points: ethyl substituted compounds have better effects than methyl substituted ones, especially in sea water and diluted form, and the best molar ratio that gave excellent dispersion of petroleum is **PSM-3** and **PSE-3**.

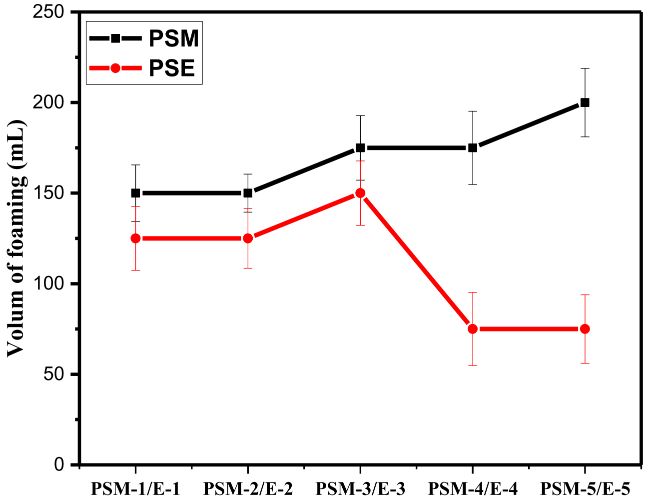

Fig. 11. The volume of foam and polymeric surfactant solutions (Molar ratios).

Table 2
Petro-collecting/dispersing properties of the synthesized polymeric surfactants (**PSM** and **PSE**).

Compd. No.	Undiluted product						2.5% wt. water solution					
	Distilled water		Fresh water		Sea water		Distilled water		Fresh water		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)
PSM-1	0–2	NE[a]	0–2	NE[a]	0–2	NE[a]	0–2	5.29 ± 0.9	0–2	3.29 ± 0.7	0–2	NE[a]
	30	3.91 ± 0.8	20	2.84 ± 0.9	5–20	3.91 ± 1.1	30	6.27 ± 1.2	30	4.30 ± 1.8	20	30.23 ± 2.3%
	60–96	4.17 ± 1.0	25–96	5.70 ± 0.5	30–60	3.30 ± 0.3	48–96	7.73 ± 1.6	40–60	6.17 ± 1.1	40–60	44.36 ± 2.3%
	–	–	–	–	70–96	4.1 ± 0.7	–	–	70–96	8.36 ± 1.9	70–96	51.34 ± 1.7%
PSE-1	0–2	2.76 ± 0.8	0–2	30.13 ± 2.3%	0–2	65.27 ± 1.3%	0–2	6.21 ± 0.7	0–2	65.27 ± 2.3%	0–2	63.17 ± 1.3%
	2–55	4.44 ± 0.1	30–60	40.21 ± 1.5%	5–20	68.02 ± 2.3%	5–20	8.32 ± 0.6	30–60	68.02 ± 1.6%	5–20	72.32 ± 2.3%
	60–96	6.23 ± 0.3	60–96	45.43 ± 2.5%	30–96	73.66 ± 2.7%	30–96	12.01 ± 0.2	60–96	73.66 ± 1.9%	30–96	85.22 ± 2.5%
PSM-2	0–2	1.67 ± 0.1	0–2	2.40 ± 0.3	0–2	32.11 ± 2.5%	0–2	6.77 ± 0.8	0–2	6.40 ± 0.3	0–2	40.23 ± 1.3%
	2–55	3.11 ± 0.2	30–60	NC[b]	5–20	39.31 ± 1.8%	2–55	NC[b]	30–60	NC[b]	5–20	45.22 ± 2.1%
	60–96	5.19 ± 0.7	60–96	NC[b]	30–96	41.42 ± 1.3%	60–96	NC[b]	60–96	NC[b]	30–96	70.56 ± 2.4%
PSE-2	0–2	2.32 ± 0.8	0–2	33.77 ± 2.1%	0–2	62.37 ± 2.3%	0–2	6.76 ± 1.0	0–2	62.37 ± 1.6%	0–2	73.17 ± 1.4%
	2–55	5.21 ± 0.1	30–60	56.23 ± 2.7%	5–20	72.12 ± 2.6%	5–20	8.23 ± 0.1	30–60	72.12 ± 2.1%	5–20	88.32 ± 2.3%
	60–96	7.25 ± 0.3	60–96	NC[b]	30–96	NC[b]	30–96	NC[b]	60–96	80.21 ± 1.8%	30–96	91.22 ± 2.7%
PSM-3	0–2	1.67 ± 0.1	0–2	2.40 ± 0.3	0–2	32.11 ± 1.3%	0–2	6.77 ± 0.8	0–2	6.40 ± 0.3	0–2	54.54 ± 1.3%
	2–55	3.11 ± 0.2	30–96	NC[b]	5–20	39.31 ± 1.9%	2–96	NC[b]	30–96	NC[b]	5–20	74.43 ± 2.6%
	60–96	5.19 ± 0.7			30–96	41.42 ± 2.5%					30–96	85.75 ± 2.1%
PSE-3	0–2	4.55 ± 0.5	0–2	35.11 ± 1.7%	0–2	NE[a]	0–2	2.21 ± 0.7	0–2	77.37 ± 1.4%	0–2	45.24 ± 1.8%
	2–55	5.87 ± 0.6	30–60	47.6 ± 2.3%	5–20	33.12 ± 2.3%	5–20	9.32 ± 0.6	30–60	89.35 ± 2.4%	5–20	75.89 ± 1.5%
	60–96	NC[b]	60–96	60.44 ± 2.7%	30–96	NC[b]	30–96	NC[b]	60–96	96.65 ± 2.9%	30–96	96.11 ± 1.3%
PSM-4	0–2	1.50 ± 0.1	0–2	2.40 ± 0.3	0–2	32.11%	0–2	4.67 ± 0.8	0–2	5.41 ± 0.3	0–2	42.44 ± 1.7%
	2–96	6.20 ± 0.2	30–96	NC[b]	5–96	NC[b]	2–96	NC[b]	30–96	NC[b]	5–96	50.11 ± 2.1%
PSE-4	0–2	3.22 ± 0.5	0–2	30.33 ± 1.4%	0–2	25.55 ± 1.8%	0–2	2.21 ± 0.7	0–2	65.30 ± 2.6%	0–2	30.22 ± 2.4%
	2–55	4.6 ± 0.6	30–60	42.21 ± 1.8%	5–96	32.12 ± 2.8%	5–20	7.55 ± 0.6	30–60	75.43 ± 2.5%	5–20	35.55 ± 1.6%
	60–96	NC[b]	60–96	55.33 ± 2.5%			30–96	NC[b]	60–96	83.21 ± 1.7%	30–96	68.54 ± 2.6%
PSM-5	0–96	5.12 ± 0.2	0–2	NE[a]	0–2	30.12 ± 1.3%	0–2	3.01 ± 0.8	0–2	2.33 ± 0.3	0–2	33.56 ± 1.3%
			30–96	1.67 ± 0.8	5–96	NC[b]	2–96	NC[b]	30–60	4.11 ± 0.3	5–20	39.82 ± 2.6%
									60–96	NC	30–96	43.67 ± 1.1%
PSE-5	0–2	4.11 ± 0.5	0–2	32.45 ± 2.3%	0–2	NE[a]	0–2	2.11 ± 0.7	0–2	60.45 ± 1.4%	0–2	30.55 ± 1.7%
	2–96	NC[b]	30–96	50.44 ± 2.7%	5–96	31.55 ± 1.3%	5–20	5.34 ± 0.6	30–60	71.66 ± 2.3%	5–20	33.67 ± 1.8%
							30–96	NC[b]	60–96	79.89 ± 2.8%	30–96	43.93 ± 2.4%

NE[a] = No Effect, NC[b] = No Change.

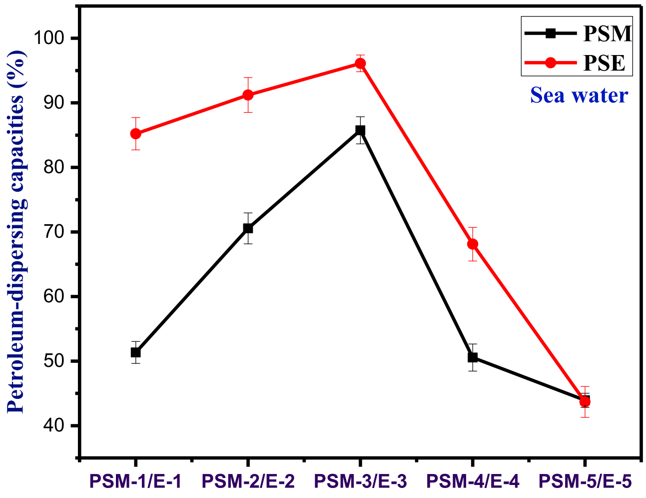

Fig. 12. Petroleum-dispersing of synthesized polymeric surfactants (Ethyl and Methyl substituents) in sea water and diluted form (%) towards molar ratio of polymerization process.

4. Conclusion

The present study reported the synthesis of novel cationic copolymeric surfactants (**PSM** and **PSE**) with good petroleum dispersing capacities in diluted and undiluted forms in waters of different mineralization degrees. The structures of synthesized copolymeric compounds based on materials obtained from natural wastes (Juagafa seed) were elucidated by FT-IR and ^{1}H NMR spectra. ^{1}H NMR spectrum was employed to quantitatively analyze of copolymers. Reactivity ratios of LMA with MAA in the copolymerization were estimated by both FR and KT methods. The data obtained from FR and KT showed that the randomly distributed monomer units in a copolymer. The values of CMC of as-prepared copolymeric surfactants were estimated using electrical conductivity and surface tension methods, in which the obtained values are very close to identical. Interestingly, the results of petroleum-collecting and dispersing properties studies revealed that ethyl substituted compounds have better effects than methyl substituted ones, especially in sea water and diluted form, and the best molar ratio that gave excellent dispersion of petroleum is **PSM-3** and **PSE-3**.

CRediT authorship contribution statement

Fahmy Adel: Investigation, Methodology, Resources, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Abdel-Fattah F. Shaaban:** Supervision, Conceptualization, Investigation, Methodology, Resources, Formal analysis, Data curation, Funding acquisition, Writing – original draft, Writing – review & editing. **Wagdy El-Dougdoug:** Supervision, Investigation, Methodology, Resources, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Ahmed H. Tantawy:** Supervision, Conceptualization, Investigation, Methodology, Resources, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Amal M. Metwally:** Supervision, Conceptualization, Investigation, Formal analysis, Funding acquisition, Writing – original draft, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2022.120579.

References

[1] Z. Chen, P. Zhang, Y. Liu, A. Mekkaoui, C. Wang, L. Zhao, B. Xu, Interfacial rheological behavior of N-acyl amino acid surfactants derived from vegetable oils, Colloids Surf. A: Physicochem. 592 (2020), https://doi.org/10.1016/j.colsurfa.2020.124600.

[2] M. Roger, I.M. Banat, Biosurfactants: a sustainable replacement for chemical surfactants, Biotechnol. Lett. 34 (2012) 1597–1605, https://doi.org/10.1007/s10529-012-0956-x.

[3] N. Joondan, S.J. Laulloo, P. Caumul, Amino acids: building blocks for the synthesis of greener amphiphiles, J. Dispers. Sci. Technol. 39 (2018) 1550–1564, https://doi.org/10.1080/01932691.2017.1421085.

[4] M.C. Moràna, A. Pinazoa, L. Péreza, P. Clapésa, M.a. Angeleta, M.T. Garcíaa, M.P. Vinardell, M.R. Infante, Green amino acid-based surfactants, Green Chem. 6 (2004) 233–240, https://doi.org/10.1039/B400293H.

[5] N. Wang, K. Yao, Y. Wang, J. Ti, J. Tan, C. Liu, G. Zhang, C. Wang, B. Xu, Green synthesis, characterization, and properties of acyl lysine, serine, threonine, and methionine derived from three types of natural oils, J. Surfactants Deterg. 23 (2020) 239–250, https://doi.org/10.1002/jsde.12365.

[6] Y.M. Xu, H.Q. Liu, B.C. Xu, G.J. Zhang, Synthesis, characterization, and surface properties of amide amine oxides based on natural vegetable oil, J. Dispers. Sci. Technol. 39 (2018) 589–593, https://doi.org/10.1080/01932691.2017.1339609.

[7] C. Liu, Y. Wang, C. Chai, S. Ullah, G. Zhang, B. Xu, H. Liu, L. Zhao, Interfacial activities and aggregation behaviors of N-acyl amino acid surfactants derived from vegetable oils, Colloids Surf. A 559 (2018) 54–59, https://doi.org/10.1016/j.colsurfa.2018.09.042.

[8] R.P.F. Melo, E.L.B. Neto, M.C.P.A. Moura, T.N.C. Dantas, A.A.D. Neto, H.N.M. Oliveira, Removal of direct Yellow 27 dye using animal fat and vegetable oil-based surfactant, J. Water Process. Eng 7 (2015) 196–202, https://doi.org/10.1016/j.jwpe.2015.06.009.

[9] H. Zhang, Y. Bai, J. Zhao, Q. Shi, Y. Zang, J. Wu, Designing, Synthesizing, and Analyzing a Comb-like Polymeric Surfactant, Poly (acrylic acid-co-octadecyl acrylate), in a Multidisciplinary Laboratory Experiment, J. Chem. Educ. 98 (2021) 2074–2082, https://doi.org/10.1021/acs.jchemed.0c01509.

[10] B. lindman, T. Nylander, Chapter 26 - Polymer–Surfactant Interactions, Cosmet. sci. technol. 17 (2017) 449-469, https://doi.org/10.1016/B978-0-12-802005-0.00026-4.

[11] P. Raffa, A.A. Broekhuis, F, Picchioni, polymeric surfactants for enhanced oil recovery;areview, J. Pet. Sci. Eng. 145 (2016) 723–733, https://doi.org/10.1016/j.petrol.2016.07.007.

[12] S. Kumar, N. Saxena, A. Mandal, Synthesis and evaluation of physicochemical properties of anionic polymeric surfactant derived from Jatropha oil for application in enhanced oil recovery, J. Ind. Eng. Chem. 43 (2016) 106–116, https://doi.org/10.1016/j.jiec.2016.07.055.

[13] H.C. Kim, E. Kim, T.L. Ha, S.G. Lee, S.J. Lee, S.W. Jeong, Highly stable and reduction responsive micelles from a novel polymeric surfactant with a repeating disulfide-based gemini structure for efficient drug delivery, J. Polym. 133 (2017) 102–109, https://doi.org/10.1016/j.polymer.2017.11.032.

[14] O. Temiloluwa, O. Tomiwa, O. Babalola, Evaluating rheological properties and recovery performance of polymeric anionic surfactant (PSURFC) synthesized from non-edible seed oil on heavy crude recovery, J. Pet. Explor. Prod. Technol. 10 (2020) 2279–2292, https://doi.org/10.1007/s13202-020-00916-2.

[15] P. Raffa, D.A.Z. Wever, F. Picchioni, A.A. Broekhuis, Polymeric surfactants: synthesis, properties, and links to applications, Chem. Rev. 115 (2015) 8504–8563, https://doi.org/10.1021/cr500129h.

[16] S. Ayirala, A. Sofi, Z. Li, Z. Xu, Surfactant and surfactant-polymer effects on wettability and crude oil liberation in carbonates, J. Pet. Sci. Eng. 207 (2021) 109–117, https://doi.org/10.1016/j.petrol.2021.109117.

[17] K. Sharma, S.S. Toor, J. Brandão, T.H. Pedersen, L.A. Rosendahl, Optimized conversion of waste cooking oil into ecofriendly bio-based polymeric surfactant-A solution for enhanced oil recovery and green fuel compatibility, J. Clean. Prod. 294 (2021) 126–214, https://doi.org/10.1016/j.jclepro.2021.126214.

[18] N.B. Samarth, P.A. Mahanwar, Modified Vegetable Oil Based Additives as a Future Polymeric Material-Review, J. Org. Polym. Mater. 5 (2015) 1–22, https://doi.org/10.4236/ojopm.2015.51001.

[19] S.M. Shaban, T. Aiad, A.H. Moustafa, O.H. Aljoboury, Some alginates polymeric cationic surfactants; surface study and their evaluation as biocide and corrosion inhibitors, J. Mol. Liq. 273 (2019) 164–176, https://doi.org/10.1016/j.molliq.2018.10.017.

[20] I. Aiad, D. Emam, A. El-Deeb, E. Abd-Alrahman, Novel imidazolium-based gemini surfactants: Synthesis, surface properties, corrosion inhibition and biocidal activity against sulfate-reducing bacteria, J Surfactants Deterg. 16 (2013) 927–935, https://doi.org/10.1007/s11743-013-1491-z.

[21] M.S. Sheikh, A.J. Khanam, R.U.H. Matto, Comparative study of the micellar and antimicrobial activity of gemini-conventional surfactants in pure and mixed micelles, J Surfactants Deterg. 16 (2013) 503–508, https://doi.org/10.1007/s11743-012-1430-4.

[22] C. Ren, F. Wang, Z. Zhang, H. Nie, N. Li, M. Cui, Synthesis, surface activity and aggregation behavior of Gemini imidazolium surfactants 1, 3-bis (3-alkylimidazolium-1-yl) propane bromide, Colloids Surf. A Physicochem. Eng. Asp. 467 (2015) 1–8, https://doi.org/10.1016/j.colsurfa.2014.11.031.

[23] O. Nacham, A. Martín-Pérez, D.J. Steyer, M.J. Trujillo-Rodríguez, J.L. Anderson, V. Pino, A.M. Afonso, Interfacial and aggregation behavior of dicationic and tricationic ionic liquid-based surfactants in aqueous solution, Colloids Surf. A Physicochem. Eng. 469 (2015) 224–234, https://doi.org/10.1016/j.colsurfa.2015.01.026.

[24] K. Parikh, B. Mistry, S. Jana, S. Gupta, R.V. Devkar, S. Kumar, Physico-biochemical studies on cationic gemini surfactants: role of spacer, J. Mol. Liq. 206 (2015) 19–28, https://doi.org/10.1016/j.molliq.2015.01.055.

[25] K. Sharma, S.S. Toor, J. Brandão, T.H. Pedersen, L.A. Rosendahl, Optimized conversion of waste cooking oil into ecofriendly bio-based polymeric surfactant-A solution for enhanced oil recovery and green fuel compatibility, J. Clean. Prod. 294 (2021), https://doi.org/10.1016/j.jclepro.2021.126214.

[26] Q.Q. Zhang, B.X. Cai, W.J. Xu, H.Z. Gang, J.F. Liu, S.Z. Yang, B.Z. Mu, The rebirth of waste cooking oil to novel bio-based surfactants, Scientific reports. 5 (2015) 1–7, https://doi.org/10.1038/srep09971.

[27] W.I.A. El-Dougdoug, K.A.H. Hebash, Amphoteric Surface Active Agents with Heterocyclic Ring Based on Industrial Wastes, Egypt. J. Chem. 54 (2011) 223–237. https://dx.doi.org/10.21608/ejchem.2011.1390.

[28] W.I.A. El-Dougdoug, M.A. Riya, B.A. Mahy, Synthesis and Surface Active Properties of Sulfonated Acrylate Esters Based on Al-Cedre Oil, J. Surfactants Deterg. 18 (2015) 681–688, https://doi.org/10.1007/s11743-015-1695-5.

[29] Q. Xu, Z. Liu, M. Nakajima, S. Ichikawa, N. Nakamura, P. Roy, T. Shiina, Characterization of a soybean oil-based biosurfactant and evaluation of its ability to form microbubbles, Bioresour. Technol. 101 (2010) 3711–3717, https://doi.org/10.1016/j.biortech.2009.12.093.

[30] Z. Chu, Y. Feng, Vegetable-derived long-chain surfactants synthesized via a "green" route, ACS Sustainable Chem. Eng. 1 (2013) 75–79, https://doi.org/10.1021/sc300037e.

[31] R. Kumar, G.C. Kalur, L. Ziserman, D. Danino, S.R. Raghavan, Wormlike micelles of a C22-tailed zwitterionic betaine surfactant: from viscoelastic solutions to elastic gels, Langmuir. 23 (2007) 12849–12856, https://doi.org/10.1021/la7028559.

[32] S.R. Raghavan, E.W. Kaler, Highly viscoelastic wormlike micellar solutions formed by cationic surfactants with long unsaturated tails, Langmuir. 17 (2001) 300–306, https://doi.org/10.1021/la0007933.

[33] M. Dierker, H.J. Schäfer, Surfactants from oleic, erucic and petroselinic acid: Synthesis and properties, Eur. J. Lipid Sci. Technol. 112 (2010) 122–136, https://doi.org/10.1002/ejlt.200900126.

[34] K. Huang, P. Zhang, J. Zhang, S. Li, M. Li, J. Xia, Y. Zhou, Preparation of biobased epoxies using tung oil fatty acid-derived C21 diacid and C22 triacid and study of epoxy properties, Green Chem. 15 (2013) 24662475, https://doi.org/10.1039/C3GC40622A.

[35] C. Liu, F.S. Chen, Y.M. Xia, Composition and structural characterization of peanut crude oil bodies extracted by aqueous enzymatic method, J. Food Compos. Anal. 105 (2022), https://doi.org/10.1016/j.jfca.2021.104238.

[36] Y. Pan, W. Jin, Q. Huang, Structure, assembly and application of novel peanut oil body protein extracts nanoparticles, Food Chem. 367 (2022), https://doi.org/10.1016/j.foodchem.2021.130678.

[37] F.D. Fernandes, L.M. Ferreira, M.L.C.P. da Silva, Evaluation of the corrosion inhibitory effect of the ecofriendly additive of Terminalia Catappa leaf extract added to soybean oil biodiesel in contact with zinc and carbon steel 1020, J. Clean. Prod. 321 (2021), https://doi.org/10.1016/j.jclepro.2021.128863.

[38] P. Rodsamran, R. Sothornvit, Lime peel pectin integrated with coconut water and lime peel extract as a new bioactive film sachet to retard soybean oil oxidation, Food Hydrocoll. 97 (2019), https://doi.org/10.1016/j.foodhyd.2019.105173.

[39] C. Chotimarkorn, S. Benjakul, N. Silalai, Antioxidative effects of rice bran extracts on refined tuna oil during storage, Int. Food Res. J 41 (2008) 616–622, https://doi.org/10.1016/j.foodres.2008.04.002.

[40] E. Kirtil, E. Kurtkaya, T. Svitova, C.J. Radke, M.H. Oztop, S. Sahin, Examination of interfacial properties of quince seed extract on a sunflower oil-water interface, Chem. Eng. Sci. 245 (2021), https://doi.org/10.1016/j.ces.2021.116951.

[41] Z. Drinić, J. Mudrić, G. Zdunić, D. Bigović, N. Menković, K. ŠavikinEffect of pomegranate peel extract on the oxidative stability of pomegranate seed oil, Food Chem. 333 (2020) 127501, 10.1007/s11694-021-01004-7.

[42] O. Emmanuel, U.M. Okezie, E.J. Iweala, E.A. Ugbogu, Pretreatment of red palm oil extracted from palm fruit (Elaeis guineensis) attenuates carbon tetrachloride induced toxicity in Wistar rats, Phytomedicine plus. 1 (2021), https://doi.org/10.1016/j.phyplu.2021.100079.

[43] Y.M. Bayisa, T.A. Bullo, Optimization and characterization of oil extracted from Croton macrostachyus seed for antimicrobial activity using experimental analysis of variance, Heliyon. 7 (2021) e08095.

[44] A.H. Tantawy, M.A. Abo-Riya, S.M. Abdallah, W. El-Dougdoug, Novel cationic surfactants based on waste frying oil for cleaning water surface from petroleum films: Synthesis, antimicrobial and surface properties, J. Mol. Liq. 253 (2018) 36–44, https://doi.org/10.1016/j.molliq.2018.01.009.

[45] M. Abo-Riya, A.H. Tantawy, W. El-Dougdoug, Synthesis and evaluation of novel cationic gemini surfactants based on Guava crude fat as petroleum-collecting and dispersing agents, J. Mol. Liq. 221 (2016) 642–650, https://doi.org/10.1016/j.molliq.2016.05.083.

[46] A.H. Tantawy, H.I. Mohamed, A.A. Khalil, K.A. Hebash, M.Z. Basyouni, Novel bioactive imidazole-containing polymeric surfactants as petroleum-collecting and dispersing agents: Synthesis and surface-active properties, J. Mol. Liq. 236 (2017) 376–384, https://doi.org/10.1016/j.molliq.2017.04.040.

[47] A. Băran, L. Aricov, G. Stîngă, A. Iovescu, A.R. Leontieş, V.V. Jerca, The effect of C12E6 nonionic surfactant on the solubilization of Eosin Y in unmodified-and hydrophobically modified poly (Acrylic acid) solutions, J. Mol. Liq. 346 (2022), https://doi.org/10.1016/j.molliq.2021.117103.

[48] F. Liu, X. Cui, S. Yu, Z. Li, X. Ge, Hydrolysis reaction of poly(ethylene terephthalate) using ionic liquids as solvent and catalyst, J. Appl. Polym. Sci. 114 (2009) 3561–3565, https://doi.org/10.1002/app.30981.

[49] H.M. Abd El-Lateef, A.H. Tantawy, Synthesis and evaluation of novel series of Schiff base cationic surfactants as corrosion inhibitors for carbon steel in acidic/chloride media: experimental and theoretical investigations, RSC Adv. 6 (2016) 8681–8700, https://doi.org/10.1039/C5RA21626E.

[50] R.A. Rahimov, I.A. Zarbaliyeva, A.H. Tantawy, Z.H. Asadov, A.H. Azizov, Synthesis of new, ecologically safe and efficient oil slick-collecting and dispersing agents based on oleic acid and its propoxylation products, Arab. J. Sci. Eng. 39 (2014) 5437–5444, https://doi.org/10.1007/s13369-014-1144-1.

[51] Z.H. Asadov, A.H. Tantawy, I.A. Zarbaliyeva, R.A. Rahimov, Synthesis of new surface-active ammonium-type complexes based on palmitic acid for removing thin petroleum films from water surface, Egypt. J. Pet. 22 (2013) 261–267, https://doi.org/10.1016/j.ejpe.2013.06.005.

[52] A.F. Shaaban, A.A. Khalil, N.N. Messiha, Estimation of reactivity ratios of N-methacryloloxyphthalimide copolymers by1H NMR, J. Appl. Polym. 37 (1989) 2051–2058, https://doi.org/10.1002/app.1989.070370724.

[53] A.F. Shaaban, A.A. Khalil, N.N. Messiha, Binary copolymerizations of N-acryloyloxyphthalimide with methyl acrylate, methyl methacrylate and acrylonitrile, Acta Polym 40 (1989) 445–448, https://doi.org/10.1002/actp.1989.010400706.

[54] A.A. Khalil, Activated polymers. II: Synthesis and exchange reactions of biologically active poly (8-acryloxyquinoline), J. Polym. Res. 20 (2013) 1–8, https://doi.org/10.1007/s10965-012-0028-x.

[55] M. Fineman, S.D. Ross, Linear method for determining monomer reactivity ratios in copolymerization, J. Polym. Sci. 5 (1950) 259–262, https://doi.org/10.1002/pol.1950.120050210.

[56] T. Kelen, F. Tudos, Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. I. A New Improved Linear Graphic Method, J. Macromol. Sci. 9 (1974) 1–27, https://doi.org/10.1080/00222337508068644.

[57] M. Fingas, C. Brown, Review of oil spill remote sensing, Mar. Pollut. Bull. 83 (2014) 9–23, https://doi.org/10.1016/j.marpolbul.2014.03.059.

[58] J.L. Gray, L.K. Kanagy, E.T. Furlong, Ch.J. Kanagy, J.W. McCoy, A.Mason, G. Lauenstein, Presence of the Corexit component dioctyl sodium sulfosuccinate in Gulf of Mexico waters after the 2010 Deepwater Horizon oil spill, Chemosphere. 95 (2014) 124–130, https://doi.org/10.1016/j.chemosphere.2013.08.049.