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As-Synthesized Oleic Amido Propyl Betaine Surfactant Mixture and the Effect on the Crude Oil–Seawater Interfacial Tension

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Abstract: As-synthesized oleic amido propyl betaine surfactant mixture was developed through a slight modification of a conventional two-step betaine synthesis process of amidation and quaternization reactions. This method is a "direct formulating through synthesis" to achieve a targeted interfacial property (interfacial tension or IFT) of the as-synthesized surfactant. Oil–water IFT was measured in the crude oil–seawater system at 96 °C. The result showed that the as-synthesized surfactant was able to reduce crude oil–seawater IFT to the ultra-low level (<0.01 mN/m). As the finding emerged, the investigation was conducted to identify the elements that would bring the characteristic of ultra-low IFT. The characterization of the surfactant using FTIR, TG-IR, and HPLC suggested that unreacted materials associated with the surfactant remained, such as the carryover of a fatty amide from the intermediate process, residues of N, N trimethylene dimethylamine and sodium chloride as a by-product, and the important newly formed sodium oleate compound that was inadvertently generated via the reaction. The performance of the as-synthesized in seawater condition has been verified and the surface tension plot shows the lowest surface tension point at 0.05 wt.% concentration before developing a plateau region at higher surfactant concentration, indicating that the formation of surfactant micelles has been interrupted by the presence of other components in the solution. The dynamic IFT test performed on the as-synthesized product revealed that it was still able to reduce the crude oil–seawater IFT to an ultra-low level, despite the multiple undesirable components in the surfactant. IFT as low as 3.4×10^{-4} mN/m for the specific seawater and crude oil composition was obtained at a temperature of 96 °C.

Keywords: surfactant; ultra-low IFT; characterization

1. Introduction

Surfactant is known for its function to reduce the surface or interfacial energy between two immiscible phases. In the case of liquid–liquid phases, the molecules of the liquid experience an imbalance in the intermolecular interactions due to attractive forces from all angles at the liquid surfaces or the internal forces in the liquid such as dipole–dipole interaction, dispersion, as well as hydrogen bonding interaction that promote the surface energy of the water [1]. For water, the typical surface tension is around 72 mN/m at room temperature. Whereas for liquids with weaker molecular attractive interactions such as apolar hydrocarbons, the surface tension is typically around 20–30 mN/m [2]. The polarity difference is the main factor for the two liquids to become immiscible and to have high

interfacial tension. The two liquids with different polarities may become miscible if the interfacial energy between the two phases is low enough. Thus, the surfactant with amphiphilic properties can practically reduce the interfacial tension according to the preference of the head and tail polarity by adsorbing at liquid–liquid interface to reduce the interfacial energy. The ability of the surfactant to lower the interfacial tension can also be influenced by many factors, such as the surfactant type, the length of the carbon tail or the head, the ionic charge, and the synergistic effect of the surfactant mixtures. Given the right factors and mechanisms, the interfacial tension of the liquid–liquid phases can be reduced to super low, usually called ultra-low Interfacial Tension (IFT) with a value less than 0.01 mN/m.

Ultra-low IFT between two immiscible liquids (oil–water) can be attained when the surfactant is accumulating at the interface and orients themselves according to their preference of charges. Hydrophilic head orients towards the water while the hydrophobic part towards the oil phase [3]. This mobilization or orientation of the surfactant molecules must take place in equal attraction such that the attraction of hydrophilic bases is towards the water and the attraction of hydrophobic towards oil. The effective area occupied and adsorbed by the hydrophobic and hydrophilic bases at the interface must also be balanced and compacted. The packing and saturated adsorption at the interface will form a tight film, which leads to clear interference of other molecules at the interface that can increase the IFT [4]. Types of surfactants also play a role in affecting the surfactant molecules saturation at the interface. The packing of molecules at the interface will be governed by the ability of the surfactant molecule to be in proximity. Ionic surfactants, either anionic or cationic surfactant, will repel each other to prevent the close packing, whilst nonionic surfactant molecules will pack more closely than ionic surfactant molecules as there is no electric repulsion, but packing of this surfactant is limited by the hydration around the head groups. Bulky ethoxylate chains can cause steric hindrance, and a local deficiency of water can invoke osmotic effects causing head groups to move apart.

Zwitterionic or amphoteric surfactant contains both cationic and anionic centers on its polar head. The ionic behavior of which is altered according to the pH of the solvent. The cationic charges in the surfactant can decrease the repulsion between the negatively charged groups, promoting closer packing, which leads to the reduction in IFT. This type of surfactant, which is normally for domestic use, has recently gained attention in the oil and gas industry, particularly for enhanced oil recovery (EOR) applications [5–7]. Numerous studies have been carried out for amphoteric surfactants in EOR applications to confirm the ability of this surfactant in reducing the IFT to ultra-low level [8] proved that this type of surfactant was the most promising to attain ultra-low IFT due to the structure and adsorption behavior of the surfactant at the interface. Out of 30 specific surfactants with various head types synthesized, they found that the betaine type of surfactant with both negative and positive charges in the head from sulfonate and carboxylate-based surfactants could reduce the interfacial tension between the oil and water to ultra-low level. Similar findings were found by [7] that sulfobetaine amphoteric surfactants were able to produce low IFT values at low concentrations and high salinity/high hardness conditions.

Synthesis of amphoteric surfactants can be initiated from a few sources of raw materials with many possible synthesis routes. A series of carboxylbetaine and sulfobetaine were synthesized by [9] from castor oil and cottonseed oil with dimethylaminoethylamine as the source of amine for quartenization, followed by the reaction with sodium chloroacetate and sodium 2-hydroxy-3-chloropropane sulfonate. [10] synthesized ultra-long amidobetaine from unsaturated fatty acids such as oleic acid (C18:1), eurecic acid (C22:1) and nervonic acids (C24:1); the products were purified but had not been tested for their crude oil–seawater IFT.

In our research, oleic acid (C18:1) from palm oil-based with 72% purity was used as the raw material for the preparation of surfactant. Through the preparation using a simplified synthesis process with no catalyst in the amidation process and no treatment applied to the final product, we found that the product had good surface activity at the interface as it was able to reduce the IFT to the ultra-low level in seawater even when it was left unpurified. The process was then repeated a few times, and we

found that it still produced ultra-low IFT when tested in seawater at 96 °C (reservoir temperature). The goal of this study was to bring some insight into the elements that influence the behavior of the surfactants through qualitative characterization of the unreacted material, which was commonly removed from the synthesized surfactant, the presence of which might be beneficial to gain dense packing of surfactant at the interface to obtain the ultra-low IFT. Thus, it can also be used as a process limitation guide for betaine preparation.

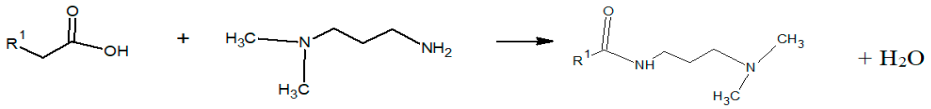
2. Materials and Methods

2.1. Materials Used

In this work, the oleic acid used for the synthesis of the surfactant was supplied by Emery Oleochemicals with a purity of 72%. The other chemicals, such as N, N dimethyl trimethylethylene, and sodium chloroacetate, both with 99% purity, were purchased from Merck. Actual crude oil from one of the Malaysian fields (Field A) was used in this study. The total acid number, gravity, and viscosity of the oil were found to be 1.064 mg KOH/g, 0.806 API, and 96 mm^2/s at 45 °C, respectively. The synthetic seawater according to the Field A seawater composition was prepared by mixing different salts (NaCl, 42.33 g/L; KCl, 1.48 g/L; $CaCl_2$, 2.43 g/L; $MgCl_2$, 19.46 g/L; Na_2SO_4, 7.09 g/L; $SrCl_2$, 0.039 g/L; KCl, 1.48 g/L; $NaHCO_3$, 0.311 g/L) in de-ionized water. All these chemicals were procured from Merck Germany, and all the chemicals are more than 98% pure.

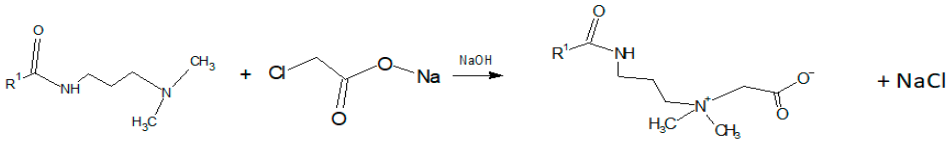
2.2. Synthesis of Surfactant

The surfactant was synthesized in a two-step reaction. In the first step, 0.125 mol of oleic acid was added into 100 mL reaction vessel, then 0.125 mol of N, N dimethyl trimethylethylene diamine was added to the oleic acid with continuous stirring at 100 rpm. The temperature of the synthesis was elevated to 120 °C and maintained at this temperature for 8–12 h under reflux. The water produced was collected during the reaction. The liquid product was then dried in a vacuum oven at 60 °C overnight or longer to further vaporize the excessive water. The amidation reaction is shown in Scheme 1.



Scheme 1. First step: Amidation reaction.

A quantity of 0.1 mol of amidation product was added into a two-pieces 100 mL reaction vessel placed in an automated synthesis reactor of the Mettler Toledo Easymax 402 system. Then, 0.1 mol of sodium chloroacetate (99%) was added into the product from the first step with continuous stirring at 400 rpm. NaOH was added dropwise, and the pH of the surfactant was maintained at 8–9. The temperature of the synthesis was set to 120 °C for 12 h, and the reaction was left unattended. No further purification was carried out for the semi-solid surfactant produced. The schematic representation of the quaternization reaction is proposed below in Scheme 2.



Scheme 2. An ideal quaternization reaction of alkyl amido propyl betaine surfactant.

2.3. High Performance Liquid Chromatography (HPLC)

HPLC was used to characterize the surfactant by separating it into the compound of its composition. Since the surfactant has not been purified, it contains other reaction-based mixtures. The separation

was, therefore, crucial to identify the possible existence of the element. The surfactant was characterized by HPLC (Agilent Model with a high sensitivity detection column; AcclaimMD Surfactant Plus LC columns from Thermo Scientific). An evaporative light scattering detector (ELSD) was used as a detector. In addition, 0.1 M acetonitrile (B) and ammonium acetate (C) were used as a mobile gradient phase with pH 5.5. The flow rate was set at 1 mL/min with an injection volume of 5 µL and a run time of 60 min. Acetonitrile and ammonium acetate with a ratio of 65:35 were used as a solvent for all the samples. The surfactant separation method was developed as per Table 1 below and the element presence was qualitatively compared with their standard samples.

Table 1. HPLC gradient Method.

Time	A%	B%	C%	D%	Flow (mL/min)	Max Pressure Limit (Bar)
0	0.00	65.00	35.00	0.00	1.00	400.00
2	0.00	52.00	48.00	0.00	1.00	400.00
6	0.00	55.00	45.00	0.00	1.00	400.00
10	0.00	50.00	50.00	0.00	1.00	400.00
30	0.00	45.00	55.00	0.00	1.00	400.00
40	0.00	55.00	45.00	0.00	1.00	400.00
60	0.00	65.00	35.00	0.00	1.00	400.00

2.4. Fourier Transform Infra-Red Spectroscopy Analysis

The functional group present in the synthesized surfactant was analyzed between 4000 cm^{-1} and 400 cm^{-1} with the FTIR 65 Perkin Elmer spectrum. This method was used to confirm the presence of the carbonyl group attached to the secondary amine as well as the carboxylate group to confirm the occurrence of amidation and quaternization.

2.5. Hyphenated Thermogravimetry-Infra-Red (TG-IR) Analysis

The Perkin Elmer hyphenated system couples the TGA to the FTIR instrument. TG-IR is capable of analyzing unknown mixtures to determine the primary components and to identify additives or contaminants. For spectral analysis, the evolved gas produced from the sample analyzed in the TGA furnace is transferred to the IR cell through the interface. The system allows analysis in real-time and the identification of decomposition of complex and unknown mixtures.

2.6. Surface Tension Analysis and Critical Micelle Concentration (CMC) Analysis

The surfactant was dissolved in deionized water at a concentration range of 0.01 wt.% to 0.5 wt.% and the surface tension for each concentration was analyzed at 25 °C using the Dunoŭy ring tensiometer to determine the surface tension and CMC of the surfactant.

2.7. Interfacial Tension (IFT) Analysis

The IFT between crude oil and as-synthesized surfactant solution and its associative mixtures was analyzed using the spinning drop tensiometer SVT 20N data physics capable of analyzing the IFT within the 0–130 °C range. The surfactant was dissolved directly in seawater at different concentrations from 0.05 wt.% to 0.3 wt.%. Specific seawater and crude oil from the same oil field have been used for this study.

3. Results and Discussion

3.1. HPLC Chromatogram of as-Synthesized Surfactant

HPLC was performed to qualitatively determine the components in this surfactant. A method has been developed to separate the individual components or elements that might coexist with the

surfactant. The retention time of the peaks was compared with that of the starting materials and intermediate such as oleic acid, N, N trimethylene dimethyl amine (amine), sodium chloroacetate, and fatty amide, respectively. Possible compounds that might be evolved from the reactions were also used as a reference. By applying the gradient method, the surfactant and all the reagents prepared at 0.5 wt.% each were well separated into several peaks, and the retention time of the reagents were shown in the figures in Appendix A.

As the first starting material, 0.5 wt.% oleic acid was prepared in the same solvent as the mobile phase. There are four separation peaks observed for the oleic acid with the widest peak area, which appeared at retention time 33.343, attributable to the main composition of C18:1. The retention time of the peaks eluted from the oleic acid are presented in Table 2 below and the separation peak is shown in Figure A1.

Table 2. Oleic acid composition and retention time.

Fatty Acids	Retention Time	% Area
C18 & below	17.638	3.968
C18:1	33.343	79.25
C18:2	29.660	11.498
others	48.987	2.63

N, N trimethylene dimethyl amine (amine), as the second starting materials, were also analyzed in the same system and method. Amine, which has higher polarity than oleic acid, was eluted as a single peak at the early retention time of 2.086 min in this reverse-phase system, as can be seen in Figure A2. The retention times of both compounds were used in the following intermediate sample as well as the surfactant as an identification method of unreacted reagent that might still exist in the intermediate and final product of untreated surfactant.

The intermediate product was also treated as a reference for the as-synthesized surfactant. The chromatogram of this intermediate is shown in Figure 1. The most intense peak appeared at 4.322 min and can be attributed to the intermediate product. It was spotted along with some other small peaks at RT 2.818 min that matched with the amine, as can be seen in the chromatogram in the Appendix A. Another peak appeared at 3.66 min, which was suspected to be another amidation product from the reaction with other fatty acids in the first starting material. Through this analysis, it can be confirmed that oleic acid (C18:1) has been completely reacted with the amine reagent as no oleic acid peak appeared in the chromatogram. The amine, however, was kept remaining and was not removed from the final product.

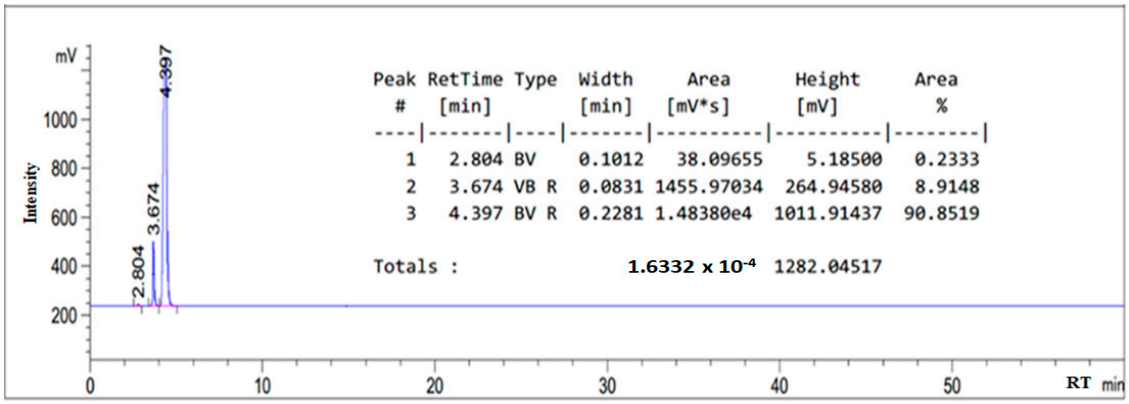


Figure 1. HPLC chromatogram for 0.5 wt.% intermediate of as-synthesized surfactant.

For the chromatogram of the final surfactant product in Figure 2, it revealed that besides the oleic amido betaine, the surfactant also consists of a significant amount of intermediate as well as some

compounds produced from the reaction, evidenced by the other intense peaks in the same figure. The presence of intermediate was confirmed based on its individual retention time at 4.407 min, which shifted slightly to the right from its individual chromatogram. The most intense peak eluted at the retention time of 2.817 min belonged to sodium oleate based on its individual reference compound analyzed using this method, as shown in Figure A3. The retention time at 3.63 min was attributable to the sodium chloroacetate, as shown in the chromatogram in Figure A4 in Appendix A.

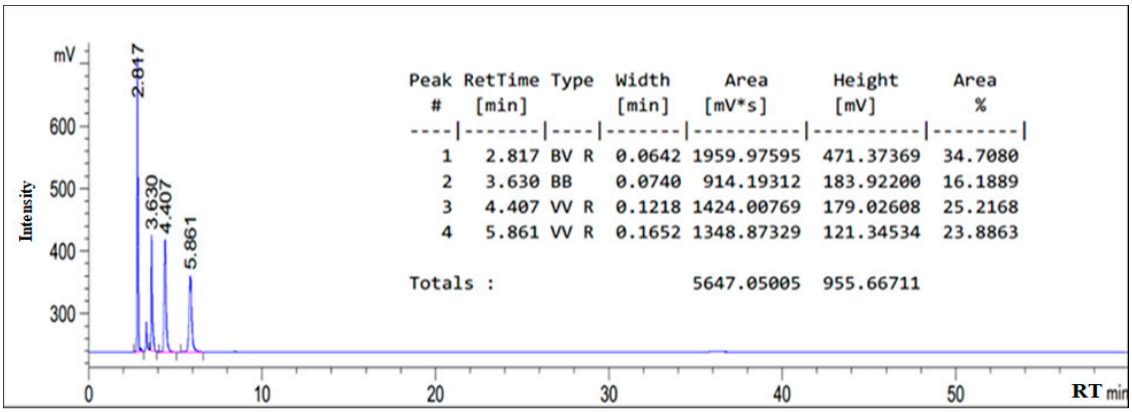


Figure 2. HPLC chromatogram for 0.5wt.% as-synthesized surfactant chromatogram.

In the quaternization reaction between sodium chloroacetate and fatty amide, given the right condition, the product formed would be the oleic amido betaine and sodium chloride as the by-product that was usually not removed from the final product [11]. However, under certain conditions, especially when NaOH was used to a catalyst, the reaction between these two components might produce other by-products that were influenced by the condition of the reaction medium. In this case, the likely reaction was the hydrolysis reaction of the amide with water, which was not removed from the first amidation step. In this quaternization step, the hydrolysis of amide can form fatty acid salts (sodium oleate) in the presence of NaOH at high temperature (120 °C) and prolonged time [12]. Thus, the peak at the retention time of 2.817 min could be attributed to the oleic acid salt as the sodium oleate. It might also overlap with the free amine peak that had a similar retention time to that of sodium oleate at 2.806 min. In many examples of quaternization reactions performed by other researchers, the temperature applied was mostly not more than 90 °C [4,13,14] as a precaution to avoid the hydrolysis reaction of amide at high temperature, especially when the reaction was carried out under the basic condition. So, for this analysis, when the reaction was carried out at 120 °C for 12 h, amide, which generally quite stable to hydrolysis as compared to an ester [15] could be hydrolyzed under the right conditions, as described above. The oleic amido betaine peak, meanwhile, was eluted at the retention time of 5.861 min (see Figure 2) as it had the longest carbon chain and the least polarity as compared to the other compounds. At the pH of the mobile phase of 5.5, this surfactant exists in its zwitterionic form as the pK_a of this betaine surfactant molecule is approximately around [4,5,16]. Thus, at pH >> pK_a, only the zwitterionic form is present. The composition of the unwashed oleic amido betaine is tabulated in Table 3.

Table 3. Unwashed as-synthesized surfactant composition and retention time.

Composition	Retention Time (min)
Oleic amido betaine	5.669
Fatty amide	4.407
Sodium oleate	2.817
Sodium chloroacetate	3.630

3.2. FTIR Analysis of as-Synthesized Surfactant

The surfactant was analyzed with the FTIR to confirm the formation of the crucial functional groups to ensure that the synthesis process had developed the desired surfactant compound. From the FTIR analysis, it was confirmed that those important functional groups were present in the surfactant and gave the amphoteric feature to the surfactant.

As presented in Figure 3, the formation of oleic amido betaine was further confirmed with the presence of the peak at 1392.87 cm^{-1} attributable to the COO-peak, indicating the formation of the carboxylate head from the oleic amido betaine itself or the fatty acid salt that was formed along with the reaction. The next significant peaks observed were the several peaks that belonged to the amide in the spectrum. The peak at 3294.75 cm^{-1} indicated the formation of secondary amide (N-H); and the peak at 1633.94 cm^{-1} indicated that the presence of (C=O) belonged to the amide functional group. The formation of amide was also supported by the presence of the peaks at 1549.25 cm^{-1} and 1464.28 cm^{-1}, attributed to secondary amide (N-H bending) and C-N stretch, respectively.

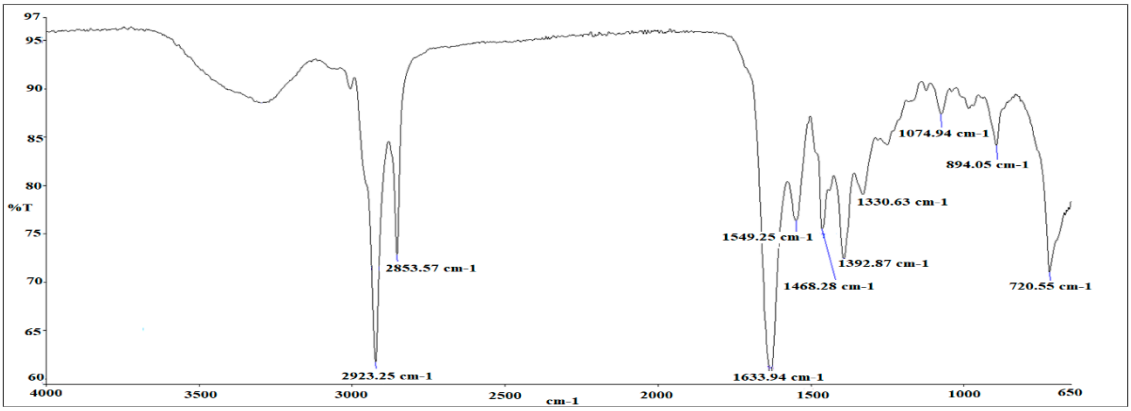


Figure 3. FTIR spectrum of as-synthesized surfactant.

Among the observed significant peaks, there were also the peaks that could be regarded as the presence of associative surfactant mixtures. For example, the appearance of water might be overlapped with the N-H peak at 3294.75 cm^{-1}. No peak was observed at (C=O) 1710 cm $^{-1}$, which can be assigned to carboxylic acid, suggesting that that the carboxylic acid has been completely converted into product as an agreement to what has been observed in the HLPC chromatogram.

3.3. Hyphenated TGA-IR-Method

The hyphenated TGA-IR method gives the proposition of component loss versus the possible functional groups. It can be a tool to confirm the presence or absence of certain components at specific decomposition temperatures. In this study, TG-IR was used to determine the conversion rate of the process based on the maximum decomposition of the surfactant and the decomposition after the maximum curve in the TG. Three mass loss regions were detected in the TG section, as shown in Figure 4 and the mass loss values are tabulated in Table 4. The first region in which the decomposition started from ambient to about 201.2 °C had 26.46% mass loss, corresponding to the loss of weakly bonded water as well as the loss of the unreacted elements such as sodium chloroacetate from the quaternization process. The decomposition was suspected at this temperature range based on its boiling point. Another decomposed product at this temperature range was fatty amide from the intermediate reaction. This statement was supported by the presence of small peaks in the IR curve in Figure 5 at 3707 cm^{-1} and 1194.2 cm^{-1}, representing the O-H bond due to water, and the C-N (stretch) as the breakdown of the amide, respectively.

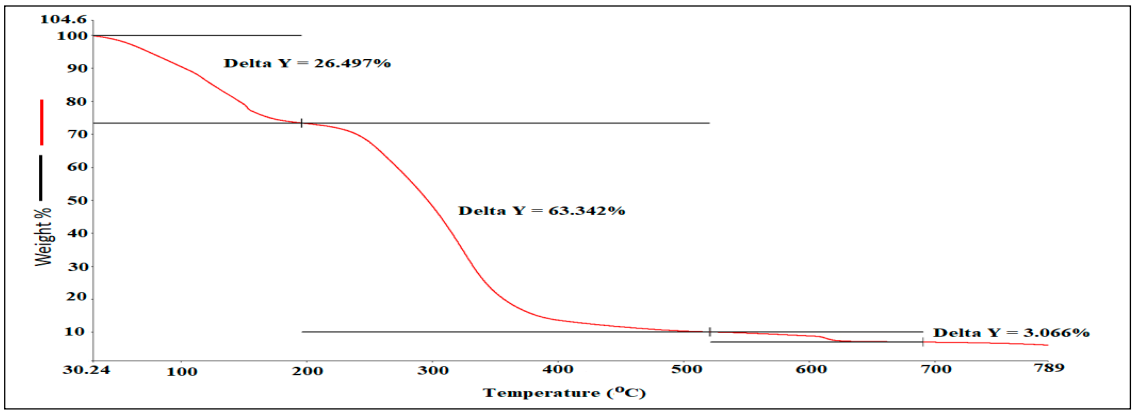


Figure 4. TG curve in hyphenated TG-IR.

Table 4. Mass loss vs. Temperature.

Mass Loss (%)	Temperature (°C)
26.46	30–201.2
63.43	210–520.5
3.066	520–690

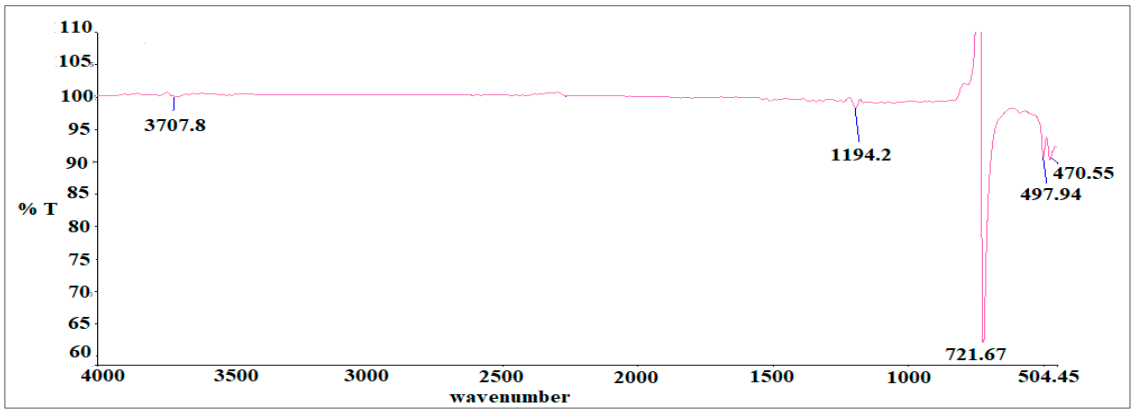


Figure 5. IR spectrum of as-synthesized surfactant in hyphenated TG-IR (curve 1).

The second decomposition region that occurred at 210 °C to 510 °C could be regarded as the major component of the surfactant. In comparison with the IR curve in Figure 6, a few peaks that belonged to the significant functional group in the surfactant appeared at this temperature region. Some of the functional groups like the carbonyl group from amide and carboxylate had been broken down into the free carbonyl group of C=O, as can be seen at the frequency of 1704 cm^{-1} with some other alkanes peaks, suggesting that the major surfactant component was still intact and its structure retained in this temperature region [17]. Another decomposition from the surfactant was observed in the range 530 °C to 690.3 °C. As can be seen in IR chromatogram for curve 3 (Figure 7), this decomposition could be attributed to the long carbon chain of the surfactant, due to the decomposition of the alkane group and some residue amine as a breakdown component of the amide from the surfactant. It also indicated that the amide was intact in the surfactant tail and was still present at high temperatures. Beyond the temperature of 690 °C, no IR peaks were recorded, indicating that the surfactant had been completely burnt off, leaving the crucible clean without any residue.

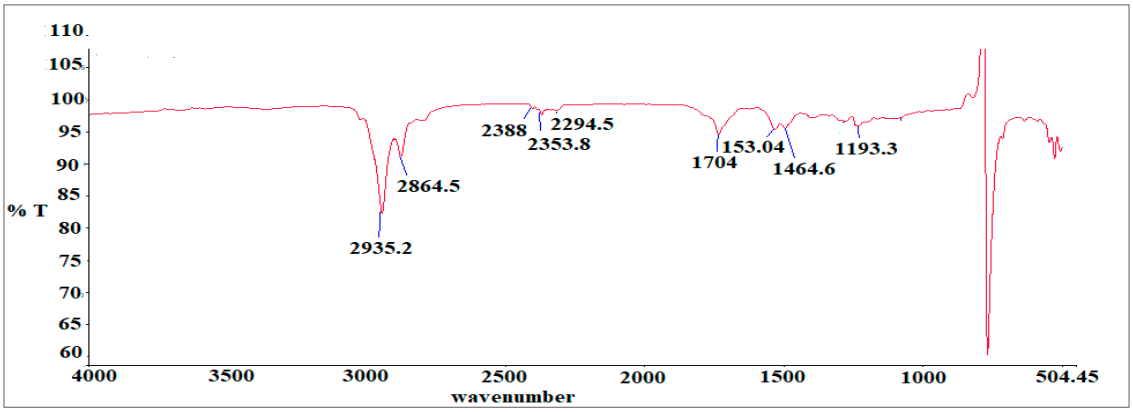


Figure 6. IR spectrum of as-synthesized surfactant in hyphenated TG-IR (curve 2).

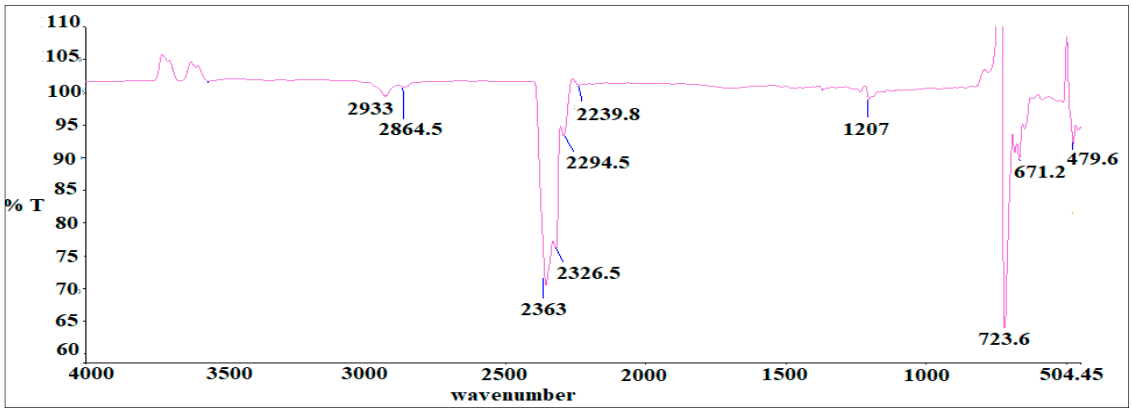


Figure 7. IR spectrum of as-synthesized surfactant in hyphenated TG-IR (curve 3).

3.4. Determination of Surface Tension

Figure 8 shows the surface tension of the as-synthesized surfactant solution at different concentrations. The critical micelle concentration is usually obtained from the intercept between the descending slope and the horizontal line in the surface tension plots against the concentration [18]. However, through this analysis, we found that the surfactant gave the lowest surface tension value of 24.7 mN/m at a concentration of 0.05wt.%. The surface tension increased when the concentration was increased to 0.1 wt.%. This finding was different from the surface tension curve of pure single surfactant that supposedly became levelled after the point of CMC. The reason for the different behavior of this surfactant could be due to the significant presence of associative mixtures, normally assumed as impurities. This finding was in agreement with the work done by [19] whereby the impure sodium dodecyl sulfate was used, and the similar trend of surface tension and point of CMC was observed. It was suspected that the impurities adsorbed at the air–water with higher surface activity than the surfactant itself. As for the as-synthesized surfactant, the phenomena could be due to the mixture of unreacted elements like amide as well as the presence of inorganic salts from the synthesis process [20].

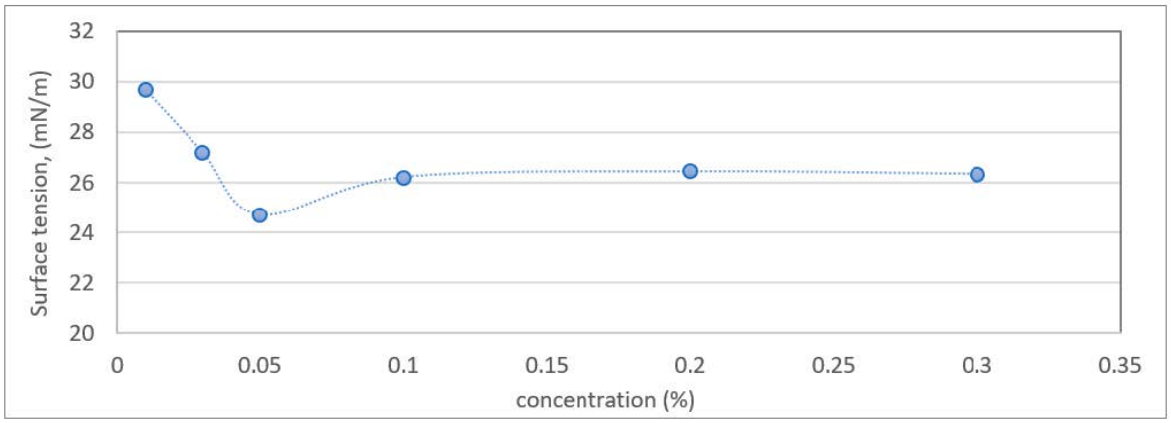


Figure 8. Surface tension of as-synthesized surfactant at different concentrations.

3.5. Dynamic Interfacial Tension (IFT) Analysis in Seawater

The dynamic IFT analysis was performed for the as-synthesized surfactant in seawater and the crude oil from Field A at the field temperature of 96 °C. The as-synthesized surfactant was regarded as 100wt.% active and was dissolved directly in seawater at different concentrations. No phase separation was observed during the IFT measurements at 96 °C and the analysis was carried out for all the concentrations in the range of 0.05 wt.% to 0.4 wt.%. The results are presented in Figure 9. At 60 min, the IFT was 3.4×10^{-4} mN/m, the lowest value recorded for 0.1 wt.% surfactant concentration. At this concentration, the dynamic IFT showed some instability, which might be due to the adsorption of the surfactant at the interface of crude oil and seawater, and/or the diffusion of surfactant back into the bulk solution [1,21].

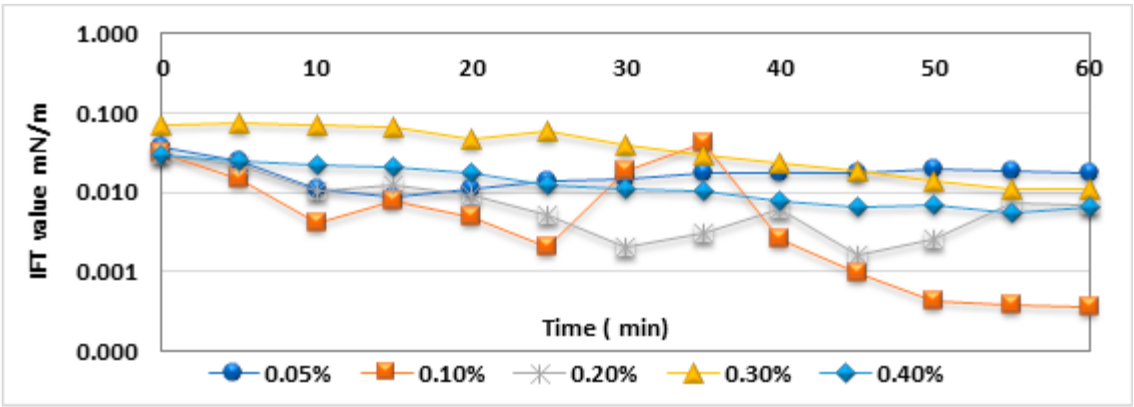


Figure 9. Dynamic Interfacial Tension (IFT) of surfactant in seawater at different concentrations.

In the presence of some other non-surfactant elements with their own behavior at the interface, this kind of dynamic IFT could be observed. For example, free amine was surface-active and able to reduce the interfacial tension if it presents as an additive in surfactants. The behavior of amine at the interface was basically influenced by the nitrogen atom that possessed a lone pair of electrons, which were prone to form hydrogen bonds with water. The hydrophobic part of the amine may also participate in the formation of micelles together with the surfactant to replace some of the water molecules at the interface [6]. Sodium Oleate was another component detected in the surfactant mixture to contribute to the IFT reduction. This by-product produced along with the reaction might have reacted as an anionic surfactant and oriented itself accordingly to promote dense packing at the interface with the presence of dual charges of amphoteric surfactant. The presence of inorganic salt (NaCl) as a by-product added up to the salinity concentration, therefore, it influenced the reduction in IFT by accelerating the migration of the surfactant molecules to the interface and helped the partitioning of

the surfactant to the oil phase [22]. As the contact time extended to 35 min or longer, the adsorption of the surfactant molecules had become more packed at the interface and reduced the interfacial tension further down to an ultra-low level. For the applications such as in EOR, the ultra-low IFT surfactant is needed for the oil recovery process [23,24]. Similar behavior was also observed for the surfactant at a concentration of 0.2 wt.%. At this concentration, the surfactant showed lower instability than the 0.1 wt.% surfactant concentration. Although the surfactant did not undergo any washing steps to eliminate the unreacted components, the proper concentration of the surfactant solutions was able to lower the IFT to the ultra-low level of below 0.01 mN/m (1×10^{-2} mN/m).

4. Conclusions

The as-synthesized surfactant with oleic acid as raw material was prepared in a conventional two step reaction with slight modifications. The synthesis product was characterized as it is without purification. Characterization of the surfactant using FTIR suggested the presence of the main functional groups, such as carbonyl from the amide group and carboxylate, attributed to the oleic amido betaine surfactant as well as sodium oleate, confirmed through the HPLC method. The formation of surfactant was further confirmed by the TG-IR method, indicating the decomposition of the carbonyl group and amide at high temperatures between 201 °C and 520.5 °C that were embedded in the main structure of the surfactant. The characterization of the as-synthesized surfactant by HPLC suggested that the final product had a mixture of oleic amido betaine surfactant, long chain amide intermediate, some unreacted sodium chloroacetate and a significant presence of sodium oleate evolved from the hydrolysis reaction of the fatty amide with water at high temperature and basic condition. In the meantime, IFT analysis confirmed the properties of the surfactant in reducing the crude oil–seawater IFT. Having unreacted elements in the surfactant as internal mixtures affected the surfactant behavior in a good way as they were part of the components that stabilized the adsorption at the oil–brine interface and had their own surface-active character, thus reducing the surface energy of the two phases to the ultralow level.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

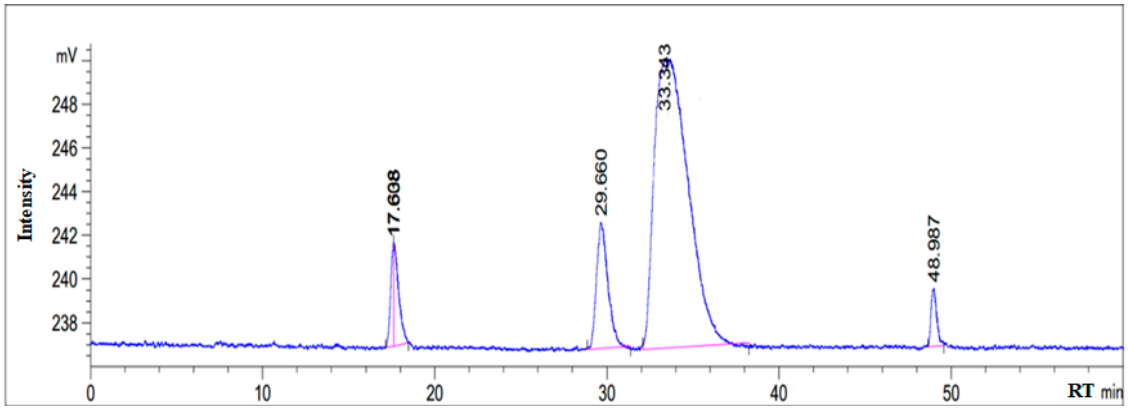

Figure A1. HPLC chromatogram for 0.5 wt.% Oleic acid.

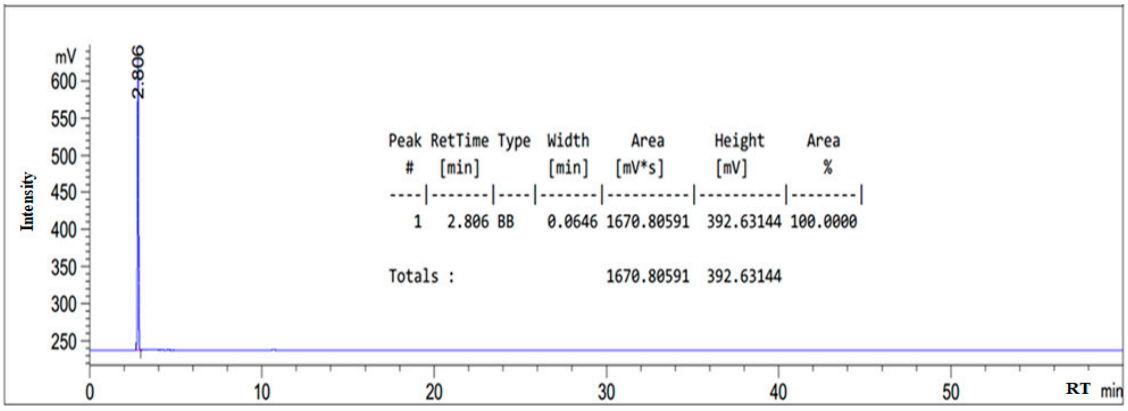

Figure A2. HPLC chromatogram for 0.5 wt.% N, N trimethylene dimethyl amine.

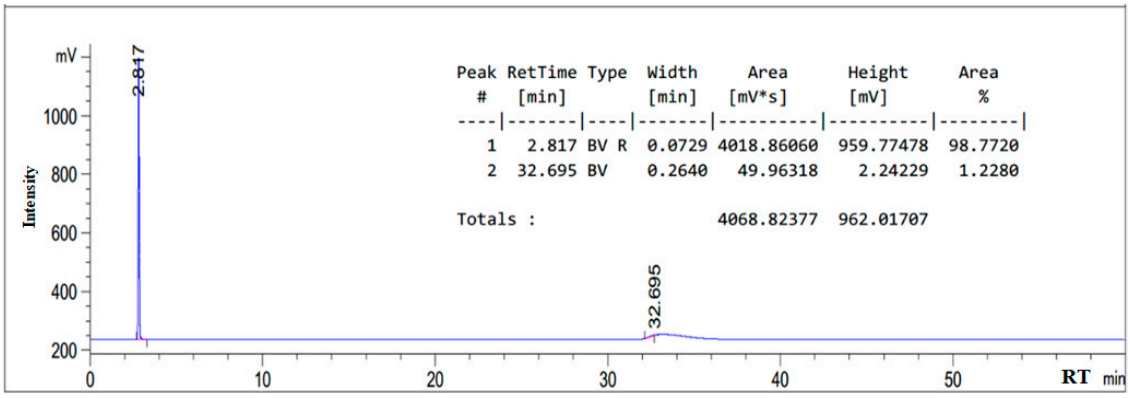

Figure A3. HPLC chromatogram for 0.5wt.% Sodium Oleate.

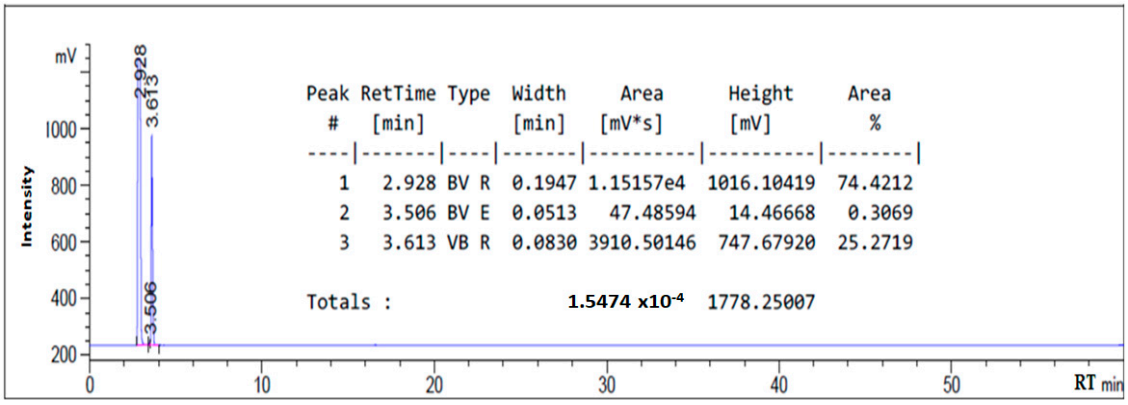

Figure A4. HPLC chromatogram for 0.5 wt.% sodium chloroacetate.

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