Ogunjobi, Joseph K and Omoruyi, Osaretin E (2025) Evaluation of surface, foam, emulsion, and clouding properties of a family of nonionic surfactants from oleic acid derivatives. Journal of Surfactants and Detergents. ISSN 1097-3958

DOI: https://doi.org/10.1002/jsde.12846

Publisher: Wiley

Version: Published Version

Received: 17 January 2025 | Revised: 17 January 2025 | Accepted: 31 January 2025

DOI: 10.1002/jsde.12846

ORIGINAL ARTICLE

AOCS WILEY

Evaluation of surface, foam, emulsion, and clouding properties of a family of nonionic surfactants from oleic acid derivatives

Joseph K. Ogunjobi[1,2] | **Osaretin E. Omoruyi**[3]

[1]DWI-Leibniz Institute for Interactive Materials, RWTH Aachen University, Aachen, Germany

[2]Manchester Metropolitan University, Faculty of Science and Engineering, Manchester, UK

[3]Department of Chemistry, The Federal University of Technology, Akure, Nigeria

Correspondence
Joseph K. Ogunjobi, Manchester Metropolitan University, Faculty of Science and Engineering, M1 5GD, UK.
Email: josephogunjobi@outlook.com; j.ogunjobi@mmu.ac.uk

Abstract

This study investigated the properties, namely: surface tension, foam, emulsion, and cloud point of a library of bio-based surfactants (represented as C_nEO_m where C is hydrophobic carbon chain and EO is ethylene oxide). The surfactants were derived from ring-opening alkyl oleate epoxides with polyethylene glycol (PEG) and monomethyl polyethylene glycol (MPEG) of varying chain lengths. Surfactants demonstrated good surface properties having surface tension at critical micelle concentration (CMC) between 35 and 38 mN/m, and recorded CMC values far lower than what was reported for most commercial ethoxylated surfactants. Foamability increased with over 30% foam increase upon increasing agitation speed from 6000 to 11,000 rpm. Branching, hydrophobic carbon chain length, and PEG chain length were seen to impact foamability and foam stability. Foam properties exhibited by the surfactants were found to be superior to those demonstrated by some known commercial nonionic surfactants. Emulsions formed by the oleate ester surfactants were stable over several weeks after formation. Surfactants showed high cloud points, which increased with increasing number of ethylene oxide units. However, the addition of co-solutes depressed the cloud point in the order Na_2SO_4 > NaCl > $NaNO_2$.

KEYWORDS

bio-based PEGylated surfactant, branching effect, cloud point, critical micelle concentration, critical packing parameter, detergency, foam stability, homogenization

INTRODUCTION

Production of surfactants, especially bio-based ones, has continued to grow over many decades even as the scopes of application widen. Bio-based surfactants are highly valued for their lower carbon footprint, rapid biodegradability, environmental sustainability, and enhanced safety compared to chemical surfactants (Adu et al., 2020; Velty et al., 2022; Zhang et al., 2014). Their resilience to high temperatures and tolerance for elevated salt concentrations makes them desirable components in a wide range of industrial products (Banat et al., 2010).

Bio-based surfactants sourced from sophorolipids, glycolipids, phospholipids, glycerols, carbohydrates, and fatty acids are particularly in high demand (Al Ghatta et al., 2022; Ismail et al., 2022; Kobayashi et al., 2023; Ortiz et al., 2022). In previous studies, the syntheses of nonionic surfactants based on oleic acid and sophorolipids via polyethylene glycol modification of its alkene moiety have been described (Ogunjobi et al., 2021; Ogunjobi et al., 2023). Recently, the synthesis of a class of nonionic surfactants with a main hydrophilic head containing 9–34 units of ethylene oxide (EO) and a hydrophobic tail containing 19–28 hydrocarbons from oleate derivatives was reported (Ogunjobi et al., 2023). The surfactants were obtained from ring-opening alkyl oleate epoxides with polyethylene glycols of varying chain length and can be represented as C_nEO_m where C is the hydrophobic carbon

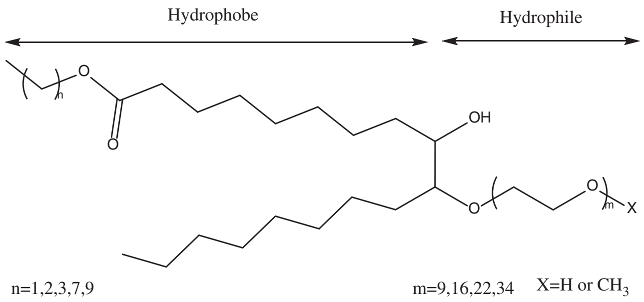


FIGURE 1 Representative structure of PEGylated oleate surfactant obtained from ring-opening alkyl oleate epoxides with polyethylene glycols of varying chain length.

chain and EO is ethylene oxide. The resulting representative structure and a list of resulting surfactants are respectively presented in Figure 1 and Table 1 with their codes (which will be adopted and hereafter referred to in our discussion) and the ethylene oxide number present in them.

In this study, we report interfacial tension, foam capacity and stability, emulsion capacity and stability as well as cloud point of this class of oleate-derived surfactants. Foam properties are among the essential factors that determine end-use applications for surfactants in the industries. Foam properties of surfactant in liquid solution include foamability and foam stability. These two are useful for application in mineral flotation, enhanced oil recovery (EOR), foam fractionation, textiles processing, firefighting, food processing, and home and personal care products (HPCs) among others (Afifi et al., 2021; Pandey et al., 2003). Foamability is the amount of foam generated while foam stability relates to how easily the generated foam collapses over time (Wilson, 2017).

Emulsion and cloud point are equally important properties determining the end-use applications for surfactants in the industries. Emulsion results from the dispersion of one phase as small droplets in the other as a continuous phase. It is the mixture of two immiscible liquids, with one of the liquids typically being oil or water, giving the possibility for either oil-in-water (o/w) or water-in-oil (w/o) emulsion. Emulsion properties of surfactants are important in determining their application in food processing, paints, plastics, cosmetics, pharmaceuticals, adhesives, bitumen emulsions, agrochemical formulations, and so on (Holmberg et al., 2014). Emulsion stability is the ability of an emulsion to retain its properties unchanged over a certain period of time. Cloud point, on the other hand, is the temperature range at which a surfactant in solutions or formulations, when heated, becomes cloudy; that is, turbid. This phenomenon results in a phase separation into two micellous phases, by which one phase has a higher concentration of surfactant solution and the other with a lower concentration of surfactant (Holmberg et al., 2003). Cloudiness of surfactant in aqueous solution and its separation into two micelles solutions are known to create certain effects for its application during product formulation. It has been reported that nonionic surfactants are highly effective close to and below the cloud point of that surfactant (Mahajan et al., 2004). Herein, we report the assessment of the properties of the C_nEO_m surfactants viz-a-viz surface tension, foamability, foam stability, emulsion capacity and stability, and cloud point.

EXPERIMENTAL SECTION

Materials

Toluene (JHD, 99.5%), sodium sulfate anhydrous (Avishkar, 99%), sodium chloride (BDH, 99.5%) and sodium nitrite (BDH, 99.5%), surfactants (previously synthesized (Ogunjobi et al., 2023) and used as obtained).

Methods

Surface tension (ST) and critical micelle concentration determination

A stock solution of surfactant (1 mg/mL) was prepared using ultra-pure 18.2 mΩ Millipore water. All surfactants were soluble in water at 25°C. This solution was thereafter diluted to obtain a series of 10 different solutions, and their densities were determined. ST measurement was done with a Kruss DSA 100 tensiometer. A 1 mL syringe was fitted with a needle whose outer diameter was measured with a micrometer gauge and was attached to the dosing unit of the device. The needle was gently lowered into the surfactant of known solution, and a suspended drop at the tip of the needle was obtained by gently controlling the dosing volume. The optical setup was adjusted until a sharp image was obtained, after which 500 images were taken, and thereafter ST was calculated and computed by the instrument using the Young-Laplace equation. Average ST was calculated, and the resulting data was processed on Origin 2022 software to obtain critical micelle concentration (CMC).

Foamability and foam stability measurement

Foamability and foam stability were done as earlier reported but with some modifications (Ogunjobi et al., 2021). Aqueous surfactant solution (50 mL, 0.25% wt/vol) was first measured into a 100 mL graduated cylinder after which foam was generated at room temperature using a homogenizer at different stirring speeds. After 1 min of homogenization, the volume of the foam height generated was read for foam capacity while foam stability was assessed by measuring the reduction in the foam volume in the graduated cylinder

TABLE 1 List of thirty-five surfactants synthesized from alkyl oleate esters via ring-opening reaction with PEG 400, MPEG 400, MPEG 750, PEG 1000, and PEG 1500.

S/N	Surfactant code	Code description	C[a] No	EO unit
1	PEMO400	Epoxidised methyl oleate ring-opened with PEG 400	19	9
2	PEEO400	Epoxidised ethyl oleate ring-opened with PEG 400	20	9
3	PEBO400	Epoxidised 1-butyl oleate ring-opened with PEG 400	22	9
4	PE2BO400	Epoxidised 2-butyl oleate ring-opened with PEG 400	22	9
5	PEOO400	Epoxidised 1-octyl oleate ring-opened with PEG 400	26	9
6	PE2OO400	Epoxidised 2-octyl oleate ring-opened with PEG 400	26	9
7	PEDO400	Epoxidised decyl oleate ring-opened with PEG 400	28	9
8	MPEMO400	Epoxidised methyl oleate ring-opened with MePEG 400	19	9
9	MPEEO400	Epoxidised ethyl oleate ring-opened with MePEG 400	20	9
10	MPEBO400	Epoxidised 1-butyl oleate ring-opened with MePEG 400	22	9
11	MPE2BO400	Epoxidised 2-butyl oleate ring-opened with MePEG 400	22	9
12	MPEOO400	Epoxidised 1-octyl oleate ring-opened with MePEG 400	26	9
13	MPE2OO400	Epoxidised 2-octyl oleate ring-opened with MePEG 400	26	9
14	MPEDO400	Epoxidised decyl oleate ring-opened with MePEG 400	28	9
15	MPEMO750	Epoxidised methyl oleate ring-opened with MePEG 750	19	16
16	MPEEO750	Epoxidised ethyl oleate ring-opened with MePEG 750	20	16
17	MPEBO750	Epoxidised 1-butyl oleate ring-opened with MePEG 750	22	16
18	MPE2BO750	Epoxidised 2-butyl oleate ring-opened with MePEG 750	22	16
19	MPEOO750	Epoxidised 1-octyl oleate ring-opened with MePEG 750	26	16
20	MPE2OO750	Epoxidised 2-octyl oleate ring-opened with MePEG 750	26	16
21	MPEDO750	Epoxidised decyl oleate ring-opened with MePEG 750	28	16
22	PEMO1000	Epoxidised methyl oleate ring-opened with PEG 1000	19	22
23	PEEO1000	Epoxidised ethyl oleate ring-opened with PEG 1000	20	22
24	PEBO1000	Epoxidised 1-butyl oleate ring-opened with PEG 1000	22	22
25	PE2BO1000	Epoxidised 2-butyl oleate ring-opened with PEG 1000	22	22
26	PEOO1000	Epoxidised 1-octyl oleate ring-opened with PEG 1000	26	22
27	PE2OO1000	Epoxidised 2-octyl oleate ring-opened with PEG 1000	26	22
28	PEDO1000	Epoxidised decyl oleate ring-opened with PEG 1000	28	22
29	PEMO1500	Epoxidised methyl oleate ring-opened with PEG 1500	19	34
30	PEEO1500	Epoxidised ethyl oleate ring-opened with PEG 1500	20	34
31	PEBO1500	Epoxidised 1-butyl oleate ring-opened with PEG 1500	22	34
32	PE2BO1500	Epoxidised 2-butyl oleate ring-opened with PEG 1500	22	34
33	PEOO1500	Epoxidised 1-octyl oleate ring-opened with PEG 1500	26	34
34	PE2OO1500	Epoxidised 2-octyl oleate ring-opened with PEG 1000	26	34
35	PEDO1500	Epoxidised decyl oleate ring-opened with PEG 1500	28	34

[a] Surfactant hydrophobic carbon chain number.

every 30 min. Foam capacity and foam stability were calculated as follows:

$$\text{Foamability} = \text{Foam volume}/\text{Initial sample volume} \times 100\% \quad (1)$$

$$\text{Foam stability} = \text{Foam volume after 30 min}/\text{Initial foam volume} \times 100\% \quad (2)$$

Emulsion capacity and stability

Surfactant (100 mg) was weighed into a 20 mL bottle, and to this was added 2 mL each of distilled water and toluene to make a solution. The solution was homogenized on an orbital shaker at 200 rpm for 15 min. Phase separation of the emulsified solution, that is, emulsion stability, was monitored at intervals for several weeks.

TABLE 2 CMC, ST_{CMC}, and efficiency concentration of the surfactants based on PEG 1500 chain length.

Entry	Surfactant code	ST_{CMC} (mN/m)	CMC (mol/L) $\times 10^{-4}$	Efficiency conc. (mol/L) $\times 10^{-5}$
1	PEMO1500	36.38	6.29	2.09
2	PEEO1500	36.12	4.51	2.89
3	PEPO1500[a]	36.94	2.90	2.41
4	PE2PO1500[a]	35.68	2.63	1.77
5	PEBO1500	36.84	1.89	1.94
6	PE2BO1500	36.11	1.78	1.24
7	PEOO1500	-	-	2.17
8	PE2OO1500	38.06	0.83	2.02
9	PEDO1500	-	-	2.35

[a] These surfactants are not part of those considered in the present study but are included in the ST measurement to balance the alkyl progression of the surfactant chain.

Cloud point determination

Aqueous solution of surfactant (1 wt%) was prepared using distilled water. 5 mL of the solution was transferred into a 10 mL test tube, sealed with aluminum foil, and immersed in a 250 mL beaker containing water fitted with a thermometer. The solution was gradually heated on a heating magnetic stirrer until the solution turned cloudy. For surfactant solutions that appeared cloudy at room temperature, the cloud point was determined by placing the solution in a bath of ice sealed with aluminum foil, with a thermometer placed inside to monitor the temperature at which the cloudiness disappears.

Cloud point determination in the presence of co-solutes

Aqueous solution of surfactant (1 wt%) and salt solution (1 wt%) was prepared. 3 mL salt solution was added to 3 mL surfactant solution in a 10 mL test tube, sealed with aluminum foil and immersed in a 250 mL beaker of water fitted with a thermometer on a heating magnetic stirrer. The solution in the test tube was gradually heated and cloudiness temperature was monitored (Mushtaq et al., 2014).

RESULTS AND DISCUSSION

ST and CMC

The CMC values of nonionic surfactants were determined using ST measurements at different concentrations and are taken into consideration at the minimum point of the decreasing surface tension curve. As ST could not be measured for all the samples listed in Table 1, CMCs, ST_{CMC}, and efficiency concentration of all surfactants based on PEG 1500 chain length are presented in Table 2. Expectedly, CMC decreased from 6.29 to 0.83 $\times 10^{-4}$ mol/L by a factor of 7.5 as the surfactant carbon chain increased from 19 to 27 (entries 1–6 and 8). This is because, as the hydrophobic chain increases, only a smaller number of these molecules can aggregate at the interface, thus lowering CMC.

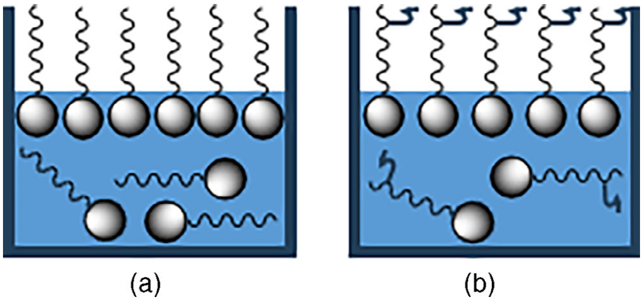


FIGURE 2 Assembly of (a) unbranched and (b) branched surfactant molecules at the air/water interface.

Of particular interest is the CMCs of the isomeric compounds (PEPO1500, PE2PO1500 and PEBO1500, PE2BO1500) which revealed that branching lowers CMC (entries 3–6) as only a smaller number of the branched molecules can adsorb and be packed at the air/water interface, as illustrated in Figure 2. However, CMC could not be determined for PEOO1500 and PEDO1500 (entries 7 and 9) as equilibrium could not be reached at set concentrations. ST at CMC for the surfactants is between 35 and 38 mN/m, indicating their ability to significantly lower ST, and favorably compare with commercially available products. Additionally, the surfactants were efficient, reducing ST by 20 mN/m at concentrations between 1.24 and 2.89 $\times 10^{-4}$ mol/L. Overall, the CMC values recorded for our C_nEO_m surfactants are by far lower than what was reported for commercial ethoxylated surfactants such as polyoxyethylene (20) stearyl ether, octyl phenol ethoxylate, and polysorbates 22, 40, 60, and 80 (Patist et al., 2000).

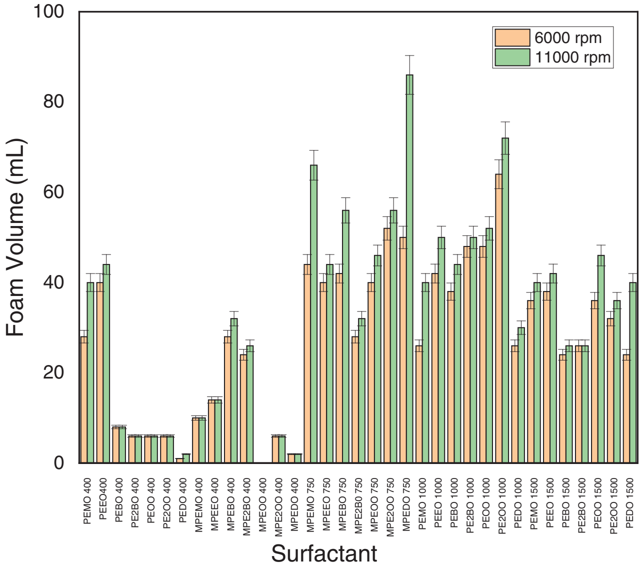


FIGURE 3 Influence of agitation speed on foam volume of 0.25% surfactant solution at 6000 and 11,000 rpm.

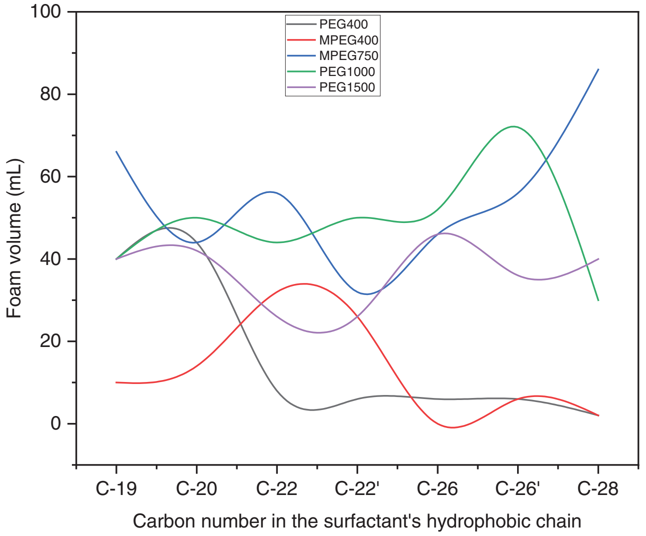


FIGURE 4 Relationship between foam volume generated at 11000 rpm against surfactant hydrophobic carbon chain over PEG 400, MPEG 400, MPEG 750, PEG 1000, and PEG 1500.

Foamability

Foam was generated for the surfactants using two different agitation speeds (6000 and 11,000 rpm), and the volume of foam generated was measured after being homogenized. Results of the influence of stirring speed on foam volume generated by the surfactants are presented in Figure 3. Foam volume generated at both speeds in all the surfactants are not significantly different, except in MPEMO750, MPEDO750, PEMO1000, and PEDO1500, with over 30% foam increase upon increasing agitation speed from 6000 to 11,000 rpm. It was observed that the increase in the alkyl carbon chain length attached to the oleate structure with uncapped PEG 400 surfactants did not have a significant effect on the foam volume produced. Rather, foam volume decreased or remained unaffected with increasing hydrophobic carbon chain length, except for PEMO400 and PEEO400 surfactants. A plot of foamability against the surfactant's hydrophobic carbon chain length shows that as the alkyl chain length increased from 19 to 28, the amount of foam formed increased, peaking at 20 before dropping at 22 and then rising a little further (Figure 4). This showed foamability was at its maximum at 20 for the PEG 400 based surfactant.

The monomethyl capped PEG 400-based surfactants, that is, MPEG 400 showed some differences in foamability compared to the uncapped counterparts. It was observed that maximum foamability was recorded on 22 alkyl chain, two carbons away from its uncapped counterpart. For both PEGs, increasing the hydrophobic carbon chain beyond 22 did not enhance foamability in the surfactants (Figure 4). There was a noticeable difference in the foamabilities of the primary and secondary chains, the former having a higher foamability than the latter.

Surfactants based on MPEG 750 had outstanding foam properties compared to all other surfactants. The highest foam volumes were recorded at 19 and 28 (Figures 3 and 4). Nearly all the surfactants in this category gave a foam volume above 40 mL at both stirring speeds. This could be attributed to a balance in the hydrophilic end in relation to the hydrophobic group of these surfactants.

In the PEG 1000-based surfactants, foam volume increased from 40 mL at 19 through 50 mL (20 and 22′) and then peaked at 72 mL (26) before dropping to 30 mL (28) as shown in Figures 3 and 4. Results showed that doubling agitation speed did not lead to much increase in foamability in the surfactant. Foamability trend in PEG 1500-based surfactants was similar to results from other surfactants, recording its highest (46 mL) at 26.

Generally, an increase in hydrophobic chain length is known to bring about a high intermolecular cohesive force leading to high foamability. However, the reverse was the case for some of the surfactants as carbon chain length increased from 19 to 28 for the different PEG chains. Reasons for this could probably be best explained using the concepts of critical molecular packing parameter (CPP) and hydrophilic–lipophilic balance (HLB). For instance, from PEBO400 to PEDO400, the hydrophobic chain increased from 22 to 28 at a fixed EO_9. Here, the CPP value is assumably above 1 and the ease of hole formation is higher, leading to reduced foamability in the PEG 400-based surfactants. But, as the number of hydrophile and lipophile reaches a balance

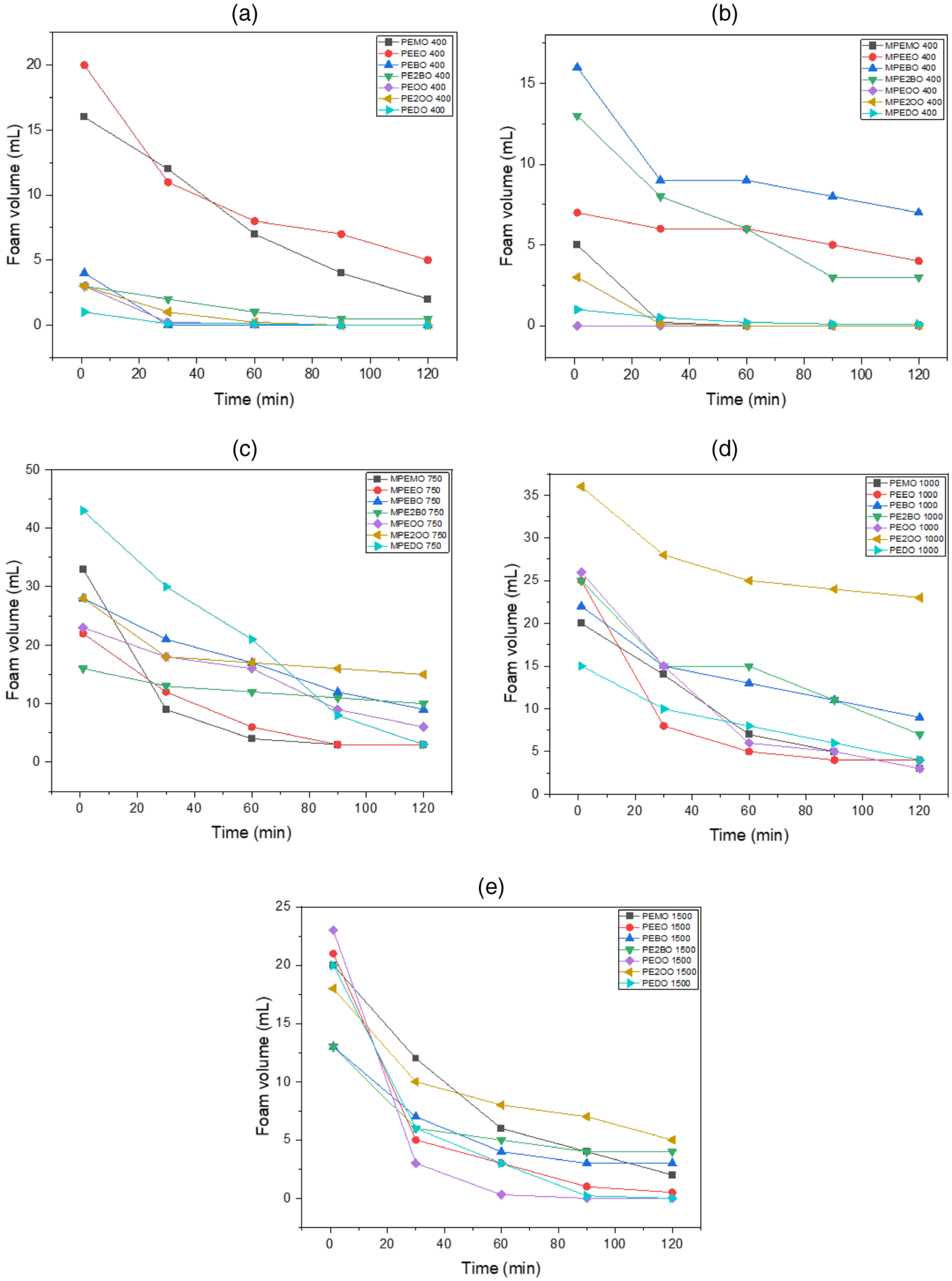


FIGURE 5 Foam stability of 0.25% wt/wt surfactant solution from: (a) PEMO400 to PEDO400. (b) MPEMO400 to MPEDO400. (c) MPEMO750 to MPEDO750. (d) PEMO1000 to PEDO1000. (e) PEMO1500 to PEDO1500 over 120 min.

that is possibly equivalent to a CPP of 1 as observed in PEG 750-based surfactants, foamability increased greatly. Surfactants are known to demonstrate their best detergency, in this case, foamability at CPP values close to 1 (Kontogeorgis & Kiil, 2016). The foamability trend recorded for the PEG 1000s and 1500s surfactants, where CPP is less than 1, showed that there is a better polarity balancing in them than in the 400 s. This agrees with an earlier report which predicted from the HLB concept that the

PEG 750, 1000, and 1500-based surfactants can be applied as detergents among others (Ogunjobi et al., 2023).

Foamabilities of these surfactants were compared with those of cetyl trimethyl ammonium bromide (CTAB)-cationic surfactant, sodium dodecyl sulfate (SDS)-anionic surfactant, and polysorbate 80 (nonionic synthetic industrial surfactant) as reported by Amaral and co-workers (Amaral et al., 2008). In the study, foam volumes for CTAB, SDS, and polysorbate 80 were 27, 27, and 24 mL respectively at ca. 0.5% wt/vol concentration prepared at 13500 rpm stirring speed. Obviously, most of the surfactants in this study present higher foaming capacities even at both lower concentrations and stirring speeds compared to these commercial products.

Foam stability

Foam stability is influenced by the following factors: the molecular packing within the adsorbed surfactant film, the surface viscosity of the film at the air-water interface, and the layering or structuring of micelles in the bulk water within foam lamellae (Holmberg et al., 2014; Patist et al., 2000). For all surfactant solutions, foam stability was assessed by measuring foam volume 1 min immediately after foam was generated, then at 30-min intervals for a period of 120 min (2 h). Foam stability of surfactants of this molecular structure was considered based on the variation of the hydrophobic chain length along a fixed PEG chain length and vice versa.

Results presented in Figure 5 showed that an increase in hydrophobic chain length had an impact on the foam stability of both capped and uncapped PEGylated surfactants. At a fixed EO unit of 9, most of the foams generated by surfactants with hydrophobic carbon greater than 22 completely collapsed before or just after 1 h of being produced. It was observed that PEEO400, with a 20 hydrophobic chain, was the most stable among them, having 25% of foam volume remaining after 2 h of being generated (Figure 5a). Their counterpart surfactants in the capped form also showed good foam stability between 20 and 22 surfactants, with MPEEO400 (20) recording the highest stability, retaining 57% of foam volume after 2 h of generation (Figure 5b). As the EO unit increased to 16, there was a shift in stability to MPE2BO750, which further shifted to PE2OO1000 as the EO unit increased to 22, and then to PE2BO1500 at the EO unit of 34, as shown in Figure 5c–d.

A look at foam stability based on the variation of hydrophilic chain length, that is, PEG chain length across a fixed hydrophobic chain length, as shown in Figure 6, it was obvious that foam stability increased with increasing carbon chain length and was highest between 22 and 24, with their isomeric secondary compounds taking the lead. According to a recent study, the longer the alkyl chain of a surfactant is increased, the greater the external force required to destroy the foam surface it produces (Zhang et al., 2023). In other words, an increase in the alkyl chain of surfactants leads to enhanced foam stability. However, in this study, the 28 surfactant did not perform accordingly. This is probably due to an imbalance in HLB value, which causes a rapid rupturing of the foam, although there is increased molecular interaction at the interface. Predominantly, the secondary surfactants in almost all the PEG chain lengths demonstrated better foam stability than their isomeric primary surfactants. This could imply that branching of the alkyl chain in the adsorbed surfactant film better stabilizes the foam generated. Branching of surfactant hydrophobic chain length has been reported to cause significant differences in the physical properties from the linear chain molecules (Chattopadhyay et al., 2020; Varadaraj et al., 1991).

Comparatively, the foam stability of the alkyl oleate-based surfactants, especially MPE2OO750 and MPE2BO750, at 0.25% concentration is higher than that of CTAB, SDS, and tween 80 at 0.5% concentration (Amaral et al., 2008). Therefore, MPE2OO750 and MPE2BO750, among others, can serve as possible replacement foam stabilizers to the commonly used synthetic industrial cationic, anionic, and nonionic surfactants.

Emulsion capacity and stability

Emulsion is the mixture of two immiscible liquids, with one phase liquid typically being an oil/nonpolar solvent and the other a water/polar solvent, where one phase is dispersed as droplets and the other is a continuous phase, or both are dispersed equally. Surfactant reduces interfacial tension; therefore, it serves as an emulsifier during the homogenization of two immiscible liquids. Emulsion capacity and stability of the surfactants were formed after homogenization of 50:50 toluene/water with 100 mg surfactant. This homogenized formulation, which is 50% each of water and oil, is noted to be of higher standard compared to a technical emulsion (25%–50% dispersed phase) (Holmberg et al., 2014).

Appearance of an emulsion after emulsifying the two immiscible liquids with the surfactant is an indication that interfacial tension between the two liquids was reduced. All the emulsions produced were oil-in-water (o/w). Some of the emulsions formed were whitish in color while others were yellowish. Others had both mixtures of colors upon emulsification as shown in Figure 7. Emulsion stability refers to the ability of an emulsion to maintain its properties unchanged over a certain period of time. The stability of the emulsion

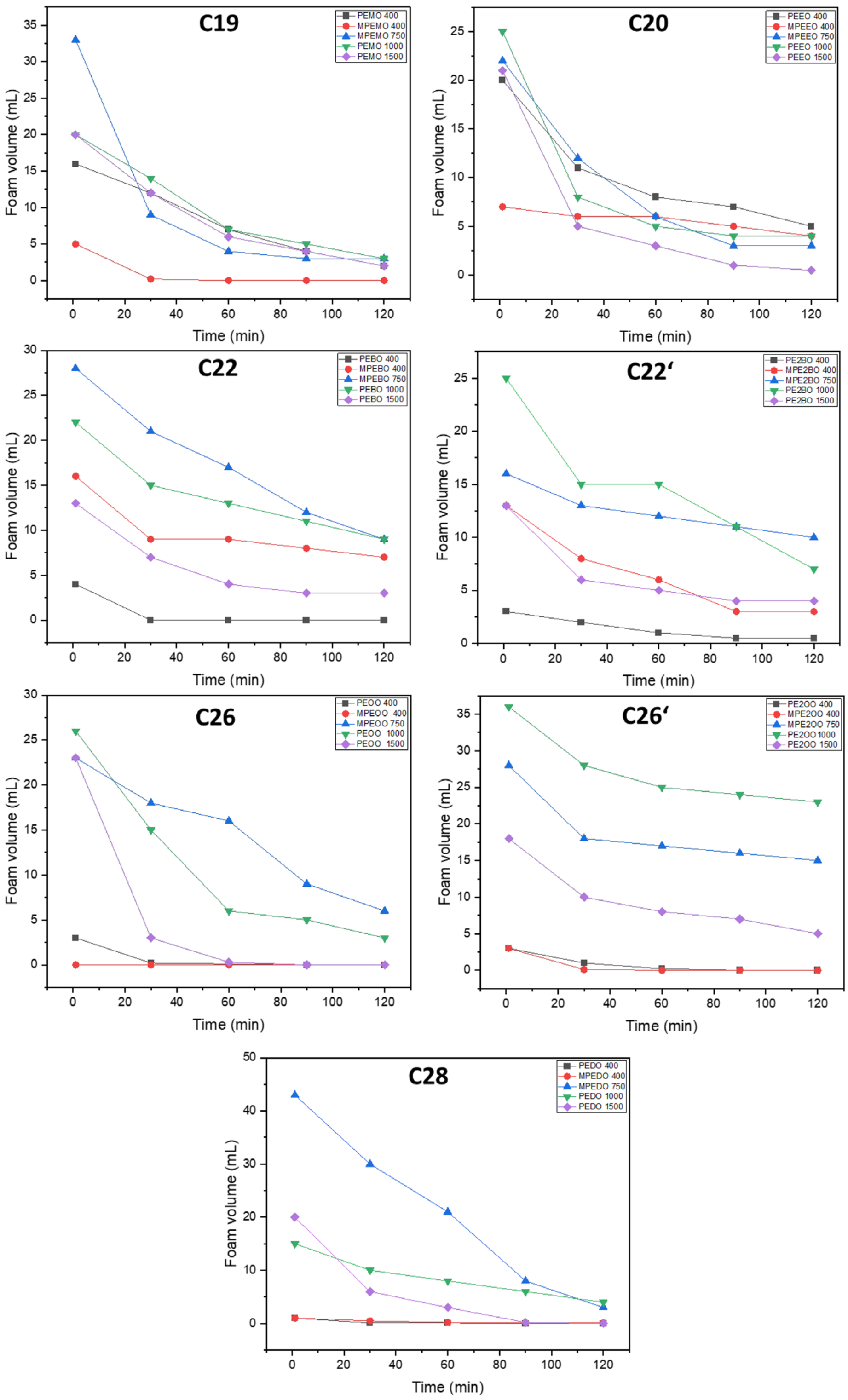
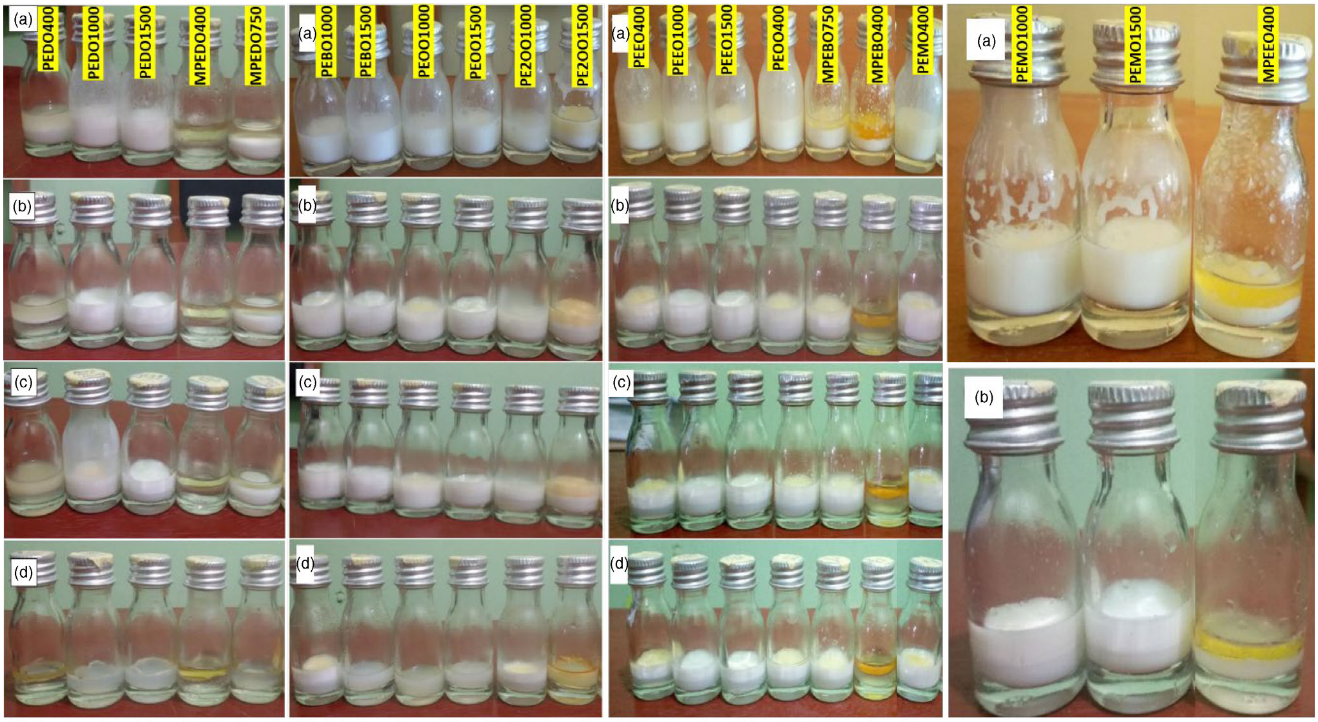


FIGURE 6 Foam stability of 0.25% wt/wt Surfactant solution from PEGs 400, 1000, 1500, monomethyl PEGs 400 and 750 based on their hydrophobic chain length 19, 20, 22, 22′, 26, 26′ and 28 over 120 min.

formed was visually accessed for weeks as the emulsion began to separate. Creaming was observed during the phase separation (stability check) as shown in Figure 7. Emulsion droplets and the continuous phase often have different densities, causing droplets to rise or sink through the continuous phase under the influence of gravity. Creaming, which was characterized by a whitish/yellowish layer at the top of the emulsion, resulted from the rise of the less dense droplets. Overall, surfactants with a higher EO number from 22 such as PEDO1000, PEEO1500 are better emulsion formers and stabilizers than those with a lower EO number 9 and 16. However, with moderate hydrophobic chain length and 9 EO units, PEMO400 and PEEO400 also formed good emulsions and, in fact, PEMO400 gave the most stable emulsion, that 2 months after, there



(a) 1st day of emulsion, (b) 6th day of emulsion, (c) 10th day of emulsion and (d) 52nd day of emulsion

(a) 1st day of emulsion (b) 7th day of emulsion, (c) 9th day of emulsion and (d) 51st day of emulsion

(a) 1st day of emulsion, (b) 7th day of emulsion, (c) 14th day of emulsion and (d) 21st day of emulsion (e) 60 days not shown.

(a) 1st day of emulsion and (b) 8th day of emulsion

FIGURE 7 Oil in water emulsion formed by the surfactants with emulsion stability monitored over weeks.

was still no visible separation noticed. Obviously, surfactants such as MPEDO400, MPEBO400, and MPEEO400 with capped PEG appeared not to have emulsion stability. Considering the high ratio of oil used in forming the emulsion, the surfactants (emulsifiers) that appeared to be unstable at this high standard might have an appreciable stability when a 30:70 oil-in-water ratio is used.

Cloud point

Clouding behavior is generally witnessed by nonionic surfactants containing PEGs. Cloud point (CP) depends largely on the chain length of the EO, but is less determined by the hydrophobic chain length or size. Longer EO chain length corresponds to a higher CP, while shorter chain length corresponds to a lower CP.

Over the years, several studies have reported on the effects of different inorganic salts on the CPs of nonionic surfactants, and finding has it that sodium salts such as sodium chloride decrease CP of nonionic surfactants (Li et al., 2009). CPs of selected surfactant solutions were studied with and without sodium sulfate, sodium chloride, and sodium nitrite to determine their effects on the CP. Expectedly, results showed an increase in CP with increasing PEG chain, as shown in Table 3.

TABLE 3 Cloud point and effect of different inorganic sodium salts (1 wt%) on the Cloud Point Behaviors of (1 wt%) Surfactants.

Entry	Surfactant	Without salt (°C)	Na_2SO_4 (°C)	NaCl (°C)	$NaNO_2$ (°C)
1	PEMO400	33	27	31	29
2	MPEBO400	53	ND	ND	ND
3	MPEBO750	88	70	67	69
4	MPEDO750	75	60	58	58
5	PE2BO1000	>100	83	82	83
6	PE2OO1000	>100	88	86	85

Abbreviation: ND, not determined.

When salts were added, the same trend was also observed as the EO unit increased from 9 to 22 with the exception of MPEDO750, which had a lower value when compared to MPEBO750. PEMO400 and MPEBO400 were cloudy when salts were added and had to be cooled in order to obtain the CP. However, the CP for MPEBO400 could not be determined even after cooling as there was no sharp fall observed in all the surfactant mixtures with the salts (Table 3 entry 2). Surfactants with 22 EO units exhibited CPs above 100°C, probably due to their higher CH_2 groups in the PEG chain but reduced when salt solutions were added (Table 3 entries 5 and 6). The depression of CP is a result of salting-out effect of Na^+, SO_4^{2-}, Cl^-, and NO_2^- present in the surfactant solutions (Marcus, 2009). Effects of SO_4^{2-} in reducing the CP of polysorbate 80 and octyl phenol ethoxylate had been reported to be dominant over Cl^- and NO_2^- (Shinoda & Takeda, 1970). Comparatively, the CP results obtained for the selected nonionic surfactants in this study, as shown in Table 3 are higher than those of corresponding ethoxylated nonionic surfactants reported in the literature (Mushtaq et al., 2014).

CONCLUSION

Surface tension, foam and emulsion properties together with cloud points of C_nEO_m type surfactants, derived from PEGylated oleate esters, were investigated. These surfactants demonstrated astounding properties as foaming agents, foam stabilizers, emulsifiers, and stabilizers even at very low concentrations. Surface activity study results showed that the surfactants are effective at lowering the surface tension of water and that their CMC values are by far lower than those for many commercial products. Branched surfactants had lower CMC values than their corresponding unbranched isomers. Foamability was seen to be influenced by agitation speed, increasing as speed increased for most of the surfactants, especially at higher PEG chains. Foam stability was enhanced by an increase in the alkyl chain of surfactants, reaching a maximum between 22 and 24. Branching in the hydrophobic chain of the surfactants was seen to influence foamability and foam stability. While branching was observed to enhance foam stability, no ordered trend could be seen for foamability. However, a definite trend might become much more obvious with increased branching in the hydrophobic chain. Additionally, results showed that this category of surfactants performed better as foaming agents and foam stabilizers even at a lower concentration when compared with commercially available surfactants, and will therefore have relevance in personal house care product industries. The surfactants showed high cloud points, especially with increasing ethylene oxide units, higher than known commercial products. Whereas a cloud point depression was recorded in the presence of inorganic sodium salts, the cloud point was still remarkably as high as 88°C. These properties show the relevance of these surfactants in detergency, emulsification, solubilization, wetting in chemical industries and product formulations, and as such can serve as possible replacements for petrochemical synthesized surfactants.

AUTHOR CONTRIBUTIONS

Conceptualization: Joseph K. Ogunjobi; *Data curation*: Osaretin E. Omoruyi and Joseph K. Ogunjobi; *Formal analysis*: Joseph K. Ogunjobi and Osaretin E. Omoruyi; *Investigation*: Osaretin E. Omoruyi and Joseph K. Ogunjobi; *Resources*: Osaretin E. Omoruyi and Joseph K. Ogunjobi; *Supervision*: Joseph K. Ogunjobi; *Writing—original draft*: Joseph K. Ogunjobi and Osaretin E. Omoruyi; *Writing—review and editing*: Joseph K. Ogunjobi.

ACKNOWLEDGMENTS

Authors would like to appreciate the initial contributions of Dr Thomas Farmer, Dr Rob McElroy and Prof. James Clark to the synthesis of the surfactants used in this study.

CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ETHICS STATEMENT

No human or animal subjects are used in this study.

ORCID

Joseph K. Ogunjobi https://orcid.org/0000-0001-9276-7310

REFERENCES

Adu SA, Naughton PJ, Marchant R, Banat IM. Microbial biosurfactants in cosmetic and personal skincare pharmaceutical formulations. Pharmaceutics. 2020;12:1099.

Afifi HR, Mohammadi S, Derazi AM, Alemi FM, Abad KFH. A comprehensive review on critical affecting parameters on foam stability and recent advancements for foam-based EOR scenario. J Mol Liq. 2021;340:116808.

Al Ghatta A, Aravenas RC, Wu Y, Perry JM, Lemus J, Hallett JP. New biobased sulfonated anionic surfactants based on the esterification of furoic acid and fatty alcohols: a green solution for the replacement of oil derivative surfactants with superior proprieties. ACS Sustain Chem Eng. 2022;10(27):8846–55.

Amaral MH, das Neves J, Oliveira ÂZ, Bahia MF. Foamability of detergent solutions prepared with different types of surfactants and waters. J Surfactant Deterg. 2008;11(4):275–8.

Banat IM, Franzetti A, Gandolfi I, Bestetti G, Martinotti MG, Fracchia L, et al. Microbial biosurfactants production, applications and future potential. Appl Microbiol Biotechnol. 2010;87(2):427–44.

Chattopadhyay AK, Ghaïcha L, Leblanc RM. Branched versus linear hydrocarbon chains in surfactants: Ellipsometric evidence of anomalous refractive indices. Surfactants in solution. Boca Raton, FL: CRC Press; 2020. p. 1–30.

Holmberg K, Jonsson B, Kronberg B, Lindman B. Surfactants and polymers in aqueous solution. 2nd ed. England: John Wiley & Sons Ltd.; 2003.

Holmberg K, Lindman B, Kronberg B. Surface chemistry of surfactants and polymers. Chichester: John Wiley & Sons; 2014.

Ismail NL, Shahruddin S, Othman J. Perspective chapter: overview of bio-based surfactant—recent development, industrial challenge, and future outlook. Surfactants and Detergents: Updates and New Insights. London: IntechOpen; 2022. p. 69.

Kobayashi Y, Li Q, Ushimaru K, Hirota M, Morita T, Fukuoka T. Isolation and characterization of novel naturally occurring sophorolipid glycerides. Bioresour Technol Rep. 2023;22:101399.

Kontogeorgis GM, Kiil S. Introduction to applied colloid and surface chemistry. Chichester: John Wiley & Sons; 2016.

Kronberg B, Holmberg K, Lindman B. Surface chemistry of surfactants and polymers. Chichester: Wiley; 2014.

Li J-L, Bai D-S, Chen B-H. Effects of additives on the cloud points of selected nonionic linear ethoxylated alcohol surfactants. Colloids Surf A Physicochem Eng Asp. 2009; 346(1–3):237–43.

Mahajan RK, Chawla J, Bakshi MS. Depression in the cloud point of tween in the presence of glycol additives and triblock polymers. Colloid Polym Sci. 2004;282(10):1165–8.

Marcus Y. Effect of ions on the structure of water: structure making and breaking. Chem Rev. 2009;109(3):1346–70.

Mushtaq M, Tan IM, Ismail L, Lee SYC, Nadeem M, Sagir M. Oleate Ester-derived nonionic surfactants: synthesis and cloud point behavior studies. J Dispers Sci Technol. 2014;35(3): 322–8.

Ogunjobi JK, Farmer TJ, Clark JH, McElroy CR. Synthesis, characterization, and physicochemical performance of nonionic surfactants via PEG modification of epoxides of alkyl oleate esters. ACS Sustain Chem Eng. 2023;11(5):1857–66.

Ogunjobi JK, McElroy CR, Clark JH. A class of surfactants via PEG modification of the oleate moiety of lactonic sophorolipids: synthesis, characterisation and application. Green Chem. 2021;23:9906.

Ortiz MS, Alvarado JG, Zambrano F, Marquez R. Surfactants produced from carbohydrate derivatives: a review of the biobased building blocks used in their synthesis. J Surfactant Deterg. 2022;25(2):147–83.

Pandey S, Bagwe RP, Shah DO. Effect of counterions on surface and foaming properties of dodecyl sulfate. J Colloid Interface Sci. 2003;267(1):160–6.

Patist A, Bhagwat SS, Penfield KW, Aikens P, Shah DO. On the measurement of critical micelle concentrations of pure and technical-grade nonionic surfactants. J Surfactant Deterg. 2000;3(1):53–8.

Shinoda K, Takeda H. The effect of added salts in water on the hydrophile–lipophile balance of nonionic surfactants: the effect of added salts on the phase inversion temperature of emulsions. J Colloid Interface Sci. 1970;32(4):642–6.

Varadaraj R, Bock J, Valint P Jr, Zushma S, Thomas R. Fundamental interfacial properties of alkyl-branched sulfate and ethoxy sulfate surfactants derived from Guerbet alcohols. 1. Surface and instantaneous interfacial tensions. J Phys Chem. 1991;95(4):1671–6.

Velty A, Iborra S, Corma A. Synthetic routes for designing furanic and non furanic biobased surfactants from 5-hydroxymethylfurfural. ChemSusChem. 2022;15(13):e202200181.

Wilson AJ. Experimental techniques for the characterization of foams. Foams. New York: Routledge; 2017. p. 243–74.

Zhang Q-Q, Cai B, Gang H, Yang S, Mu B. A family of novel biobased zwitterionic surfactants derived from oleic acid. RSC Adv. 2014;4(72):38393–6.

Zhang Z, Qiao M, Zhao H, Ran Q, Yuan S. Effect of sodium alkyl sulfate chain length on foam stability: a molecular dynamics study. Colloids Surf A Physicochem Eng Asp. 2023;656:130394.

How to cite this article: Ogunjobi JK, Omoruyi OE. Evaluation of surface, foam, emulsion, and clouding properties of a family of nonionic surfactants from oleic acid derivatives. J Surfact Deterg. 2025. https://doi.org/10.1002/jsde.12846