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Research Article

Synthesis, Characterization, and Physicochemical Performance of Nonionic Surfactants via PEG Modification of Epoxides of Alkyl Oleate Esters

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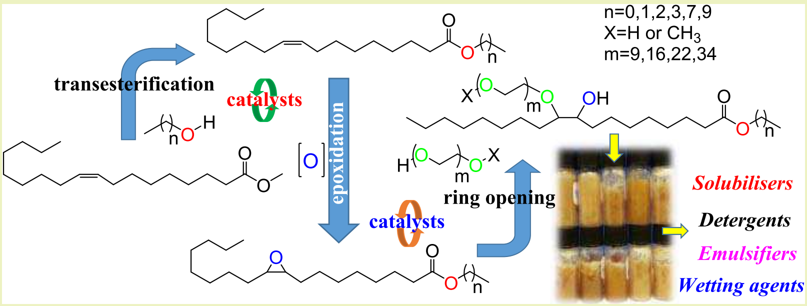

ABSTRACT: The synthesis of surfactants from fatty acid esters via epoxide chemistry has been known for its accompanying challenges, which usually involve the use of toxic homogeneous catalysts in the ring-opening reaction step and generation of many side reaction products. This paper presents environmentally benign routes to a library of nonionic surfactants via a three-step synthesis involving transesterification of methyl oleate to alkyl oleates, epoxidation of the oleate alkene, and solventless heterogeneously catalyzed ring opening of the epoxides with poly(ethylene glycols) of varying chain length under a short reaction time (60 min). The processes were highly atom efficient and afforded a minimum surfactant yield of 80% with limited or negligible side reaction products. The intermediate molecules and synthesized surfactants were purified and comprehensively characterized, including physicochemical measurements: dynamic surface tension and equilibrium surface tension. Additionally, the hydrophilic−lipophilic balance (HLB) concept was used to comprehensively scan through the polarity behaviors of the surfactants' head and tail in solution as a prediction of their end use. The results showed that surfactants have a critical micelle concentration (CMC) lower than 0.1 mg/ml as the alkyl oleate increases in length from ethyl to decyl and that the lower-molecular-weight surfactants reached equilibrium faster than the higher-molecular-weight surfactants. HLB results showed that the surfactants can be applied as oil-in-water emulsifiers, detergents, solubilizers, and wetting agents. In general, the synthesized surfactants potentially possess switchable properties for use in industrial formulations, as the alkyl chain length and the ethylene oxide number in the surfactant's structure are varied.

KEYWORDS: *biobased chemical, heterogeneous catalyst, spectroscopy, surface tension, ring opening, oleic acid, transesterification*

INTRODUCTION

Oleic acid is arguably the most abundant mono-unsaturated fatty acid found in nature. It is largely found as triglycerides in vegetable oils such as rapeseed oil, sunflower oil, olive oil, and peanut oil and is also present in many animal fats. Oleic acid is a C18 molecule whose ester derivatives have found wide applications in home and personal care product industries as the hydrophobic component in surfactants. Oleate-derived surfactants are considered more biodegradable than any other surfactants whose hydrophobes are from petroleum feedstock; the oleate being incorporated makes the hydrophobic region of the surfactants long and bulky enough to lower the CMC and decrease the surfactant dosage used by consumers.[1−5]

Epoxidation is one of the means of functionalizing unsaturated fatty esters, with many different approaches presented in the literature. The typical oxidants used include chlorohydrin, organic peroxides, and peracids, but there has been a growing need to curtail the side reaction products and use of toxic and hazardous reagents and oxidants.[6−9] Challenges in fatty ester epoxidation include hydrolysis of the ester group, with low yields resulting from acid-catalyzed ring-opening side reactions, separation of acidic byproducts,

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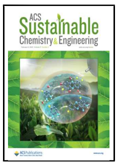

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and corrosion of reaction vessels.[10] Hydrogen peroxide is a relatively environmentally benign oxidant that has a high content of active oxygen, decomposes to give water as the only byproduct, and is not expensive.[11,12] This increased content of active oxygen means the use of hydrogen peroxide is a more atom economic (AE) epoxidation process. For example, the AE in soybean oil epoxidation using hydrogen peroxide is 90%, which is a significant improvement as against using meta-chloro peroxy benzoic acid, where AE = 51%.[13]

One of the earliest studies of functionalizing epoxidized fatty esters *via* ring opening of the epoxy ring resulting in amphiphilic compounds was reported by Hedman and co-workers.[14] In their report, methyl oleate epoxide was ring-opened with different monomethylated polyethylene ethers using a homogeneous boron trifluoride catalyst. Other studies have reported epoxy ring opening of methyl and ethyl oleate epoxides with nucleophiles such as alkyl glycosides and oligoethene glycols using erbium(III) triflate and tin tetrachloride as catalysts.[15,16] However, these syntheses employed catalysts and solvents that present issues such as difficulty in removal and reuse of the catalyst, corrosiveness, and toxicity. Recently, functionalization of the double bond of the fatty ester unit of lactonic sophorolipid via epoxy ring opening with polyethylene glycols was demonstrated.[17] The resulting surfactants gave promising results that could further be exploited in personal and home care products. A comprehensive list of the nucleophiles most commonly used to functionalize fatty derivatives, as well as the chemistry of fatty epoxide ring-opening reactions leading to valuable chemicals was recently reported by Moser and co-workers.[18]

The properties of surfactants resulting from epoxy ring opening of methyl oleate epoxide such as earlier reported can be tailored to have a more hydrophilic influence and to give a broader application by introducing polyethylene glycol (PEG) of varying chain lengths. PEGs are short-chain polyethers soluble in water and a number of organic solvents, including toluene, acetone, ethanol, and dichloromethane, depending on their molecular weight. They are nontoxic and are readily available in various functionalities such as amine, hydroxyl, and thiol end groups.[19] Additionally, increasing the alkyl chain length of the ester of oleic acid and ring opening its epoxide will lead to systems with a nonpolar moiety having two unequal chain lengths, about the same size for the methyl ester, but with more different sizes as the alkyl length changes. Consequently, it would be interesting to investigate how this chemical modification will influence the physicochemical performances and as such end use of the targeted oligomeric surfactants when compared with the methyl oleate-based molecule.

Hence, herein methyl oleate was transesterified into various oleate ester analogues. The oleate alkenes were epoxidized and the resulting epoxides subsequently ring-opened with PEGs of varying chain length to generate a range of nonionic surfactants. The synthetic routes employed involve the use of recoverable heterogeneous catalysts and an atom economic oxidant, H_2O_2.

■ EXPERIMENTAL SECTION

Reagents. Titanium(IV) isopropoxide; silica-supported boron trifluoride; iron(III) nitrate nonahydrate; iron(III) chloride; PEG 400; PEG av. Mn 950-1050; PEG 1500; aluminum nitrate hexahydrate; ammonium-Y-zeolite; phosphotungstic acid hydrate (PTA); tungsten powder; >30% hydrogen peroxide solution in H_2O; Adogen 464; Celite 545 coarse molecular sieve; cyclohexene oxide Amberlyst 15 ion exchange resin; and 2-methoxyethanol were all purchased from Sigma-Aldrich. Triethylene glycol was purchased from Acros Organics. Polyethylene glycol monomethyl ether (MePEG) 400 and MePEG 750 were purchased from Alfa-Aesar, with the numbers 400 and 750 referring to the average molecular weights of the MePEG. Orthophosphoric acid and ethanediol were purchased from Fisher Scientific.

Preparation of Catalysts. Potassium fluoride on alumina (KF/Al_2O_3), treated magnesium oxide catalyst (MgO-T600), Fe-montmorillonite catalyst (Fe-mont), Fe-K30-montmorillonite catalyst (Fe-K30mont), and Al-Y zeolite catalyst were prepared as described in the Supporting Information (SI) section 3.0.

Synthesis of Alkyl Oleates from Methyl Oleate. Methyl oleate (MO, 20 g, 67.2 mmol) and the desired alcohol (403 mmol) were weighed into a 250 mL round-bottom flask fitted with a Dean-Stark trap and condenser. $Ti(O\text{-}i\text{-}Pr)_4$ or KF/Al_2O_3 or MgO-T600 (2 g, 10 wt % with respect to MO) was added and the reaction was agitated under reflux. The reaction progression was monitored by GC-FID. 2 mL of the corresponding alcohol was added at 1-h intervals for the first 3 h into the reaction. After 24 h, the resulting product was vacuum filtered to recover the KF/Al_2O_3 catalyst and a rotary evaporator was used to remove the solvent to yield an amber oil. For reactions involving $Ti(O\text{-}i\text{-}Pr)_4$, 25 mL of distilled water was added to the reaction product to generate titanium(IV) oxide and isopropanol, and the resulting solution was transferred into a separating funnel and shaken with dichloromethane. The organic phase was collected, dried over anhydrous magnesium sulfate, filtered, and the solvent removed *in vacuo* to yield an amber oil. For the MgO-T600 catalyst, after 24 h, the resulting product was allowed to cool down and centrifuged at 3500 rpm at 20 °C for 20 min. The supernatant was transferred into a round-bottom flask and a rotary evaporator was used to remove the solvent to yield an amber oil. Purity and product identification were confirmed by GC-FID, GC-MS, IR spectroscopy, ESI-MS, and ^1H and proton-decoupled ^{13}C NMR spectroscopy as provided in the SI.

Synthesis of Alkyl Oleate Epoxides. The desired alkyl oleate (100.15 mmol), hydrogen peroxide solution (>30% H_2O_2, 40 mL), water (30 mL), phosphotungstic acid (6 wt % with respect to alkyl oleate), and Adogen 464 (3 wt % with respect to alkyl oleate) were added into a 250 mL round-bottom flask and heated at 50°C with vigorous stirring for 3 h. The resulting product was extracted in ethyl acetate (EtOAc, 50 mL), transferred into a separating funnel, and then washed with deionized water (30 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered, and the filtrate passed through a plug of neutral alumina. EtOAc was removed *in vacuo* to yield a light amber oil. The product was analyzed by IR spectroscopy, GC-MS, ESI-MS, ^1H and proton-decoupled ^{13}C NMR spectroscopy, and quantified by GC-FID as provided in the SI.

Ring Opening of Alkyl Oleate Epoxides with Polyethylene Glycol (diol) or Polyethylene Glycol Monomethyl Ether. Polyethylene glycol (PEG, 10 mmol) or polyethylene glycol monomethyl ether (MePEG, 10 mmol) was heated to 80 °C in a 50 mL round-bottom flask followed by addition of catalyst (5 wt % of PEG or MePEG) and allowed to mix thoroughly for 2 min. The desired alkyl oleate epoxide (5 mmol) was added in drops through a dropping funnel for over 5−10 min and the temperature was raised to 100 °C while stirring rigorously. The progress of the reaction was monitored with ^1H NMR spectroscopy with portions taken for analysis. The reaction was stopped when complete or after 50 min (whichever came first), and the resulting product was extracted in EtOAc (50 mL) and vacuum filtered to recover the catalyst. The filtrate was transferred to a separating funnel and washed with distilled water (25 mL) followed by saturated brine (20 mL). The organic phase was collected and dried over anhydrous $MgSO_4$, run through a narrow column packed with Amberlyst 15 ion exchange resin, and the resulting solution concentrated on the rotary evaporator. Product identification was done by IR spectroscopy, ESI mass spectrometry, CHN elemental analysis, and ^1H and proton-decoupled ^{13}C NMR spectroscopy. The total product mass recovered, spectroscopic assignment (NMR, IR, and ESI-MS), and elemental analysis for the ring-opened epoxides are provided in the SI.

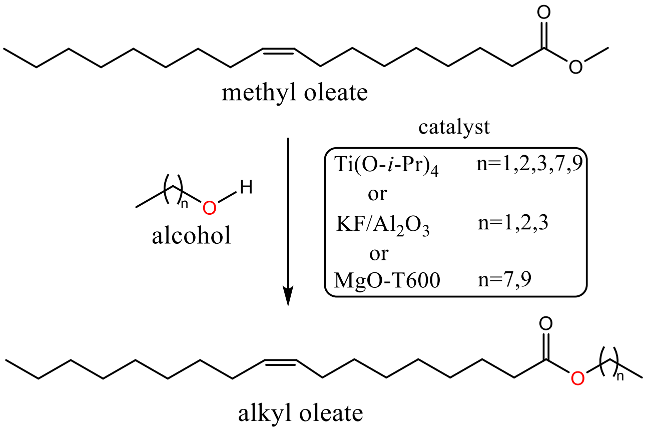
Dynamic Surface Tension (DST) Measurement of Synthesized Surfactants. To a sodium chloride solution (100 mL, 10 mmol) was added 0.1 g of surfactant to give a 1 g/L surfactant solution and left to age for 24 h. Thereafter, 5 mL of the solution was measured in a beaker and placed under a maximum-bubble-pressure tensiometer, and a precision capillary was immersed automatically to a depth of 10 mm from the liquid surface. The other end of the capillary was connected to a gas supply with a pressure sensor, and the tensiometer was operated to obtain a set of data. The surface lifetimes of the bubbles were measured until 100 s.

Equilibrium Surface Tension (EST) Measurement of the Synthesized Surfactants. To a sodium chloride solution (100 mL, 10 mmol) was added 0.1 g of surfactant in a 100 mL sample bottle to give a 1 g/L surfactant solution, which was left to age for 24 h. Thereafter, 30 mL of the solution was measured in a clean beaker and placed under a Kruss K100 tensiometer fitted with a platinum plate (Wilhelmy plate). The dilute aqueous surfactant solution was then allowed to attain 25 °C, after which the plate was automatically lowered into the solution by the automatic interface detection method to start the experiments. A bottle on a Dosino unit coupled to the tensiometer was filled with 10 mmol/L sodium chloride solution, from which the sample was multiply diluted and the instrument run under preset conditions. An extended surfactant program was used and sets of measurements were taken until the change in surface tension was less than 0.1 mN/m. The plate was washed each time sequentially with ethanol and acetone, dried on a spirit lamp, and then allowed to cool prior to and after each time the measurement was made.

■ RESULTS AND DISCUSSION

Synthesis of Alkyl Oleates *via* Transesterification of MO. A set of oleate esters were synthesized from methyl oleate *via* transesterification with ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-octanol, 2-octanol, and 1-decanol using potassium fluoride on alumina support (KF/Al_2O_3), magnesium oxide treated at 600 °C (MgO-T600), and titanium(IV) isopropoxide ($Ti(O\text{-}i\text{Pr})_4$) as catalysts (Scheme 1). Transesterification of methyl oleate with the various alcohols was observed to be fastest in reactions involving $Ti(O\text{-}i\text{Pr})_4$, presumably as the catalyst was homogeneous with the reactants.

Scheme 1. Transformation of Methyl Oleate into Alkyl Oleate Esters Using Both Homogeneous and Heterogeneous Catalysts



Transesterification generally gave high conversions, yields, and selectivities, becoming close to quantitative in most reactions (Table 1, entries 1−10). However, in the syntheses of 1-octyl oleate, 2-octyl oleate, and 1-decyl oleate, the selectivity was reduced to between 95 and 98% (entries 11−15). The conversion remained quantitative, with formation of some side products (Scheme 2 and SI section 6).[20] GC-FID and GC-MS data showed the presence of the corresponding epoxides and diols in both the crude and final products.

The colors of the synthesized oleates and catalytic studies (other heterogeneous supports, optimum catalyst loading, catalyst reuse, and catalyst recovery) were also investigated in this study and are presented in section 6 of the Supporting information SI. Alkyl oleates were characterized with FT-IR spectroscopy, GC-MS, ESI-MS, and one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy. Full details of NMR assignment and analytical data are included in the SI.

Epoxidation of Alkyl Oleates. All of the oleate esters synthesized and methyl oleate for comparison were epoxidized effectively using H_2O_2 as the oxidant in the presence of a catalyst. Two catalytic methods were used to synthesize the epoxides. The first method involved the use of a preformed commercial phosphotungstic acid (PTA), while the second method involved the preparation of PTA *in situ* by the reacting tungsten powder, hydrogen peroxide, and orthophosphoric acid (H_3PO_4), and both methods used Adogen 464 as the phase transfer catalyst (PTC), as shown in Scheme 3. Typically, a catalyst concentration of 6 wt % relative to alkyl oleate and 3 wt % Adogen 464 concentration relative to oleate were applied in all epoxidation reactions.

Conversion, yield, and selectivity were calculated and are presented in Table 2. Alkyl oleate conversion up to 99%, yield up to 93%, and selectivity up to 95% for synthesis involving the preformed PTA catalyst were obtained. Side reactions are commonly observed with fatty acid alkyl ester (FAAE) epoxidation.[7,21,22] As such, the following side products were detected alongside the desired epoxides: nonanal, 9-oxo-alkyl ester nonanoic acid, cis-9,10-epoxy octadecanoic acid, and diol. The reaction times were determined by monitoring the conversion and yield and differed from one epoxide to the other. It was noted that those oleates in which waxes were formed (Table 2 entries 1, 2, 3, and 5; SI section 6.0 and Figure SI-4a) took longer reaction times to reach a comparable level of conversion compared with those in which there were no waxes (entries 4 and 6). This could be due to reduced molecular collision of reactants resulting from the increased viscosity and reduced mobility of the oleate molecules. Comparing the two epoxidation methods, preformed PTA catalysis gave the least side products and as such was preferred.

Precise carbon and proton NMR spectra assignment was achieved by a combination of COSY, HSQC, and DEPT carbon as detailed in the SI Section 4.0. IR spectral analysis (Figure SI-8) equally showed the disappearance of the ca. 3004 cm^{-1} band belonging to the olefinic C−H stretch and appearance of vibrations belonging to the epoxy band between 953 and 979 cm^{-1} (asymmetric deformation) and between 822 and 837 cm^{-1} (symmetric ring deformation). The epoxy bands are in line with the values reported in the literature.[23,24] Electrospray ionization mass spectrometry was employed to determine the accurate masses for all of the epoxides synthesized.

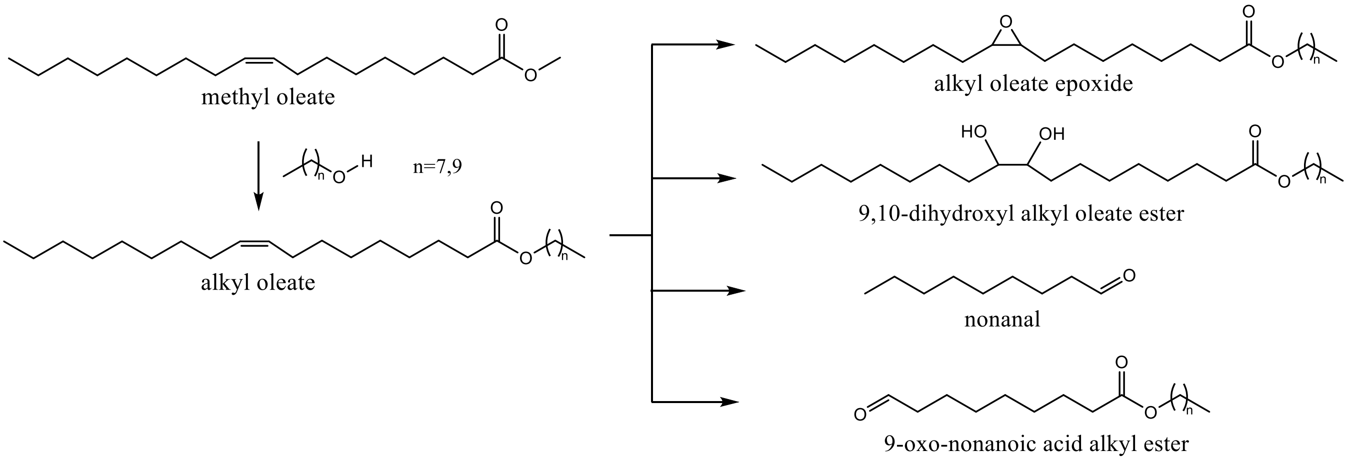
With respect to the appearance of the alkyl oleate epoxides synthesized, it was observed that there was a change in color from deep to light amber shades in the compounds formed as shown in Figure SI-9. This was probably due to the bleaching of the oleates by hydrogen peroxide.

Table 1. Comparative Effectiveness of $Ti(O\text{-}i\text{-}Pr)_4$, MgO-T600, and KF/Al_2O_3 Catalysts for Alkyl Oleate Synthesis

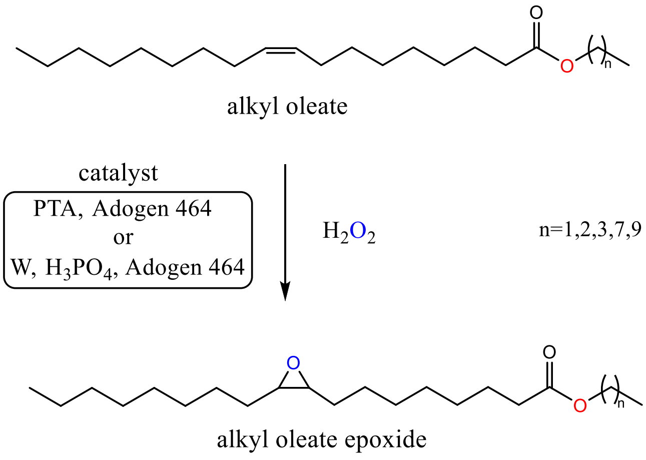
entry	alcohol	oleate ester product	catalyst	time (h)	conversion[a] (%)	selectivity (%)	yield[a] (%)
1	ethanol	ethyl oleate	KF/Al_2O_3	30	99	100	99
2	ethanol	ethyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	10	99	100	99
3	propan-1-ol	1-propyl oleate	KF/Al_2O_3	30	99	100	99
4	propan-1-ol	1-propyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	10	99	100	99
5	2-propanol	2-propyl oleate	KF/Al_2O_3	36	98	100	98
6	2-propanol	2-propyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	24	100	100	100
7	butan-1-ol	1-butyl oleate	KF/Al_2O_3	24	100	100	100
8	butan-1-ol	1-butyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	10	96	100	96
9	butan-2-ol	2-butyl oleate	KF/Al_2O_3	30	100	100	100
10	butan-2-ol	2-butyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	10	98	100	98
11	octan-1-ol	1-octyl oleate	MgO-T600	24	100	95	95
12	octan-1-ol	1-octyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	13	100	88	88
13	octan-2-ol	2-octyl oleate	MgO-T600	39	100	98	98
14	octan-2-ol	2-octyl oleate	$Ti\ (O\text{-}i\text{-}Pr)_4$	17	100	97	97
15	decan-1-ol	1-decyl oleate	MgO-T600	24	100	98	98

[a] Calculated by GC. Reaction conditions: methyl oleate (20 g, 67.2 mmol), alcohol (403 mmol), and catalyst (2 g, 10 wt % with respect to methyl oleate) under reflux temperatures of the respective alcohol.

Scheme 2. Formation of Aldehydes, Keto Esters, Epoxides, and Diols Observed in Higher Alkyl Oleates during Transesterification of Methyl Oleate Leading to Reduced Selectivity



Scheme 3. Synthesis of Alkyl Oleate Epoxide from the Oxidation of Alkyl Oleate in the Presence of Hydrogen Peroxide *via* Either Preformed PTA or In Situ PTA Catalysis



Ring Opening of Alkyl Oleate Epoxides with PEGs. Many of the previous studies involving ring opening of methyl oleate and fatty acid epoxides utilized the boron trifluoride catalyst.[14,18,25,26] However, boron trifluoride's acceptance as an effective catalyst for this reaction continues to wane not only because it is a homogeneous catalyst but also because of its high toxicity. Some heterogeneous catalysts such as saponite clays and Nafion-silica have been reported as being effective for epoxide ring opening of epoxy methyl oleate.[27,28] However, their effectiveness with longer-chain fatty esters is unknown. This study sought to catalyze the ring-opening step using heterogeneous catalysts that are eco-friendly and cheap.

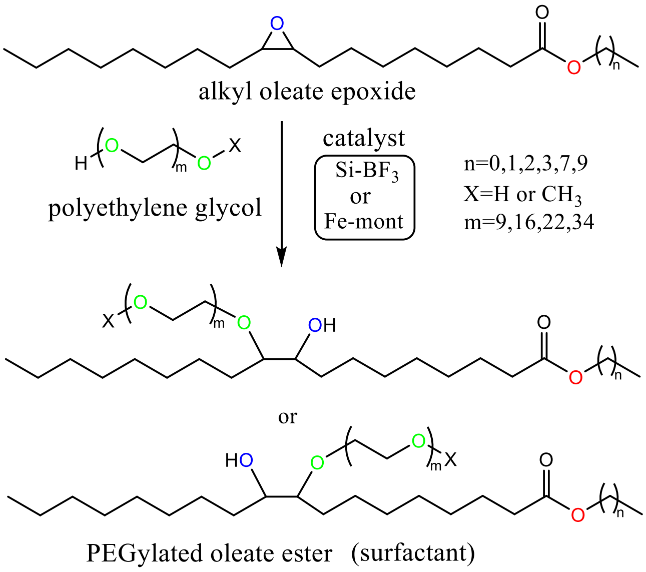
The synthesized epoxides were ring-opened with monomethylated PEGs (MePEG) and uncapped PEG diols (PEG) using Lewis acid catalysts (Scheme 4). A wide range of homogeneous and heterogeneous metal and non-metal Lewis acid catalysts were first screened at different reaction conditions: ytterbium(III) triflate, $Yb(TFA)_3$; indium(III) triflate, $In(TFA)_3$; iron(III) triflate, $Fe(TFA)_3$; scandium(III) triflate, $Sc(TFA)_3$; silica-supported boron trifluoride, Si-BF_3; boron trifluoride diethyl etherate, BF_3-Et_2O; sulfuric acid, H_2SO_4; iron(III) chloride, $FeCl_3$; iron-exchanged montmorillonite clay, Fe-mont; aluminum-exchanged montmorillonite clay, Al-mont; and aluminum-exchanged zeolite clay, Al-zeolite. Most of these catalysts are less well known for this

Table 2. Table Effectiveness of Preformed PTA for Synthesis of Alkyl Oleate Epoxides

entry	oleate epoxide	time (h)	conversion[a] (%)	selectivity (%)	yield[a] (%)
1	methyl oleate epoxide	3.5	99	73	73
2	ethyl oleate epoxide	5.5	98	95	93
3	1-propyl oleate epoxide	5.5	95	92	88
4	2-propyl oleate epoxide	3.0	100	93	93
5	1-butyl oleate epoxide	6.0	95	83	79
6	2-butyl oleate epoxide	3.0	99	82	81
7	1-octyl oleate epoxide	3.0	99	84	83
8	2-octyl oleate epoxide	3.5	95	81	77
9	1-decyl oleate epoxide	3.0	99	90	90

[a] Calculated by GC. Reaction conditions: alkyl oleate (100.15 mmol), H_2O_2 (40 mL), water (30 mL), PTA (6 wt % with respect to alkyl oleate) and Adogen 464 (3 wt % with respect to alkyl oleate) at 50°C, t = 3 h.

Scheme 4. Synthesis of PEGylated Oleate Esters from the Ring Opening of Alkyl Oleate Epoxides with PEGs of Varying Chain Length Catalyzed by Heterogeneous Lewis Acids



type of reaction.[29,30] The metal-exchanged montmorillonite catalysts were prepared as earlier reported.[17,31,32]

Results of catalyst screening (SI section 9.0 Table SI-4) showed that Si-BF_3 gave high selectivity toward the PEGylated oleate esters. Heterogeneous silica-supported BF_3 is corrosive but significantly less hazardous than its unsupported free form.[33,34] In order to accurately characterize the resulting PEGylated oleate esters owing to their high molecular masses, model reactions with lower-molecular-weight compounds (<726 g/mol) of the same functionalities as PEGs were investigated and the products were characterized with GC-FID, GC-MS, IR spectroscopy, and proton-decoupled NMR spectroscopy. The reactions involved ring-opening cyclohexene oxide (CHexO) and methyl oleate epoxide (EMO) with ethylene glycol (EG), triethylene glycol (TEG), poly(ethylene glycol) (PEG), and 2-methoxyethanol (MeEG).[20] From the model reaction, based on the yield and selectivity, the best catalysts selected for synthesis were determined to be Si-BF_3 and Fe-mont. Subsequently, epoxides of methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 1-butyl, 1-octyl, 2-octyl, and 1-decyl oleates were ring-opened with poly(ethylene glycol) 400 (PEG 400), poly(ethylene glycol) 1000 (PEG 1000), poly(ethylene glycol) 1500 (PEG 1500), methoxy poly(ethylene glycol) 400 (MePEG 400), and methoxy poly(ethylene glycol) 750 (MePEG 750). PEGs with molecular weight less than 1000 are viscous and colorless liquids, while higher-molecular-weight PEGs are waxy white solids.

Synthesis of the PEGylated oleate esters was typically performed by heating PEGs or MePEGs to 80 °C and adding the catalyst, followed by dropwise addition of the fatty epoxide over 5 to 10 min depending on the amount of epoxide added. The initial ring-opening reactions were catalyzed by the Si-BF_3 catalyst with a typical reaction time of 50 min. A catalyst loading of 1 and 2 wt % amount of Si-BF_3 relative to PEG or MePEG was first applied, but there was no conversion after 2 h of reaction; thus, 5 wt % Si-BF_3 was used for further synthesis. Different catalyst concentrations were initially applied for the metal-exchanged mont catalysts, but 20 wt % catalyst concentration gave the best conversion in 2 h. Interestingly, 20 wt % each of Al-mont, Fe-mont (NO_3^-) was prepared from the nitrate salt of iron, and Fe-mont (Cl_3^-) was prepared from the chloride salt of iron; catalysts relative to PEG were found as effective as the 5 wt % Si-BF_3 catalyst in 2 h of the reaction. However, Fe-K30-mont was not effective at these conditions as a large portion of the epoxide was instead converted to diol. The metal-exchanged mont catalyst generates products with a pale amber color (Figure SI-12), which will easily blend with

Table 3. Description of PEGylated Oleate Esters Synthesized from PEGs of Different Chain Lengths

PEG	color	appearance and texture	mass recovery (%)	av. molecular weight range (g/mol)
PEG 400	golden amber	viscous	∼77	726−852
MePEG 400	a different shade of amber	less viscous	97	739−865
MePEG 750	golden amber	gel-like viscous	90	1049−1175
PEG 1000	amber	viscous when hot but solidify into hard-to-cut-through materials at room temperature	95	1298−1424
PEG 1500	golden amber	golden amber hard-to-cut-through materials at room temperature	93	1826−1952

most cosmetic formulations. Completion of the reaction was usually marked with a change in the reaction mixture color from amber to golden amber or brown. Excess PEG was removed by transferring the filtrate (the resulting solution following catalyst removal) into a separating funnel; after adding water, the solution was shaken to form an emulsion, which was broken up with the addition of brine. However, attempts to remove excess MePEG by the same method were unsuccessful. Therefore, syntheses involving MePEG and other higher PEG chains were subsequently carried out using an equimolar amount of epoxide and PEG.

A descriptive summary of the synthesized PEGylated oleate esters from different PEGs is presented in Table 3. The average molecular weight ranges from 726 to 1952 g/mol with a minimum product recovery of over 77%. The amber-shaded products varied from viscous to hard-to-cut-through waxy materials.

Characterization of Synthesized PEGylated Oleate Esters. Model reactions of methyl oleate epoxide with TEG and PEG 400 using the Si-BF_3 catalyst already gave a minimum product yield of 75%. The final PEGylated oleate esters were characterized with 1D and 2D NMR spectroscopy, FT-IR spectroscopy, electrospray ionization mass spectrometry, CHN elemental analysis, and inductively coupled plasma mass spectrometry (ICP-MS).

NMR, IR, and ESI Analyses. Full details of the characterization and peak assignments of all synthesized surfactants are provided in sections 5.0 and 9.0 of the SI. Specific details of NMR, IR, and ESI using PEGylated methyl ester as an example are provided in sections 9.1−9.4 of SI.

CHN Elemental Analysis. It became apparent that some of the synthesized PEGylated oleate esters contained residual Adogen 464; thus, the PEGylated oleate ester-ethyl acetate mixture was passed through a narrow column packed with Amberlyst 15 ion exchange resin to remove the cationic surface-active impurity and the resulting compounds were investigated using a CHN elemental analyzer. The results are presented in Table 4 and it was attested that nitrogen was not detected (ND) in any of the surfactants after purification with Amberlyst 15 resin, which implies that Adogen 464 impurity had been successfully removed by this approach.

Table 4. CHN Elemental Composition of Epoxide and PEGylated Oleate Esters after Treatment with an Ion Exchange Resin

		percentage found after ring opening and treatment		
entry	compound code	C	H	N
1	PEMO 400	60.673	10.089	ND
2	MPEMO 750	57.262	9.637	ND
3	PE2BO 400	63.418	10.395	ND
4	PEMO 1500	55.236	8.782	ND

ICP Mass Spectrometry. Determination of residual metal catalysts in PEGylated oleate esters was achieved using ICP-MS. Results for PEEO 400 obtained via Fe-mont catalysis showed 0.002 wt % (20 ppm) aluminum (Al), 0.009 wt % (90 ppm) potassium (K), 0.011 wt % (110 ppm) iron (Fe), and 0.06 wt % (600 ppm) tungsten (W). Al and K were likely resulting from use of the KF/Al_2O_3 transesterification catalyst, while W most likely comes from phosphotungstic acid used to catalyze the epoxidation process. Fe has come from the Fe-mont catalyst used for the ring-opening reaction. This indicates that there has been some degree of catalyst leaching in each step of the synthesis, although the presence of these metals may not impair surfactant end-application performances as their overall concentrations are low (W is the highest at 600 ppm). The Al content is below that typically found in many foodstuffs;[35] potassium and iron are not problematic, while dermal exposure to W is not problematic at the concentrations recorded.[36]

Physicochemical Performance of the Synthesized Compounds. *DST of the Synthesized PEGylated Oleate Esters.* Dynamics studies of the synthesized PEGylated oleate esters including surface tension and critical micelle concentration (CMC) measurements were recorded using a Sinterface maximum-bubble pressure tensiometer and a Kruss K100 tensiometer coupled with Metrohm 700 dosino. The extended surfactant characteristic method was used to measure the CMC. DST gave information on surface tension as a function of time. The results for some of the compounds are shown in Figure 1. The synthesized molecules demonstrated surface activity with good dynamics. PEMO 400 (hydroxyl end group to PEG chain) had the lowest surface tension (32 mN/m), while PEOO 400 had the highest surface tension (53 mN/m). MPEMO 400 (methoxy end group to PEG chain) with a surface tension of 33 mN/m did not perform any differently from the hydroxyl end group to the PEG chain and appeared to have reached equilibrium in 20 s. It was observed that PEEO 400 had a lower surface tension (32 mN/m) but quicker equilibrium time compared to PEEO 1500 with higher surface tension (42 mN/m) and it took a bit longer to equilibrate due to the dominance of the hydrophilic chain over the hydrophobic chain. PEOO 400 had a high surface tension (53 mN/m) but slow equilibration, which could be due to the presence of an inadequate hydrophilic character over a long hydrophobe. PEOO 1500 also was slow but not at equilibrium due to the high molecular weight, which delays self-aggregation. However, the latter has a lower surface tension

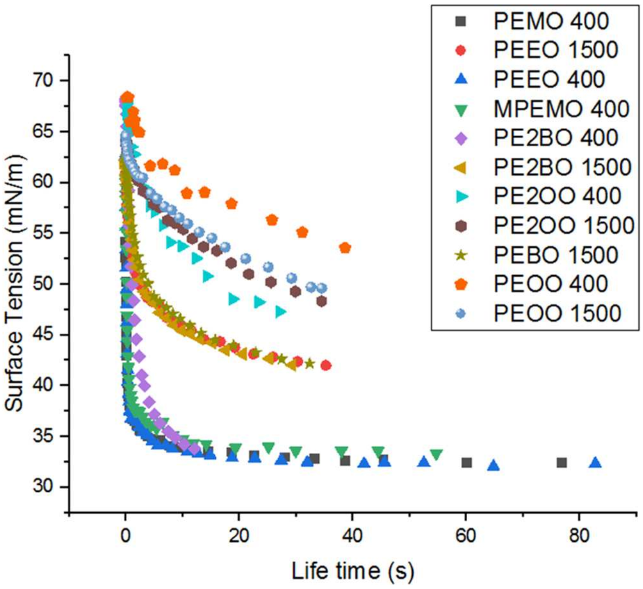


Figure 1. Dynamic surface tension of unpurified PEMO 400, MPEMO 400, PEEO 400, PEEO 1500, PE2BO 400, PE2BO 1500, PEOO 400, PEOO 1500, PE2OO 400, and PE2OO 1500.

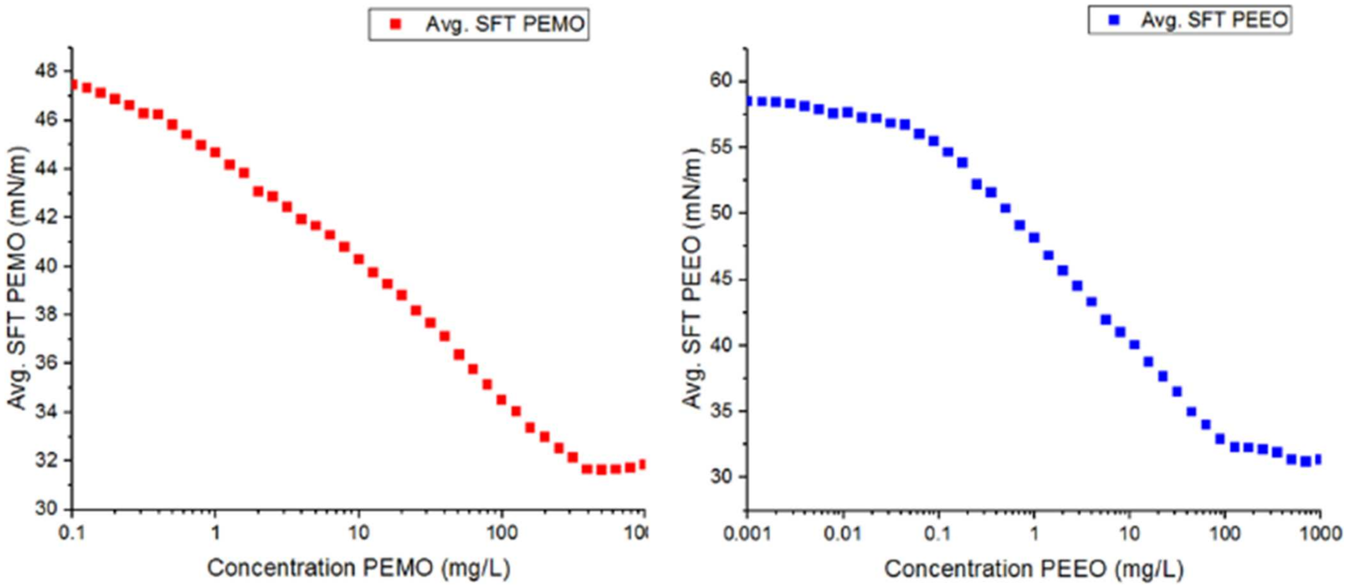


Figure 2. Surface tension versus the logarithm of surfactant concentration for purified PEMO 400 (1 mg/mL) and PEEO 400 (1 mg/mL) at ~26 °C.

(49 mN/m) than the former, thus having a better balance between hydrophobic and hydrophilic regions.

Structurally contrasting between the PEGylated molecules, it was observed that as the PEG chain length increased from 400 to 1500, although surface tension increased due to increasing hydrophilicity in the PEG chain except in PEOO where it decreased, equilibrium times were longer. Increasing the alkyl group on the ester functionality across the same PEG chain length did not significantly increase the surface tension and equilibrium time upon the addition of four CH_2 groups. However, a significant increase was recorded with the addition of eight CH_2 groups to the ester.

EST of the Synthesized PEGylated Oleate Esters. Measurements of equilibrium surface tension using a Kruss K100 tensiometer showed the variation between the surface tension and change in surfactant concentration. A surfactant loading of 1 mg/mL was prepared and diluted by the instrument while changes in surface tension were measured. Continual dilution to a concentration low enough to give the surface tension of water (72 mN/m) was not achieved for all measurements. Initial attempts with unpurified surfactants are reported in the ESI section 11. Results for the purified samples are shown in Figure 2 and compared with the unpurified samples (Figure SI-13). The surface tension vs concentration curves showed that PEEO 400 at 0.001 mg/L concentration when purified was 58 mN/m, while when unpurified it was 45 mN/m.

The higher surface tension in the purified sample is as a result of the removal of surface-active impurities. The same trend was observed in the purified and unpurified PEMO 400 surfactant curves in which surface tension increased from around 40 mN/m to over 46 mN/m at 0.3 mg/mL concentration after removing the impurities. CMC values for both purified PEMO 400 and PEEO 400 were ~0.7 and ~0.1 mg/mL, respectively, close to what was recorded for the unpurified samples. With both having the same hydrophilic head group, CMC is eight times lower for PEEO 400 with an addition of one CH_2 to the hydrophobic tail. This observed factor of 7 reduction is far more than a factor of about 3 that Traube's rule states upon adding a methylene group to nonionics.[37−39] The structural difference in surfactant types could be the likely reason for this observation. However, it is not obvious how this is linked with surface tension and CMC reduction. With a lower CMC, PEEO 400 is a better surfactant than PEMO 400 depending on their area of application. Both PEEO 400 and PEMO 400 surfactants have an effectiveness of ~40.5 mN/m when extended to the surface tension of water (Figure 2). Efficiency could not be evaluated for PEMO 400 (unless the concentration was extended), but PEEO 400 recorded an efficiency of 0.018 mg/mL. Efficiency is the concentration required to reduce the solution surface tension by 20 mN/m. This value is similar to that obtainable in commercial nonionic surfactants.[40] CMC is sensitive to both the presence of alkyl chain length and EO number in polymeric surfactants. However, it is more sensitive to an increase in the former than in the latter.[38] Therefore, for other surfactants where measurements were not taken, CMC values will be higher for all surfactants on increasing the alkyl chain length attached to the ester at a constant EO number, but lower CMCs will be expected for those having the same alkyl chain length as the EO number increases from 9 to 16 and from 22 to 34.

Hydrophilic−Lipophilic Balance (HLB). The HLB concept using the extended contribution effective chain length (ECL) method was employed as a rapid and facile approach to predict the possible properties and applications of the PEGylated oleate esters as surfactants (Figures 3−6, further details of the calculations are in the SI, section S11). HLB values decrease with increasing alkyl group in the fatty chain, but increase with increasing EO number in the hydrophilic head. Based on the HLB values and range in Figures 3 and 4, surfactants with PEG 400, MePEG 400, and MePEG 750 (EO number 9 and 16) will likely find applications as either oil-in-water emulsifiers or detergents. Surfactants with higher EO number (PEG 1000) spread between three potential applications. For PEMO 1000 to PE2BO 1000 with HLB values between 16.70 and 15.33, their potential application will be as solubilizing agents, while PEOO 1000, PE2OO 1000, and

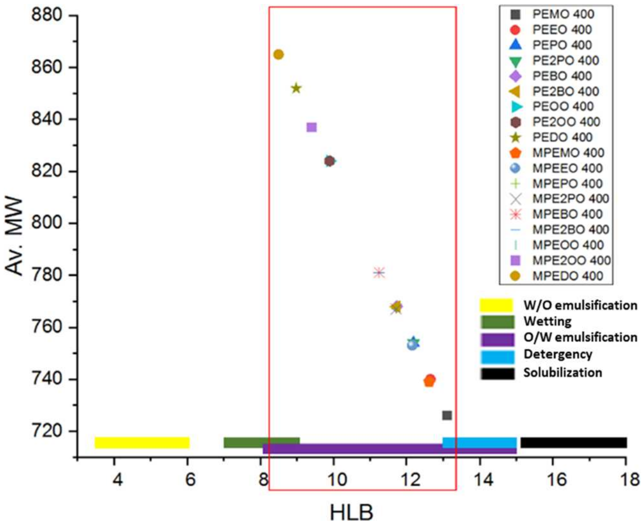


Figure 3. HLB values and average molecular weight obtained for alkyl oleate surfactants based on PEG 400 and MePEG 400.

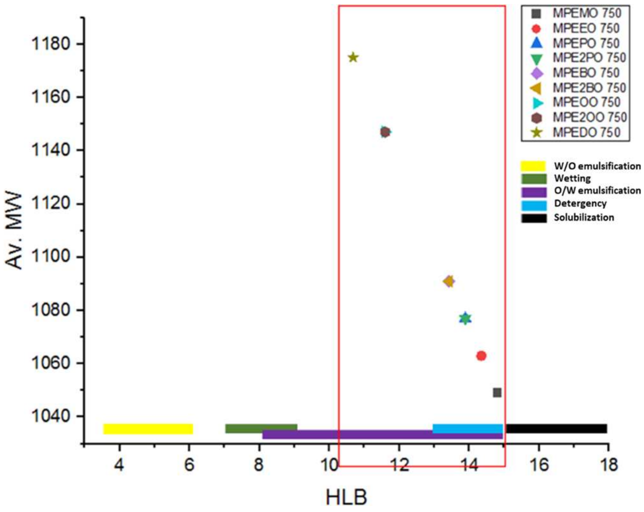


Figure 4. HLB values and average molecular weight obtained for alkyl oleate surfactants based on MePEG 750.

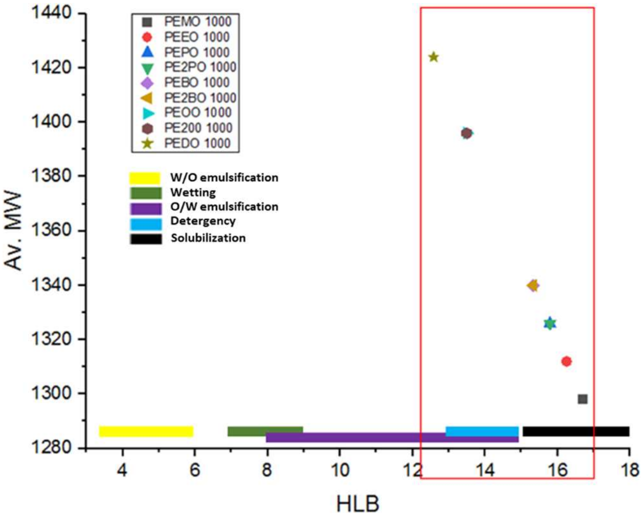


Figure 5. HLB values and average molecular weight obtained for alkyl oleate surfactants based on PEG 1000.

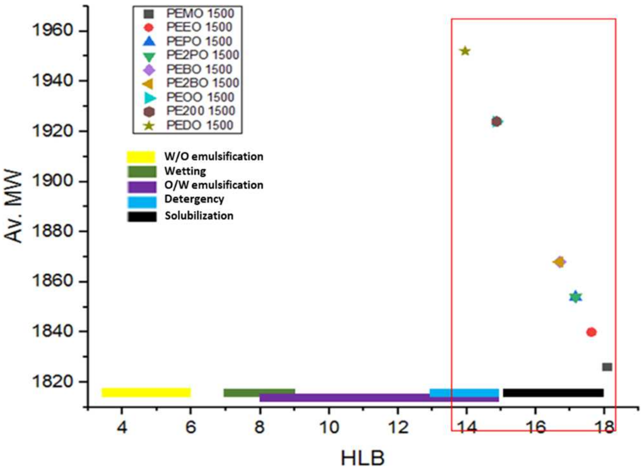


Figure 6. HLB values and average molecular weight obtained for alkyl oleate surfactants based on PEG 1500.

PEDO 1000 surfactants have potentials as either oil-in-water emulsifiers or detergents (Figure 5). Surfactants with PEG 1500 attached also have three potential applications. The methyl-, ethyl-, 1-propyl-, 2-propyl-, 1-butyl-, and 2-butyl-oleate PEGylated surfactants will most likely find applications as solubilizing agents while the 1-octyl-, 2-octyl-, and 1-decyl-oleate PEGylated surfactants have potentials as oil-in-water emulsifiers and detergents (Figure 6). Although HLB values obtained for isomeric surfactants of the same EO chain length, for example, 1-propyl oleate- and 2-propyl oleate-based surfactants, showed no obvious difference, it is believed critical parking parameter (CPP) values will be different for these surfactants.

CONCLUSIONS

Forty-five renewable nonionic surfactants have been successfully prepared from alkyl oleate epoxides *via* ring-opening reaction with PEGs of varying chain lengths using cheap heterogeneous catalysts, affording ~80% surfactant yield. The surfactants so formed took the physical form of the PEG attached to them and were extensively characterized. Treatment of surfactants with Amberlyst 15 resin helped in removal of the residual Adogen 464 impurity in the epoxidation step, but it contained trace amounts of residual catalyst metals used in transesterification, epoxidation, and ring opening processes.

DST studies revealed that structural modifications in the PEG chain length and alkyl group on the ester functionality had influence on the surface tension and equilibrium time of the traditional methyl molecule. The lower-molecular-weight surfactants were more spontaneous in reaching equilibrium than the higher-molecular-weight surfactants. EST measurements showed that the surfactants tested have low CMCs (0.1−0.7 mg/mL) and are efficient and effective. These results clearly demonstrate that the synthesized surfactants have suitable properties for use in formulations and that structure variation has altered these properties accordingly. Based on the theoretical HLB results, the family of synthesized surfactants will potentially find applications as oil-in-water emulsifiers, detergents, solubilizers, and wetting agents, their final use being heavily dependent on the structure (size of alkyl group on the ester and length of the PEG chain).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c06298.

> synthesis of methyl oleate; spectroscopic assignment (NMR, IR and ESI-MS) analysis for synthesized methyl oleate and alkyl oleates; synthesis of alkyl oleates *via* transesterification of methyl oleate; preparation of catalysts; spectroscopic assignment (NMR, IR and ESI-MS) analysis for alkyl oleate epoxides; spectroscopic assignment (NMR, IR and ESI-MS) and elemental analysis for ring-opened alkyl oleate epoxides; details of transesterification reactions and catalyst loading and reuse; epoxidation of alkyl oleate; screening of ring-opening catalyst and characterization of pegylated oleate esters; synthesized surfactants and their colors; equilibrium surface tension of synthesized surfactants; HLB calculations (PDF)

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Notes

The authors declare no competing financial interest.

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