Synthesis and Performance of Surfactants Based on Epoxidized Methyl Oleate and Glycerol

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ABSTRACT: A small series of surfactants based on methyl oleate and glycerol was synthesized. The synthesis utilizes an epoxidation reaction of methyl oleate followed by a simple esterification. The resultant products have between two and seven glyceride units, and their performance properties, including aqueous surface tensions and dynamic aqueous surface tensions, were studied. The droplet size of soybean oil/water emulsions made with each surfactant was also studied. The surfactants show properties similar to alcohol ethoxylates, such as the reduction of aqueous surface tension to ~34 mN m^{-1}. Additionally, because the synthesis leaves the epoxide functionality in the surfactant, further modification for performance optimization is possible.

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KEY WORDS: Bio-based surfactant, emulsifier, environmentally friendly, epoxidized methyl oleate, glycerol, polyglyceride, surface tension, surfactant.

In 2002, the North American and world surfactant markets were 3.5 billion metric tons and 11.2 billion metric tons, respectively (1), with 3% growth forecast until 2010. Despite this large market, surfactant makers are faced with a higher costs (2,3) and the need for innovation (4–6) in order to meet consumer demands. The use of agriculturally derived natural carbohydrates and oleochemicals is becoming more attractive to producers (7).

Conventional nonionic surfactants utilizing oleochemicals are often made via catalytic reaction of ethylene oxide with long-chain alcohols, often of petrochemical origin (8). Work using oleochemically derived alcohols, or more recently, oleochemically derived esters and oils (9–11) has also been performed. One drawback to these surfactants is the requirement of large quantities of ethylene oxide, which is not only potentially dangerous, but it is becoming more expensive as the cost of ethylene increases. The cost of ethylene oxide increased from \$0.45 lb^{-1} to \$0.60 lb^{-1} between 2004 and 2006. Meanwhile, the cost of glycerol has been decreasing due to biodiesel production (12). This makes the study and production of glycerol based surfactants an attractive area.

Novel polyglycerides (13–15) and polyglyceride oleochemicals (16–21) have been synthesized, characterized (22), and are potentially useful in the food (23,24), cosmetic , and biomedical industries(13,25,26). However, there is still potential for significant progress in the area.

Herein, a series of surfactants based on glycerol and epoxidized methyl oleate (EMO) is synthesized. These surfactants are also tested for their surface tension reduction and emulsion stabilizing capability. These surfactants offer similar performance to alcohol ethoxylates and have built in functionality for further chemical modification to achieve desired physical properties.

EXPERIMENTAL PROCEDURES

Materials. Methyl oleate (Sigma-Aldrich, St. Louis, MO, technical grade, 70%), hydrogen peroxide (Sigma-Aldrich, ACS reagent grade, 30% solution), formic acid (Sigma-Aldrich, 96%, ACS reagent grade), hexanes (Sigma-Aldrich, >95%, HPLC grade), acetone (Sigma-Aldrich, Chromasolve for HPLC, 99.9%), NaCl (Fisher, Fairlawn, NJ, ACS reagent grade), $NaHCO_3$ (Fisher, ACS reagent grade), NaOH (Fisher, ACS reagent grade), Na_2SO_4 (Sigma-Aldrich, 99+%, ACS reagent grade), butanol (Fisher, ACS reagent grade), glycerol (Fisher, ACS reagent grade), solketal (Sigma-Aldrich, 98%), HBr in acetic acid (Fluka, Buchs, Switzerland, >33% assay), crystal violet (Sigma-Aldrich, ACS reagent grade), acetic acid (EM science Gibbstown, NJ, 99.7%, potassium acid phthalate (Sigma-Aldrich, ACS standard grade, 99.95%), chlorobenzene (Sigma-Aldrich, ACS reagent grade, 99.6%), sodium dodecyl sulfate, (Sigma-Aldrich, 99.%), Brij® 72, 76, 78 (Sigma-Aldrich), and soybean oil (Nexsoy, Springfield, IL, expeller pressed, refined, bleached, degummed) were used as received. The surfactants, Pluronic® L43 (BASF, Spartanburg, SC), Pluronic® L64 (BASF, Spartanburg, SC), and Caprol® MPGO (Abitec Corporation, Janesville, WI), were obtained from the manufacturers as free samples, and

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Abbreviations: EMO, epoxidized methyl oleate.

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used as received. Ethylene glycol dimethyl ether (Sigma-Aldrich, 99.5%, ACS reagent grade) and toluene (Sigma-Aldrich, 99.5%, ACS reagent grade) for RSN titrations were mixed by volume, 2.6% toluene, and allowed to dry over molecular sieves overnight. The water used in the surfactant tests was purified to at least 18.0 M cm^{-1} by a Barnstead (Dubuque, IA) Easy Pure II RF/UV water purification system.

Instrumentation and equipment. FTIR spectra of the starting material and products were recorded on a Thermonicolet (Madison, WI) Nexus 470 FTIR with a Smart ARK accessory containing a 45^o ZeSe trough. Data was collected and processed on a Windows 2000–equipped Dell Optiplex GX260 Pentium 4, 2.46 GHz computer running Omnic 6.2 software.

NMR was performed on a Bruker (Boston, MA) Avance 500 NMR operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Bruker Icon NMR software was used running on an HP x1100 Pentium 4 workstation. Peaks were referenced to sodium 3-trimethylsilylpropionate-2,2,3,3-d_4 (TSP) at 0.0000 ppm. Simulations of ^{13}C NMR spectra were performed by ACD/Labs 6.00 ACD/CNMR predictor software, running on a Gateway Pentium 4 CPU with a 2.53 GHz processor.

Dynamic surface tension measurements were taken with a Sita t60 bubble pressure tensiometer (Desden, Germany) using Sita online V2.1 software. Dilutions were made using an Ingenieurbüro (Staufen, Germany) Cat M 26 stir plate and an Ingenieurbüro (Staufen, Germany) CAT contiburette µ-10M-C burette using Sita Labtool V1 software. They were all controlled by an IBM (White Plains, NY) Pentium 4 computer with a 3.0 GHz processor and a Windows XP operating system.

Static surface tension and critical micelle concentration were measured on a Krüss K10t digital tensiometer. The duNouy ring method was used for surface tension measurement.

Emulsion droplet size was measured by a Malvern (Southborough MA), Mastersizer/E instrument equipped with a small volume sample presentation unit. Data was analyzed and processed using Malvern Mastersizer software.

Viscosity of the polyglyceride was measured using a Brookfield Model DV-III Programmable Rheometer ran by Rheocalc v. 2.4. A CP-52 spindle was used, and the resulting sheer stress vs sheer rate plot was analyzed by the Bingham model.

Oxirane titrations were preformed by AOCS official Method Cd 9-57. The samples of ~0.2 g were dissolved in 30 mL of a 2:1 volume ratio chlorobenzene/acetic acid solution, and titrated with a standardized 0.1 M HBr in acetic acid solution. The titrations were performed on a Metrohm 836 Titrando titrator equipped with an 801 stirrer and a Metrohm 6.0229.100 Solvotrode electrode. The titrator was ran by Tiamo 1.1 light software. The titration endpoint was determined by the titrator, and visually verified using crystal violet indicator.

Higher oil content emulsion stability was measured by LUMisizer demonstration instrument. Transmission profiles were analyzed by SepView software.

Relative Solubility Number (RSN) titrations were preformed by dissolving 0.1 g of sample in 10 g of a 2.6% (vol/vol) toluene in ethylene glycol dimethyl ether solvent. Water was slowly added to the solution until cloudiness was apparent visually. A linear relationship between HLB and RSN was made from using commercial surfactants of known HLB, Brij® 72, 76, 78. These surfactants were chosen because their similar nature to the surfactants studied, and to have a wide range of HLBs. Sample HLBs were determined by comparison to this linear relation.

Epoxidation of methyl oleate. The epoxidation reaction was based on a Swern epoxidation (27–29) and used by this laboratory in the past (30). Using 420.0 g (1.4 mol) of methyl oleate, 15 g (0.3 mol) of formic acid, and 254 g of 30% hydrogen peroxide (2.2 mol), 410 g of product was produced (1.3 mol; 93% yield). The product was characterized by GC, FTIR, and ^{1}H and ^{13}C NMR analysis showing similar results to past syntheses (30).

Synthesis of EMO glyceride esters. Our synthesis of polyglyceride was designed to directly utilize glycerol. First, sodium polyglyceride was made by stirring 27.0 g (0.293 mol) of glycerol with 2.69 g (0.067 mol) of NaOH pellets and heating in an oil bath. The reaction was run at 140^{o}C for 2 h yielding a gelled product, which was used without further purification. The polymerized product had a viscosity of 23,000 ± 3,000 m Pa S, which was measured by a Brookfield Rheometer. The products were characterized by FTIR spectroscopy. FTIR (ATR) ν 3280 (O-X stretch), 2924, 2873 (C-H stretch), 1416, 1322, 1212, (C-H bend), 1109, 1028 (C-O stretch), 993, 919, 849 cm^{-1}.

The sodium polyglyceride was stirred with EMO in 2:1, 1:1, and 1:2 mass ratios. The reactions were run at 70^{o}C with overhead stirring for 10–16 h. The product in all three cases was a highly viscous gel. Products synthesized with the higher two ratios of polyglyceride were water soluble, whereas the product produced using more EMO was not water soluble. The products were characterized FTIR and NMR spectroscopies: 2:1 weight ratio FTIR: (ATR) ν 3316 (O-X stretch), 2921, 2853 (C-H stretch), 1739 (C=O stretch), 1593, 1560, 1450–1250 (unresolvable signals), 1109, 1035 (C-O stretch), 995, 923, 850 cm^{-1}, 1:1 weight ratio FTIR: (ATR) ν 3316 (O-X stretch), 2922, 2853 (C-H stretch), 1739 (C=O stretch), 1561, 1450–1250 (unresolvable signals), 1110, 1038 (C-O stretch), 996, 924, 850 cm^{-1}. 1:2 weight ratio FTIR: (ATR) ν 3316 (O-X stretch), 2924, 2854 (C-H stretch), 1740 (C=O stretch), 1593, 1560, 1450–1197 (unresolvable signals), 1110, 1038 (C-O stretch), 995, 923, 847 cm^{-1}. The product of 2:1 weight ratio ^{1}H NMR (MeOD): δ: 4.82 (solvent peak prevents integration), 3.35–3.67 (multiple peaks, 35H polyglyceride backbone), 2.94 (b, 1.1 H residual epoxide), 2.17 (t, 2 H, carbon α to carboxy), 1.63–1.36 (multiple signals, 26 H, fatty backbone) 0.92, (b, 3 H end of fatty chain). ^{13}C NMR (MeOD): δ: 74, 65 (glyceride signals), 59 (residual epoxide carbons), 33–24 (fatty chain carbons), 14 (end of fatty chain). The product of 1:1 weight ratio ^{1}H NMR (MeOD): δ: 4.82 (solvent peak prevents integration), 3.3–3.68 (multiple peaks, 28.5 H polyglyceride backbone), 2.94 (b, 1.1H residual epoxide), 2.36 (m, not identified), 2.18 (t, 2H, carbon · to carboxy), 1.62–1.36(multiple signals, 26H, fatty backbone)

0.92, (b, 3H end of fatty chain). ^{13}C NMR (MeOD): δ: 75, 74, 64 (glyceride signals), 59 (residual epoxide carbons), 33–24 (fatty chain carbons), 14 (end of fatty chain). The product of 1:2 weight ratio ^{1}H NMR (MeOD): δ: 4.82 (solvent peak prevents integration), 3.36–3.68 (multiple peaks, 10 H polyglyceride backbone), 2.95 (b, 1.2 H residual epoxide), 2.36 (m, not identified), 2.17 (t, 2 H, carbon · to carboxy), 1.62–1.36 (multiple signals, 26 H, fatty backbone) 0.92, (b, 3 H end of fatty chain). ^{13}C NMR (MeOD): δ: 75, 73, 64 (glyceride signals), 59 (residual epoxide carbons), 52 (residual methoxy carbon), 35–24 (fatty chain carbons), 15 (end of fatty chain).

Surfactant performance. The 1% o/w emulsions, used for droplet size comparison, were prepared in the Malvern small volume sample stirring unit. First, surfactant solutions (0.1 and 0.5 weight percent) were prepared by stirring on a stir plate. Next, 100 mL of this solution was flowed through the instrument flow cell, and an appropriate blank measurement was taken. Next, 1.0 mL of soybean oil (SBO) was then added, and the solution was rapidly stirred in the Malvern small volume sample stirring unit for at least 5 min. The resulting emulsion was then allowed to flow through the instrument cell, and appropriate measurements were taken.

Emulsion stability for 50% water/SBO by first preparing the emulsion using 5 g of SBO and 5 g of purified water. Surfactant was then added to the solution to give the appropriate 0.3–2.3% solutions which were stirred overnight. The surfactants were loaded into cuvettes and analyzed in the Lumisizer emulsion stability analyzer. They were centrifuged at 1000 RPM for 20 min at 23°C to obtain transmission profiles of each sample.

Static surface tension measurements were taken by dissolving 10.0 mg of surfactant in 10.0 mL of pure water to form a 0.1% solution. Serial dilutions of the surfactant were made and the surface tension was measured at 25°C using a Krüss K10t digital tensiometer equipped with a duNouy ring. A similar experiment was done using 0.1 M NaOH solution, yielding surface tension results within experimental error to the values obtained in pure water.

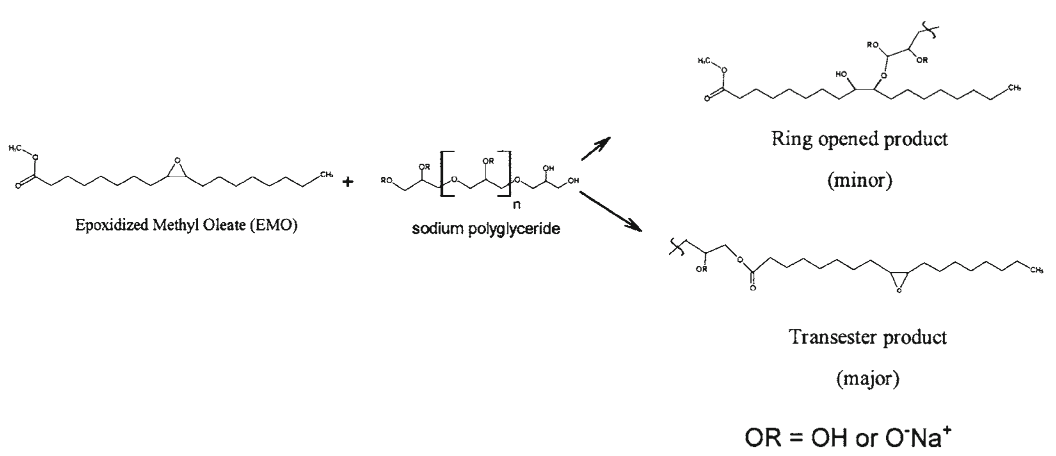
Dynamic surface tensions were measured by preparing 10 mL of the appropriate concentration of surfactant, then measuring with the Sita t60 bubble pressure tensiometer at 30°C. The tensiometer was programmed to vary bubble lifetime from 30 ms to 60 s. The critical micelle concentration (CMC) unit of the tensiometer was set up by preparing 100 mL of 0.4% solution, then running the program which automatically performs dilutions and measurements. Bubble lifetimes of 8 s and 45 s were used in these measurements.

RESULTS AND DISCUSSION

Synthesis. The straightforward epoxidation of methyl oleate went as expected, and as demonstrated in the past (30). Closely monitoring the reaction via GC ensured that the over reaction product, 9,10-dihydroxy methyl stearate, was not formed. The resultant product was characterized by FTIR and NMR, giving identical results to past syntheses (30).

This synthesis of sodium polyglyceride has the advantage of forming the polyglyceride directly from glycerol, instead of from a potentially petroleum based epoxy compound, as has been described in the literature (13,31). A relatively low temperature was used to minimize the possible formation of acrolein. Glycerol was mixed with sodium hydroxide catalyst (10 wt %) at 140°C for 2 h. The reaction progress was confirmed by measuring the viscosity of the product, showing an increase from ordinary glycerol at 948 ± 14 mPa S to a thick gel of 23,000 ± 3000 m Pa S. These values confirm that there is significant polymerization of the glycerol. The FTIR spectrum of the polyglyceride was similar to that of glycerol, but the ratio of the signal of the C-H bands at ~ 2873–2933 cm^{-1} compared to the O-H signal at 3280 cm^{-1} increased significantly.

The EMO polyglyceride ester was synthesized using a method similar to that in literature of other fatty esters glycerides (18–20,32). The weight ratio of polyglyceride and EMO were varied. When excess polyglyceride was used, there is the possibility for formation or either the ring opened and/or the transesterified product (Scheme 1). The ^{13}C



SCHEME 1. The reaction to produce surfactant products from EMO to form the major transester product, and the minor ring opened product.

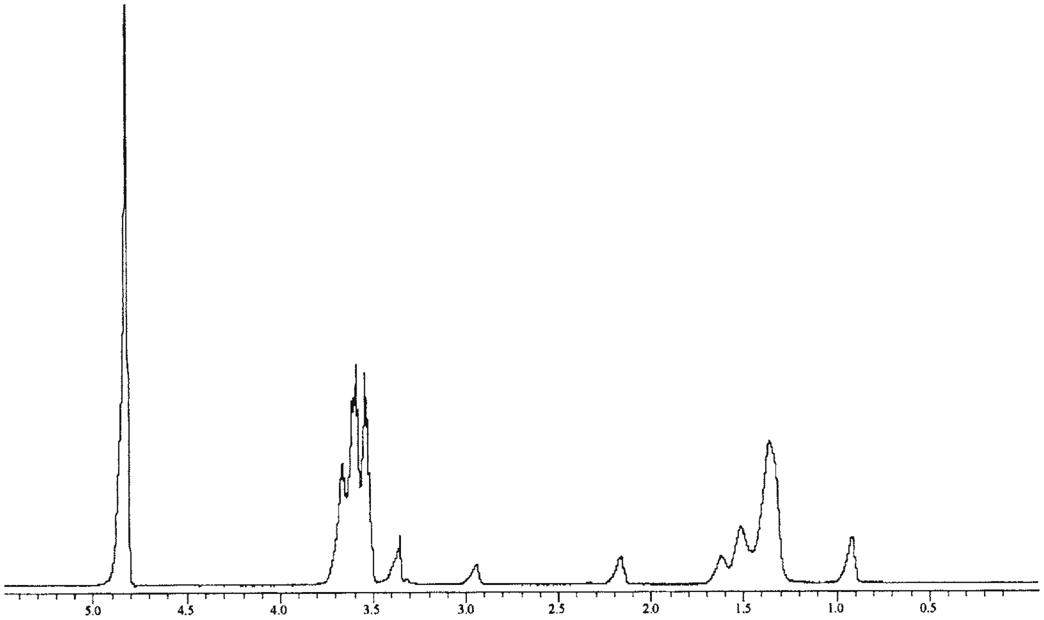


FIG. 1. The ^{1}H NMR of the heptaglyceride ester (2:1 ratio) surfactant material. Using the signals from the glyceride region (δ 3.35–3.67), and the end of the fatty chain (δ 0.92), we were able to estimate the number of glyceride in each of the products.

NMR of the isolated products was used to estimate the amount of each product. The peak at ~58 ppm, carbons in the epoxy ring, was still evident in all of the spectra of the products indicating that there is significant epoxy functionality remaining. The peak at ~52 ppm, methoxy carbon, was only present in the sample with the largest amount of EMO, and even in that spectrum, it was quite small. This indicates that transesterification is the more rapid reaction under these conditions. Using ^{1}H NMR (Fig. 1), it was possible to quantify the amount of remaining epoxide by comparison of the signals at ~2.9 ppm, corresponding to the 2 epoxy carbon bound protons, with the signal at ~ 0.9 ppm, corresponding to the 3 protons bound at the end of the fatty chain. These results show that in all cases, the surfactant product retains 55–85% of its epoxide functionality. This result was confirmed by performing oxirane titration of the resultant surfactants using an official AOCS method. All of the surfactants display a % oxirane value in the range of 3.4–3.6%. This again confirms that the epoxy functionality is conserved, and the transester is the major product.

The ^{1}H NMR (Fig. 1) also allows estimation of the surfactants synthesized at 2:1, 1:1, and 1:2 ratios contain 7, 5.7, and 2 glyceride units, respectively. This is confirmed qualitatively the FTIR results. A comparison of the C=O signal at ~1740 cm^{-1} with the O-H signal at ~3400 cm^{-1} show much more O-H signal in the spectra of the product containing more glyceride units. Overall, the ability to synthesize a variety of materials was demonstrated, and because the surfactants still contain a functional epoxide group, further modification may be easily attained.

Estimation of HLB. The hydrophile-lipophile balance (HLB) can be estimated using a general formula $[20 \times (M_{\text{hydrophile}}/(M_{\text{hydrophile}} + M_{\text{lipophile}})]$ (8) and the structural information given in the NMR. The estimated HLBs (Table 1) range from 13 for the heptaglyceride ester product, down to 7 for the diglyceride ester product. These estimates are rein-

TABLE 1
Data on the Glyceride Units, Surface Tension, and the VMD and Span Surfactants Studied

Surfactant	Glyceride units[a]	HLB calculated by formula[b] (and from Fig. 2)	γ (mN/m) of water solution	VMD[c] (μm) and (span)[d] 1% SBO in water 0.1 wt% surfactant	VMD (μm) and (span) of 1% SBO in water 0.5 wt% surfactant
2:1 ratio	7	13 (13.1)	33.9 ± 0.3	42 (1.6)	42 (1.6)
1:1 ratio	5.7	12 (9.2)	34.7 ± 0.3	42 (1.6)	42 (1.6)
1:2 ratio	2	7 (9.0)	NA[e]	20 (2.1)	18 (4.1)

[a] Calculated by ^{1}H NMR integrations.
[b] Calculated by the formula $[20 * (M_{\text{hydrophile}}/(M_{\text{hydrophile}} + M_{\text{lipophile}}))]$.
[c] VMD (volume media diameter), also written $D_{v0.5}$; 50% of the spray volume is composed of larger droplets, 50% of the volume is composed of smaller droplets.
[d] Span $((D_{v0.9} - D_{v0.1})/D_{v0.5})$, where $D_{v0.n}$ is defined above. Span is a measure of droplet size uniformity.
[e] Was not measured due to solution cloudiness.

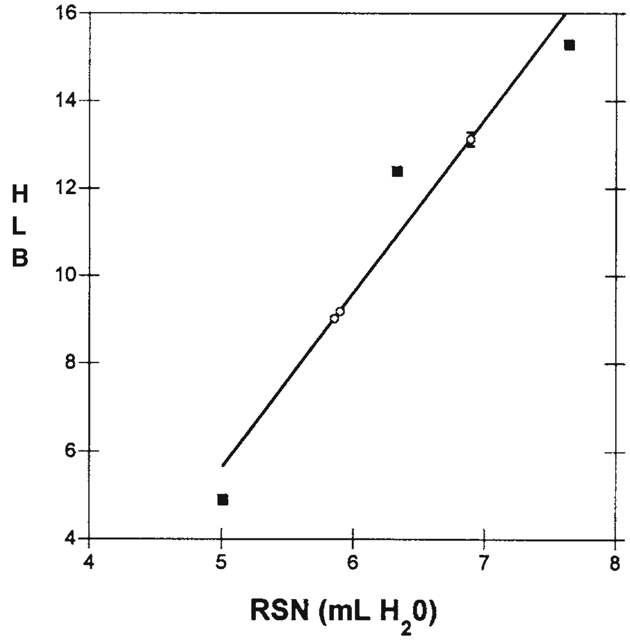


FIG. 2. A plot of the value of HLB vs RSN for the Brij® 72, 76, and 78 surfactant series (■) and for the polyglyceride surfactants studied herein (○). From this plot, HLB values of 13.1, 9.2, and 9.0 can be calculated.

forced by the water behavior of the products, where the more hydrophilic products form translucent solutions and the more lipophilic one forms a cloudy solution. This places them in the range where they may be considered suitable o/w emulsifiers (33).

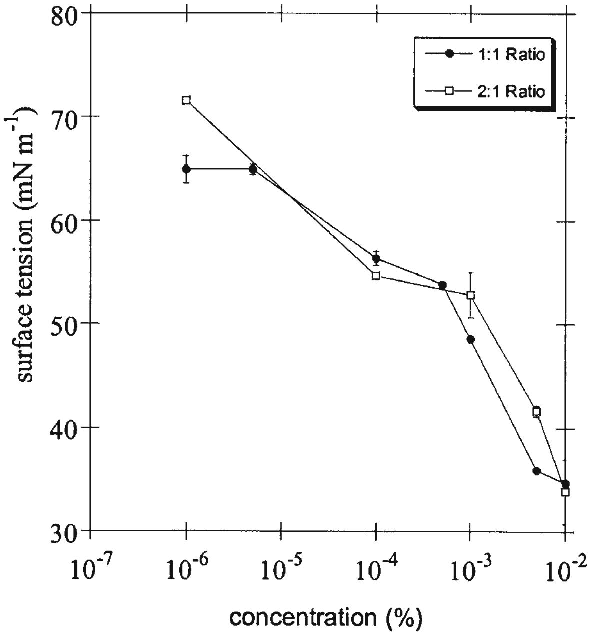


FIG. 3. The aqueous surface tension of the hexaglyceride ester (1:1 ratio) and heptaglyceride ester (2:1 ratio) surfactants, as a function of the log of the concentration, measured by the duNouy ring method.

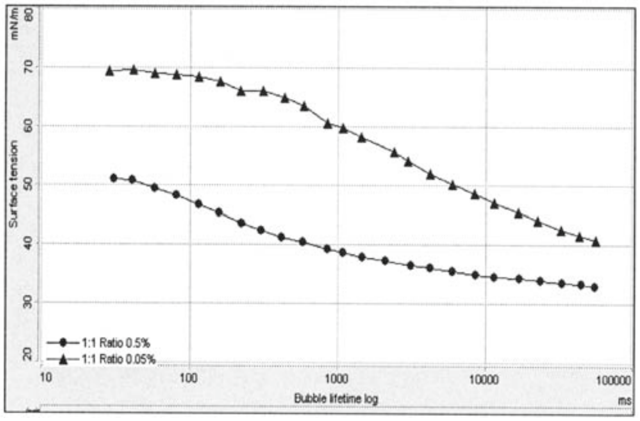


FIG. 4. The aqueous surface tension of two concentration of the hexaglyceride ester (1:1 ratio) material as a function of bubble lifetime. The 0.5% solution shows much lower surface tension at longer bubble lifetime.

Determination of HLB. HLB was also measured experimentally by a literature relative solubility number (RSN) method (34). This method measures how much water can be solubilized in a solution of EGDE (ethylene glycol dimethyl ether) and toluene. A series of polyoxyethylene fatty ethers, Brij® 72, 76, and 78, were used to determine the linear relationship between HLB and RSN under the conditions used in this study (Fig. 2). A HLB of 13.1 was obtained for the heptaglyceride using the similar type nonionic surfactants, and down to 9.0 for the diglyceride product, similar, but slightly higher than estimations from the general formula.

Static and dynamic surface tension measurements. The surface tension of multiple concentrations of the more soluble surfactants was measured using the duNouy ring method (Fig. 3). Both the heptaglyceride ester and hexaglyceride ester material show significant surface tension reduction and both reduce the surface tension to ~34 mN m^{-1} with no obvious critical micelle concentration observed below 0.01%. This is similar behavior to commercial surfactants of the formula $C_{11\text{-}12}H_{23\text{-}25}(OC_2H_4)_{7\text{-}14}Cl$ or $C_{12}H_{25}(OC_2H_4)_{9\text{-}12}OH$ (35). This data shows that the hydrophilic polyglyceride moiety behaves as a reasonably large hydrophilic head group.

The dynamic surface tensions of two different concentrations of the hexaglyceride ester material were performed (Fig. 4). In the higher concentration, the surface tension using a bubble lifetime of 115 ms was 46.7 mN m^{-1}, but when the bubble lifetime was increased to 1,103 ms the surface tension was reduced to 38.6 mN m^{-1}. This is also similar behavior to a commercial ethoxylate surfactants, this time of the formula $C_{9\text{-}11}H_{21}(OC_2H_4)_6OH$ (35). It is expected behavior for surfactants with a large hydrophobic group.

The surfactants in this study were compared with a commercial surfactant, Caprol® MPGO, which is described as a polyglyceryl-6-dioleate (Fig. 5). A bubble pressure tensiometer was used with a bubble lifetime of 42 s. From the data, it is easy to see that the surfactant in this study reduces surface tension significantly better than this commercial solubilizer.

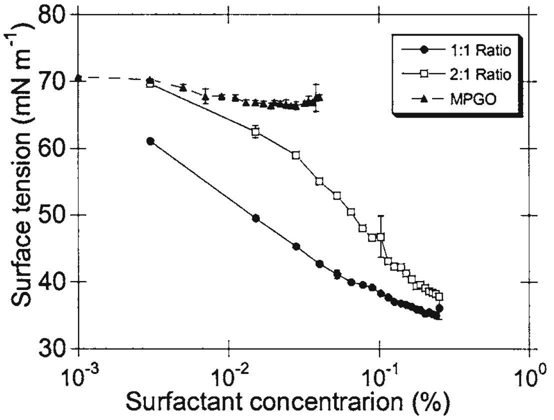


FIG. 5. The aqueous surface tension vs the log of concentration of our surfactants and a commercial surfactant, Caprol MPGO.

Emulsions. The study of the drop size of emulsions has been shown to be an important in surfactant performance parameter (36). Comparisons were made for droplet size of a 1% SBO in water emulsion. The emulsions were stabilized by the polyglyceride surfactants, as well as that of Caprol® MPGO and Pluronic® L43, at 0.1 and 0.5%. Caprol® MPGO, is a polyglyceryl-6-dioleate, and the Pluronic® series of surfactants are a widely used ethylene oxide–propylene oxide copolymer. A Malvern particle size analyzer was used to determine the droplet size formed in these stirred systems (Fig. 6). The diglyceride ester material formed the smallest, and therefore most solubilized droplets. The other surfactant systems and the Pluronic® L43 emulsion, showed slightly smaller droplets than emulsions using glycerol as a stabilizer, but the droplets were still fairly large. The best solubilizer, as expected was the commercial emulsifier, Caprol® MPGO, which formed very small droplets.

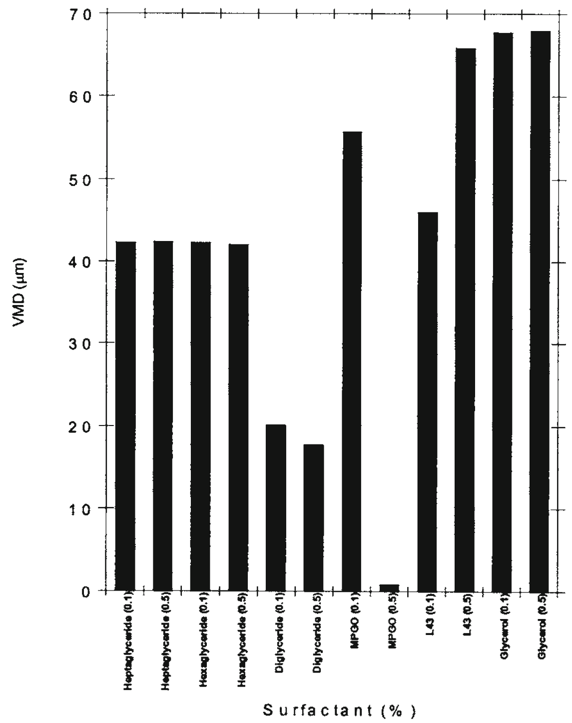


FIG. 6. The VMD (volume median diameter) of the droplets in a 1% SBO in water emulsion stabilized by 0.1 or 0.5% of each of the surfactants studied.

Emulsion stability of a 50% SBO and water emulsion were also studied using a Lumisizer (Table 2). This instrument gave both the oil clarification rate, and the water clarification rate, with lower values indicating more emulsion stability. Of the surfactants tested, only the Pluronic® L64 was able to stabilize both phases. The data show that the polyglycerides, as well as Pluronic® L43, are effective in keeping the oil in the water phase, but highly ineffective in keeping the water in the oil phase. Similar results were obtained using the popular anionic surfactant sodium dodecyl sulfate (SDS). This is the expected result from HLB estimation, and shows that modification of the surfactants will be necessary to stabilize W/O emulsions or high concentration O/W emulsions.

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TABLE 2
Rate of Clarification of the Oil and Water Phases of a 50% SBO in Water Emulsion, Measured by the LUMisizer

Surfactant	Oil clarification rate (% h^{-1})	Water clarification rate (% h^{-1})
None	55 ± 9.5	85 ± 0.7
Heptaglyceride ester (2:1 ratio) (0.3%)	14 ± 3.0	81 ± 7.1
Hexaglyceride ester (1:1 ratio) (0.4%)	18 ± 5.5	79 ± 5.6
Diglyceride ester (1:2 ratio) (0.6%)	33 ± 7.8	84 ± 1.2
Pluronic L64 (0.4%)	18 ± 3.3	14 ± 0.9
Pluronic L43 (0.6%)	32 ± 4.4	77 ± 7.0
SDS (1.0%)	29 ± 0.5	78 ± 11
SDS (0.2%)	17 ± 4.6	81 ± 11

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