Structural Aspects of Surfactant Selection for the Design of Vegetable Oil Semi-Synthetic Metalworking Fluids

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This paper presents a set of surfactant-selection guidelines that can be used to design bio-based semi-synthetic metalworking fluid (MWF) microemulsions as a renewable alternative to conventional petroleum formulations. Ten surfactant classes (six anionic and four nonionic) with different head and tail structures and three vegetable base oils (canola oil, soybean oil, and a fatty acid trimethylolpropane ester) were investigated as representatives of oil and surfactant options currently under consideration in the MWF industry. All combinations of these surfactants and oils were formulated at the full range of oil to surfactant ratios and surfactant concentrations. The stability of each formulation was evaluated based on visual transparency, light transmittance, and droplet diameter. The experimental results yield the following guidelines that produce stable bio-based MWF microemulsions with minimum necessary concentrations of surfactants: (1) a combination of two surfactants, one nonionic and one water soluble co-surfactant (either nonionic or anionic) is preferred over a single surfactant; (2) the nonionic surfactant should have a carbon tail length greater than or equal to the nominal carbon chain length of the fatty acids in the oil as well as a head group that is not excessively small or large (e.g., 10−20 ethylene oxide groups for a polysorbitan ester, ethoxylated alcohol, or ethoxylated glyceryl ester); (3) the difference in tail lengths between the surfactant and the co-surfactant should be less than 6 to maximize the feasible range of oil to surfactant ratios yielding stable emulsions. These guidelines are consistent with general results of micelle solubilization theory and evidence is provided to suggest that common semi-synthetic MWF systems can be thought of as swollen micelle systems.

1. Introduction

Metalworking fluids (MWFs) serve as coolants, lubricants, and corrosion inhibitors in manufacturing (*1*). They are ubiquitous in the machine tool industry, with estimates of consumption in North America exceeding 2 billion gallons in 2000 (*2*). Conventional MWF formulations are based on petroleum feedstocks, which result in high treatment and disposal costs due to their ecotoxicity and low biodegradability (*3−5*). These factors, along with increasing crude oil prices and the national security concerns associated with imported oil, serve as motivations to consider alternatives to petroleum-based MWFs.

To address these issues research efforts have focused on (1) reducing or eliminating MWF use in manufacturing through dry or damp machining (*6, 7*); (2) extending the usable life of MWFs by reformulating them for improved resistance to in-process deterioration (*8−10*); (3) extending the usable life of MWFs by applying membrane-filtration-based recycling to remove contaminants (*11−14*); and (4) developing petroleum-free, bio-based MWFs (*15, 16*). Bio-based formulations offer a renewable and domestically produced alternative to petroleum-based MWFs. Due to their inherently higher biodegradability, bio-based formulations have the potential to reduce the waste treatment costs required to meet the new MWF effluent limitation guidelines and standards published by the U.S. EPA in the Metal Products and Machinery Rule (*17*). Also, bio-based formulations could reduce the occupational health risks associated with petroleum-oil-based MWFs due to their lower reported toxicity (*18*), while providing an alternative that has been shown to perform better in many manufacturing operations such as thread cutting (*19*). The principle technical limitation of vegetable oil lubricants, their low oxidative stability, has been addressed by genetic alteration, chemical modification, and use of various additives (*20*). The principle economic limitation of vegetable-based lubricants, their high cost relative to petroleum oils, is diminishing as petroleum prices increase (*21*).

This paper focuses on the use of bio-based feedstocks to formulate semi-synthetic MWF emulsions. Semi-synthetic MWF formulations are composed of water, a base oil, surfactants, and specialty additives (*3*). In general, semi-synthetic MWFs are sold as concentrates with 10−30% petroleum oil. These concentrates are diluted 10−20 times with water before use as metalworking fluids. The diluted fluids are stable, translucent, and often called "microemulsions", with emulsified oil droplet sizes less than 100 nm. The selection of surfactants to disperse the oil and other hydrophobic additives in water is critical for producing a stable microemulsion. This research focuses on surfactant selection for base MWF microemulsion systems consisting of water, oil, and surfactants.

Formulation of petroleum-based MWFs has long been carried out using empirical rules developed through trial and error experience (*3*), as well as using the HLB (hydrophile−lipophile balance) method (*22*). Recently, Zimmerman et al. (*9*) designed both canola oil and petroleum oil based semi-synthetic MWFs by screening binary mixtures of ethoxylated alcohol surfactants and sulfonate surfactants. It was found that stable vegetable oil microemulsions can be achieved with a wide range of HLB values (from 6 to 18), while stable petroleum formulations required a narrower HLB range (from 6 to 12). This suggests that the HLB method may not provide sufficient insight to facilitate surfactant selection when designing vegetable oil MWFs. It was also pointed out in ref *9* that emulsion stability correlated with nonionic surfactant head group size. To our knowledge the fundamental structure−stability relationships driving surfactant selection for semi-synthetic MWFs have yet to be identified in the academic literature.

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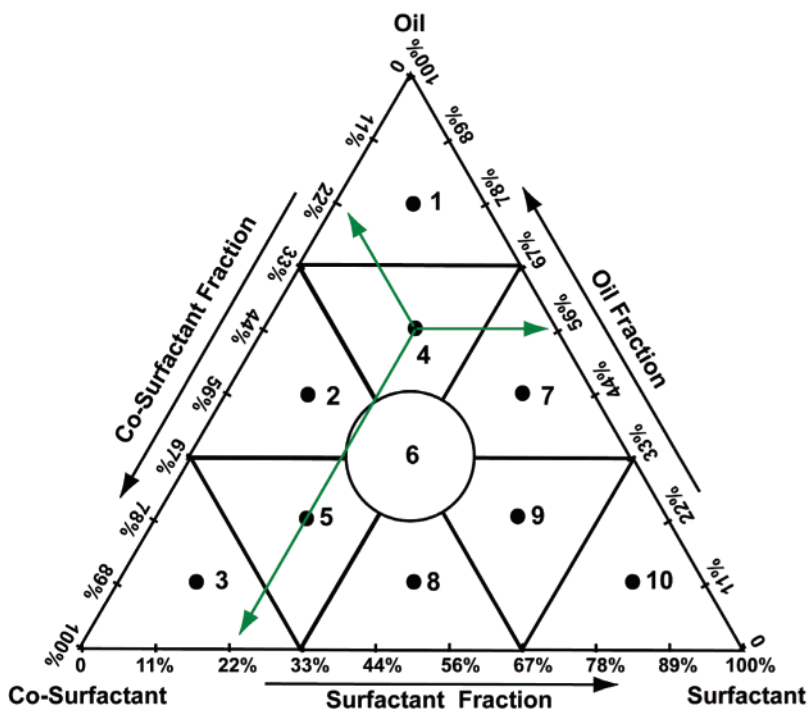‡ Department of Civil and Environmental Engineering.

FIGURE 1. Formulation triangle representing different oil/surfactant molar ratios for a system of two surfactants and one oil.

Oil-in-water microemulsions can be viewed either as a specific class of emulsion, with the oil dispersed as nanoscale droplets in water (23), or they can be viewed as swollen micelles formed by micelle solubilization (24). Shah et al. (25) noted that microemulsions with a ratio of dispersed phase molecules to surfactant molecules less than 2 are likely to be swollen micelle systems. In semi-synthetic MWF dilutions, the molar ratio of oil to surfactant is about 1:1 and the volume fraction of oil can be as low as 0.5%. We therefore begin our analysis with the hypothesis that semi-synthetic MWFs behave like swollen micelle systems.

It has been long understood that the molecular structure of a surfactant such as its head group size and tail length can greatly affect its surface active properties including its ability to solubilize hydrophobic constituents (26, 27). For a given surfactant, the molecular structure of the hydrophobic substance such as its carbon chain length also has a significant effect on micelle solubilization (28). While existing literature considers these issues for the micelle solubilization of alkane hydrocarbons, halogenated hydrocarbons, and polycyclic hydrocarbons, to the authors' knowledge there is no research reported in the literature on the development of structure-based guidelines for the selection of surfactants for vegetable oil microemulsions, especially MWF microemulsions, by viewing such microemulsions as swollen micelle systems.

This paper reports on the development of surfactant selection guidelines for the design of vegetable-based semi-synthetic metalworking fluids. Commercially available anionic and nonionic surfactants from ten major classes of surfactants with varying head and tail characteristics were considered for their ability to emulsify three representative vegetable base oils: canola oil, soybean oil, and fatty acid trimethylolpropane (TMP) ester. The experimental results are interpreted from the swollen micelle perspective to facilitate the selection of bio-based surfactants for producing stable microemulsions.

2. Materials and Methods

Materials. Three representative vegetable base oils were used in this research: a canola oil (AgriPure 75, Cargill, Inc), a soybean oil (Technical Grade, Cargill, Inc.), and a TMP ester

(Priolube 1427, Uniqema, Inc.). Their fatty acid compositions and molecular structures are given in the Supporting Information. Commercially available surfactants from the major classes listed in refs 26 and 29 were selected for investigation. Anionic surfactants were selected from six different classes: fatty acid soaps, alcohol sulfates, alcohol ether sulfates, alkane sulfonates, alkyl aryl sulfonates, and sulfo-carboxylic esters. Nonionic surfactants were selected from four classes: ethoxylated alcohols, ethoxylated glyceryl esters, polysorbitan esters, and alkyl polyglucosides. The Supporting Information lists the molecular structures and molecular weights of the surfactants investigated. All of the oils and surfactants were used as received from their manufacturers. In this research, the average tail carbon chain lengths and head group ethylene oxide (EO) numbers given by the manufacturers were adopted for data analysis as suggested by Kibbey et al. (30).

Formulations with Single Surfactant. Since oil concentration impacts emulsion stability (3), all MWFs were tested at a fixed oil molarity 0.019 mol/L, which is the same as a representative semi-synthetic MWF previously investigated by the authors (9). For every surfactant of the 31 anionic and nonionic surfactants considered during this research, MWFs were prepared with a surfactant to oil ratio at 1:8, 1:3.5, 1:2, 1:1.25, 1.25:1, 2:1, 3.5:1, and 8:1. Prior to stability evaluation, all formulations were aged for 12−15 h at approximately 25 °C.

Formulations with Two Surfactants. In industrial applications it is common to use a binary surfactant mixture as the emulsifier package for MWFs (3, 9). Normally this surfactant package consists of one surfactant and one co-surfactant. In Figure 1, all possible oil to surfactant ratios and surfactant concentrations are represented as a "formulation triangle" for a given surfactant package and fixed oil concentration. Ten points are uniformly selected within the triangle and each point corresponds to a MWF formulation with different oil to surfactant ratio and a different surfactant to co-surfactant ratio. Ten formulations are considered sufficient since any stable formulation that could not be detected by the ten points is essentially too sensitive to composition variations that would be unavoidable in field
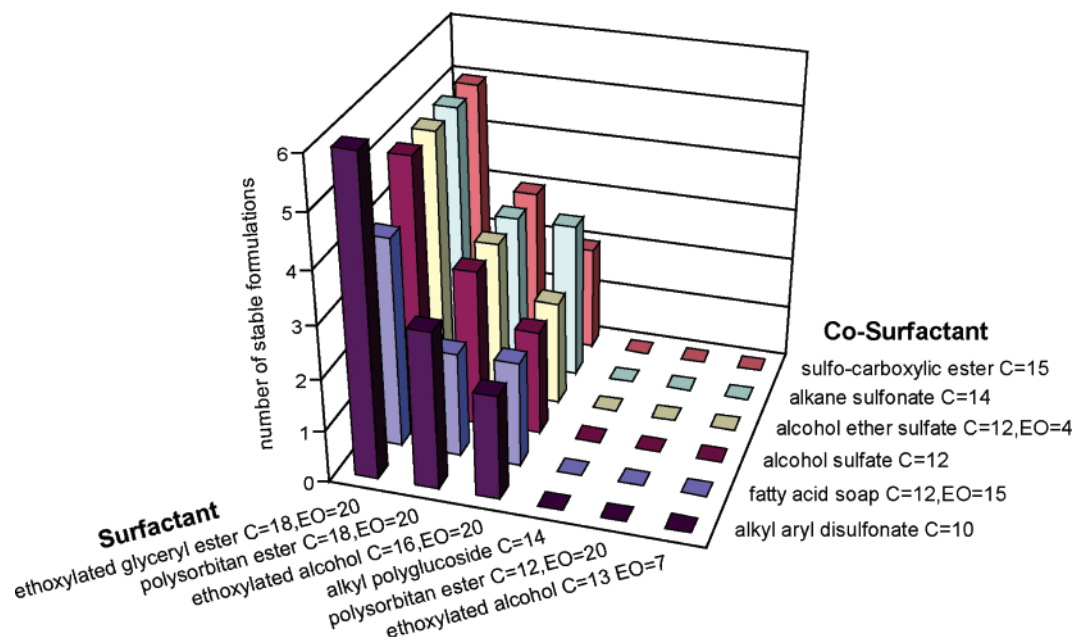
FIGURE 2. Number of stable formulations out of ten achieved for each surfactant combination when nonionic surfactants with different tail lengths are used to emulsify canola oil.

applications and therefore would have very limited practical significance. All formulations were aged for 12−15 h at approximately 25 °C prior to stability evaluation.

MWF Stability Evaluation. In this paper, three metrics are used to develop an index of MWF stability: visual transparency, light transmittance, and droplet diameter. The measurements were interpreted as a score with possible values being 1, 3, or 9, where 9 corresponds to the most stable fluids (see Supporting Information for details). In order to determine the long-term stability of the fluids, the three measurements were performed again after 7 days. One additional visual inspection was performed after 6 months. It was found that the score from visual inspection after one week was always the same as the score obtained after 6 months, which suggests that stability metrics determined after 7 days are correlated with long-term stability.

For each formulation, an aggregate score was calculated as the sum of the three stability metrics measured after 7 days, with a maximum of 27 and a minimum of 3. As an operational definition of emulsion stability, we only considered fluids with score of 27 to be stable. Only surfactants or surfactant packages that led to at least one stable formulation received further consideration. In this research, we began by only considering formulations with canola oil. In all, 31 surfactants and 150 surfactant packages were tested. Given the knowledge gained from the research with canola oil, it was possible to narrow down the number of surfactants and surfactant packages considered for soybean oil and TMP ester. For the soybean oil and the TMP ester, only 60 surfactant packages using ethoxylated alcohols, ethoxylated glyceryl esters, and polysorbitan esters as the nonionic surfactant were randomly selected from 150 packages tested for canola oil. The TMP and soybean oil results were compared with the canola oil results to investigate emulsion stability differences.

3. Results and Discussion

To achieve a stable semi-synthetic MWF, a surfactant or a surfactant package has to be selected such that the required oil concentration is below the oil solubility limit. This solubility limit is determined by the micelle solubilization capacity (amount of oil solubilized per micelle) and the surfactant solubility (amount of dissolved surfactant mono-

mers available to form dispersed micelles). We focus here on how surfactant structural characteristics affect the oil solubility limit by influencing the micelle solubilization capacity and the surfactant solubility.

Formulations with Single Surfactant. To start, semi-synthetic MWF emulsions produced using one surfactant and canola oil were evaluated. Among the 31 anionic and nonionic surfactants investigated, the following nonionic surfactants were the only ones that were found to produce stable emulsions: the ethoxylated alcohols with 16 carbon atoms in the tail (denoted as $C = 16$) and 20 ethylene oxide groups in the head (denoted as EO = 20), the ethoxylated glyceryl esters with $C = 18$ and EO = 40, and the polysorbitan esters with $C = 18$ and EO = 20. For all these systems, the required surfactant to oil ratio was at least 3.5:1. This high surfactant to oil ratio would be impractical for manufacturing operations due to the high cost of surfactants and difficulties controlling foam and treating the waste emulsions. Since it has been observed that surfactant packages can have higher oil solubility than those obtained with either component alone (*30*), formulations with binary mixtures of surfactants were investigated in order to achieve MWF systems with a practical surfactant to oil ratio.

Formulations with Two Surfactants. Figure 2 shows the number of observed stable formulations (out of the ten possible formulations indicated in Figure 1) when using the selected binary surfactant packages to emulsify canola oil. For some nonionic surfactants, no stable formulation was achieved regardless of which anionic was used in combination. This indicates that the nonionic surfactant is more important than the anionic surfactant with respect to microemulsion stability. Figure 2 also indicates that in order to obtain at least one stable formulation, the tail length of the nonionic surfactant should be at least 16, which is close to the carbon chain length of the fatty acid compositions in canola oil. This is in agreement with the results reported in the literature for the solubilization of alkane hydrocarbons (*28*, *32*), and provides support for the hypothesis that vegetable oils and alkane hydrocarbons are similarly solubilized by micelles as suggested by ref *29*.

Figure 2 suggests that ethoxylated glyceryl esters, ethoxylated alcohols, and polysorbitan esters with tail lengths longer than 16 carbon atoms can be selected as the primary
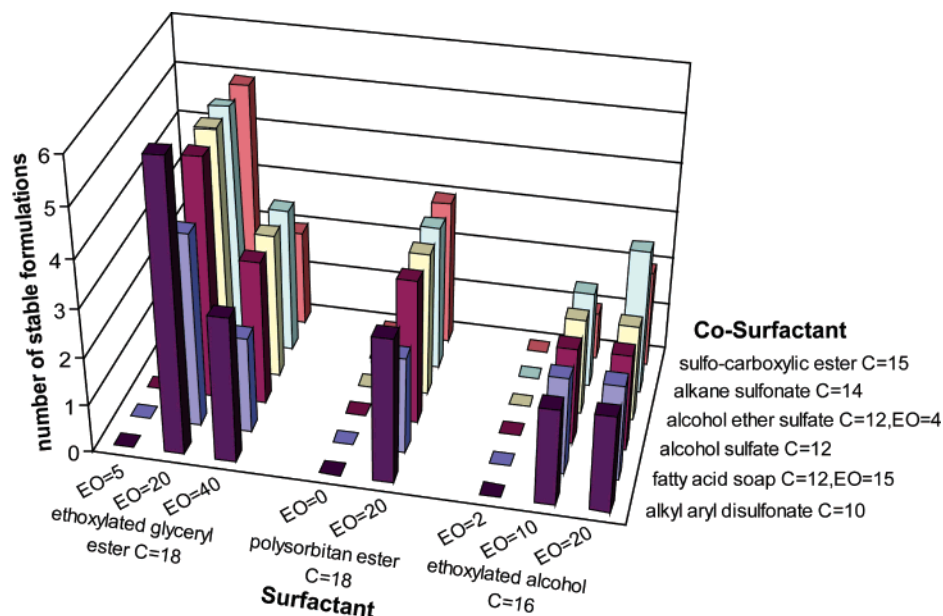
FIGURE 3. Number of stable formulations out of ten achieved for each surfactant combination when nonionic surfactants with different head group size are used to emulsify canola oil.

surfactant. To investigate the effect of head group size, surfactants with tail lengths of at least 16 carbon atoms were investigated. The results in Figure 3 show that stable formulations can be achieved when the size of the head group in the nonionic surfactant has an EO number of at least 10. One possible explanation for this is that when the head group is very small (e.g., the number of EO units is less than 5), the nonionic surfactant may form large micelles that are too hydrophobic, leading to low surfactant solubility due to weak repulsion between micelles. As a result the total amount of oil solubilization is small and no stable formulation can be achieved. However, when the size of the head group is large, such as for the ethoxylated glyceryl ester with $C = 18$ and EO = 40, stable formulations were only observed when a very high concentration of nonionic surfactant was present (e.g., oil/nonionic molar ratio of at least 1:3.5). As the head group size increases, the micelle size decreases, leading in turn to a reduced micelle solubilization capacity. The micelles on the whole become more hydrophilic and surfactant solubility increases, leading to stable formulations if high surfactant concentrations are utilized.

To support the above explanation, the micelle droplet diameter, surfactant solubility, and oil solubility limit of three ethoxylated alcohol nonionic surfactants with $C = 16$ and EO = 2, 10, and 20 were experimentally measured. For each surfactant, the micelle droplet diameter was measured at a concentration of 2 times its reported critical micelle concentration (CMC). To yield an operational definition of surfactant solubility, the surfactant concentration was increased until the micelle droplet diameter increased by 50%. Starting from this surfactant solubility concentration, oil was then introduced gradually until the droplet diameter exceeded 100 nm. At this point the oil solubility was operationally defined by considering the amount of oil necessary to increase the droplet diameter above 100 nm. It can be seen from Table 1 that when the head group is small (e.g., EO = 2), large micelles are formed as indicated by the aggregation number and micelle diameter. In this case the oil solubilization limit is very low (less than 4×10^{-5} M) due to low surfactant solubility. When the head group is large (e.g., EO = 20), much smaller micelles are formed. In this case, the oil solubilization limit is high since a large amount of surfactant (0.089 M or 10% w/w) can be dissolved in water, leading to a large number of dispersible micelles.

TABLE 1. Micelle Droplet Size and Oil Solubility Limit of Three Ethoxylated Alcohol Nonionic Surfactants with $C = 16$ and EO = 2, 10, and 20[a]

no. of EO	CMC (M)[b]	aggregation number[b]	micelle diameter (nm)	surfactant solubility	oil solubility limit
2	1.6×10^{-6}	~2400	49 ± 9	6.1×10^{-05} M	4×10^{-05} M
10	2.1×10^{-6}	~180	17 ± 3	0.016 M	0.004 M
20	3.9×10^{-6}	~60	12 ± 2	>0.089 M	>0.019 M

[a]Micelle diameter was measured using dynamic light scattering apparatus NICOMP 370 (PSS, Santa Barbara, CA). [b] Aggregation numbers and CMCs are from refs *25* and *28*.

Selection of Co-Surfactant. Figure 4 shows the number of stable formulations produced when three nonionic surfactants are paired with various co-surfactants (either anionic or nonionic) representing different head structures and tail lengths. The results illustrated in Figure 4A reveal that at most one stable formulation out of ten defined in Figure 1 is achieved when the co-surfactant used has a small head group, corresponding to low water solubility. The results illustrated in Figure 4B reveal that with the same surfactant, the number of stable formulations out of the ten is larger when the co-surfactant tail length is close to that of the surfactant (e.g., the tail length difference is less than 6) than when the tail length is significantly different from the tail length of the surfactant (e.g., the difference is larger than 6).

The data presented here suggest that when the oil-soluble surfactant is applied alone, the oil solubility is limited by the surfactant solubility in water. When the water-soluble co-surfactant is applied alone, the oil solubility is limited by the micelle solubilization capacity. When a mixture of one oil-soluble and one water-soluble surfactant is applied, it is possible that molecules of the two surfactants form mixed micelles with increased surfactant solubility and unchanged micelle size, which in turn leads to a significant increase in the oil solubility.

To support the hypothesis that mixed micelles are being formed in the semi-synthetic MWF systems considered in this paper, we measured the droplet diameter of micelles formed by an ethoxylated glyceryl ester ($C = 18$) alone and when it was used in combination with an alkane sulfonate
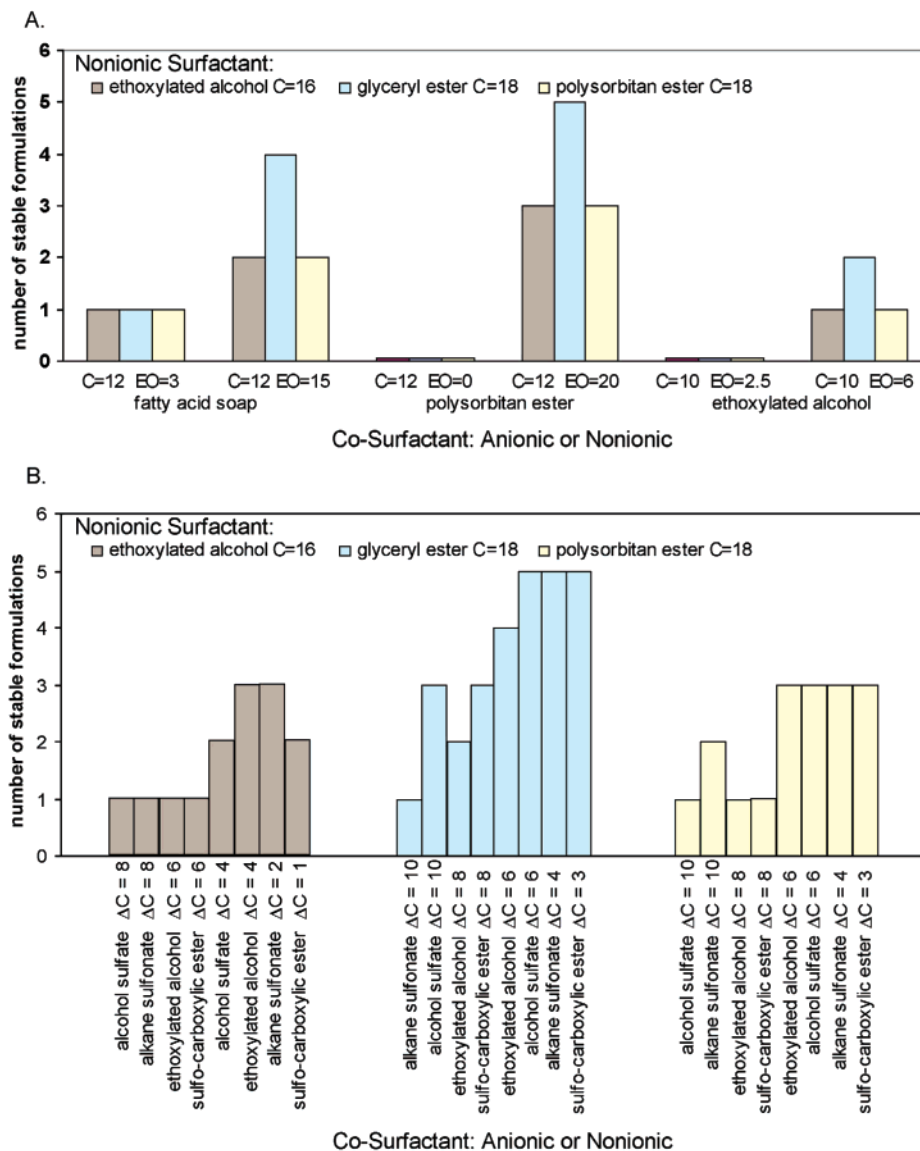
FIGURE 4. Effect of co-surfactant on number of stable formulations achieved from each surfactant combination: (A) effect of head group size; (B) effect of carbon chain length difference.

co-surfactant with different tail lengths ($C = 14$ or 8). As shown in Figure 5, when the ester surfactant is used alone, the micelle diameter stays at 15 nm at concentration below 0.2 mM but increases significantly at about 0.5 mM. If a sulfonate co-surfactant with $C = 14$ is introduced, the micelle diameter remains close to 15 nm at an ester surfactant concentration up to 2 mM. These observations indicate that the introduction of the water-soluble co-surfactant encourages the formation of mixed micelles with significantly improved surfactant solubility (2 mM vs 0.2 mM), without changing micelle size (remaining at 15 nm). If the ester surfactant is used in combination with an alkane sulfonate co-surfactant with $C = 8$, the micelle diameter begins to increase at a lower ester surfactant concentration (1 mM). A comparison of these two surfactant mixture systems suggests that more mixed micelles with stronger inter-micelle repulsion are formed when the tail length difference between the surfactant and co-surfactant is small. This is in agreement with the observations of Abe et al. (*33*), where an investigation of the formation of mixed micelles using anionic fatty acid soaps with tail lengths 8−12 and nonionic ethoxylated alcohols with tail length 12−18 indicated that the tendency to form two simultaneously existing micelles of different

compositions increases with increasing alkyl chain length difference.

From a practical standpoint, a surfactant package leading to stable formulations with a low total surfactant to oil ratio is preferred over a package with a high ratio in order to reduce foaming in factory production systems. Figure 6 illustrates the relationship between surfactant concentration and foaming tendency as measured based on ASTM D3519 (*34*). It can be seen that emulsions formed using a high concentration of surfactants, especially polysorbitan ester, tended to create long lasting foams. These foams are undesirable since they can reduce the cooling and lubrication properties of MWFs and shorten the life of pumps due to cavitation (*3*). From the foaming perspective, formulations produced using ethoxylated glyceryl ester ($C = 18/EO = 20$) which have the lowest surfactant to oil ratio (1:3.5) are preferred over ones produced using ethoxylated glyceryl ester ($C = 18/EO = 40$), polysorbitan ester ($C = 18/EO = 20$), and ethoxylated alcohol ($C = 16/EO = 20$) which have the highest surfactant to oil ratio (3.5:1).

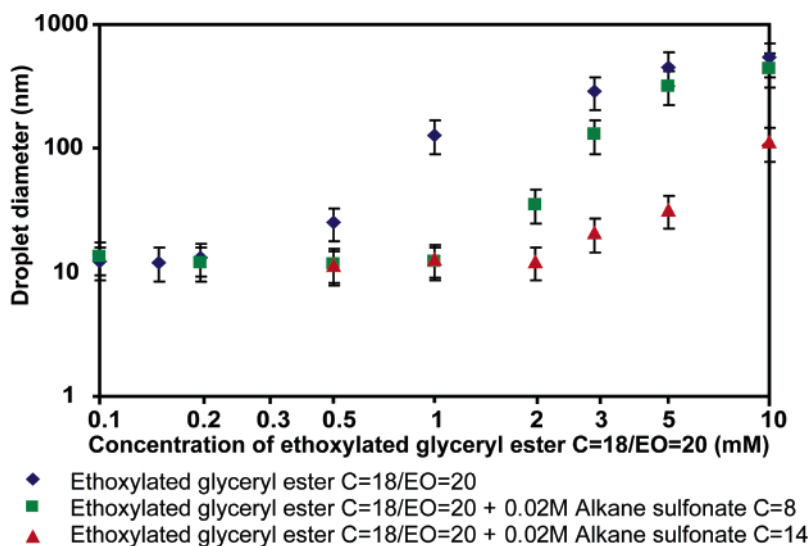**Effect of Vegetable Oil Type.** In all of the above experiments, canola oil was used as the dispersed phase. To

FIGURE 5. Diameter of micelles formed by ethoxylated glyceryl ester $C = 18$ alone, and with 0.02 M alkane sulfonate $C = 8$ or alkane sulfonate $C = 14$ at different concentrations. The error bars were determined based on three replications of droplet size measurements.
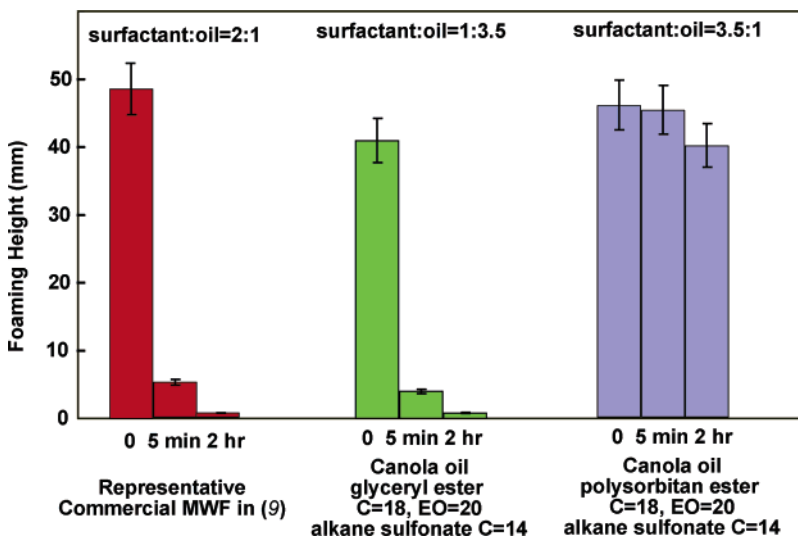

FIGURE 6. Foaming height measured at $t = 0$, 2 min, and 2 h for MWF formulations with different oil/surfactant ratios based on ASTM D3519 (*34*).

TABLE 2. Similarity of Microemulsion Stability for Three Vegetable Oils Formulated with 60 Different Surfactant Packages

oils compared:	soybean vs canola				canola vs TMP				soybean vs TMP			
no. of formulations out of ten showing stability difference:	0	1	2	>2	0	1	2	>2	0	1	2	>2
surfactant used in the package and no. of packages tested												
ethoxylated alcohol (no. of combinations = 20)	90%	10%	0%	0%	60%	20%	20%	0%	70%	20%	10%	0%
ethoxylated glyceryl ester (no. of combinations = 24)	75%	17%	8%	0%	59%	25%	16%	0%	66%	17%	17%	0%
polysorbitan ester (no. of combinations = 16)	87%	13%	0%	0%	62%	25%	13%	0%	75%	12%	13%	0%
total number of packages = 60	84%	13%	3%	0%	60%	23%	17%	0%	70%	17%	13%	0%

investigate the impact of vegetable oil type on stability, 60 of the surfactant packages using ethoxylated alcohols, ethoxylated glyceryl esters, and polysorbitan esters as the nonionic surfactant were randomly selected from the 150 packages tested for canola oil. For each package the number of stable formulations out of ten was determined for soybean oil and TMP ester and compared with the corresponding number of stable formulations observed for canola oil. As shown in Table 2, there were at most two formulations out of ten that showed stability difference from canola oil. Over

80% of the combinations either showed identical formulation stability or had only one formulation out ten that showed stability difference. This is reasonable to expect given that all three vegetable oils have similar molecular structures and fatty acid compositions. Considering that TMP ester is less similar to the other two oils due to its additional ethyl group, a larger difference in the number of stable formulations out of ten in Figure 1 was expected between TMP ester and canola oil than between soybean oil and canola oil. The data in Table 2 support this hypothesis.

Surfactant Selection Guidelines. Based on the results presented in Figures 2–6 and Tables 1–2 the following guidelines can be used to facilitate the formulation of vegetable-oil-based semi-synthetic MWFs based on canola oil, soybean oil, or TMP ester:

(1) Surfactant packages consisting of one nonionic surfactant and one water soluble co-surfactant (either anionic or nonionic) are preferable to single surfactant systems in order to reduce the amount of surfactant needed.

(2) A nonionic surfactant with tail length at least 16 and an intermediate size of head group, such as ethoxylated glyceryl ester with $C = 18$ and $EO = 20$, is preferable.

(3) The co-surfactant should have a tail length similar to that of the nonionic surfactant (e.g., the tail length difference should be less than 6).

To use these guidelines to select surfactants based on bio-based constituents rather than petroleum, it can be noted that among all the surfactants used in this research, only the anionic surfactants of the sulfonate class are currently manufactured exclusively from petroleum feedstock (*35, 36*). All other surfactants can be manufactured without using petroleum although most are still at least partially derived from petroleum. To replace sulfonates, one can use an anionic surfactant from the classes of fatty acid soap, alcohol sulfate, alcohol ether sulfate, or sulfo-carboxylic ester. Alternatively, one can use a suitable nonionic surfactant available from any of the chemical classes considered in this paper. For other additives that are generally present in semi-synthetic MWF formulations such as extreme pressure (EP) additives, corrosion inhibitors, and chelating agents, research is ongoing to develop bio-based alternatives (*37–39*). The combinations of vegetable oil and bio-based surfactant packages investigated in this research serve as a starting point for the development of 100% petroleum-free formulations. It is expected that the guidelines developed here will facilitate the transition from petroleum-based MWFs to renewable bio-based MWFs in the machine tool industry.

Acknowledgments

Supporting Information Available

Details on (1) the fatty acid composition and molecular structure of three vegetable oils, (2) molecular structure of surfactants, and (3) preparation and stability measurement of MWFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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