STRUCTURAL ASPECTS OF SURFACTANT SELECTION FOR THE DESIGN OF VEGETABLE OIL SEMI-SYNTHETIC METALWORKING FLUIDS

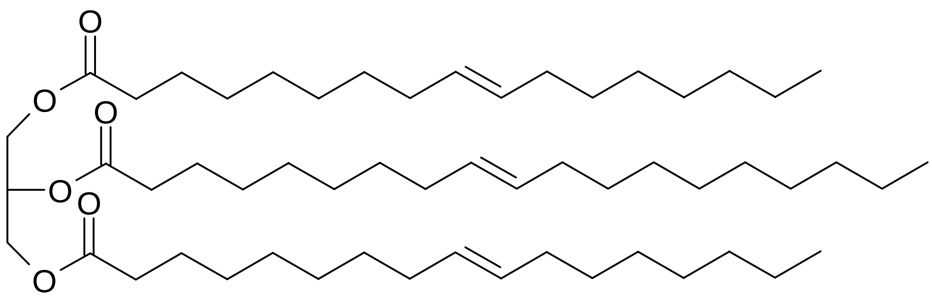
Fu Zhao[1], Andres Clarens[2], Ashley Murphree[1,2], Kim Hayes[2], Steven J. Skerlos[1]*,
Environmental and Sustainable Technologies Laboratory
1. Department of Mechanical Engineering
2. Department of Civil and Environmental Engineering
University of Michigan at Ann Arbor, Ann Arbor, MI, 48109-2125
Telephone: 734-615-5253; Fax: 734-647-3170; Email: skerlos@umich.edu
e-mail of other authors: Fu Zhao: fzhao@umich.edu; Andres Clarens: aclarens@umich.edu
Ashley Murphree: anmurph@umich.edu; Kim Hayes: ford@umich.edu

A. MATERIALS AND METHODS

A.1 Materials.

In this research three representative vegetable base oils were used: a canola oil (AgriPure 75, Cargill, Inc), a soybean oil (Technical Grade, Cargill, Inc.), and a fatty acid trimethylolpropane (TMP) ester (Priolube 1427, Uniqema, Inc.). Figure S.1 gives the fatty acid compositions and molecular structures for these oils. 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. Tables S.1 and S.2 list the molecular structure, molecular weight, head and tail structure characteristics, and HLB of the surfactants investigated. All of the oils and surfactants were used as received from their manufacturers.

Structure of canola oil and soybean oil:



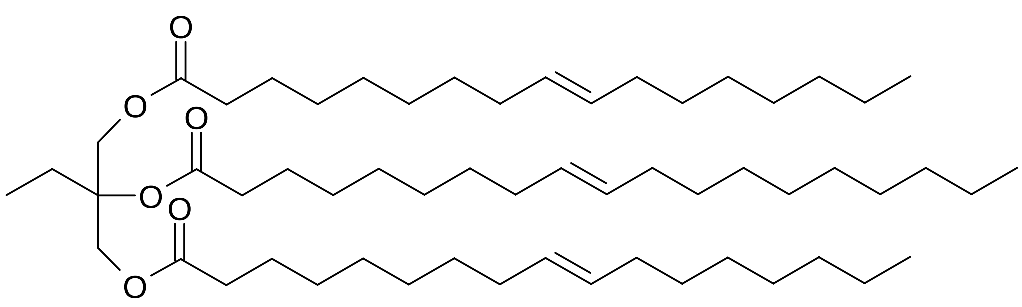
Fatty acid component distribution in canola oil:

C16:0=4%; C18:0=2%; C18:1=74%;C18:2=12%;C18:3=4%;Other=4%

Fatty acid component distribution in soybean oil:

C16:0=5%; C18:0=5%; C18:1= 61%; C18:2=7%; C18:3=3%; Other=19%

Structure of TMP ester:



Fatty acid component distribution in TMP ester:

C18:0=1%; C18:1=58%; C18:2=24%;C18:3=10%; Other=7%.

Figure S.1 Fatty acid component distribution and molecular structure of vegetable base oils investigated.

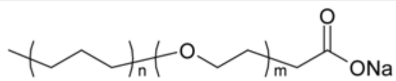
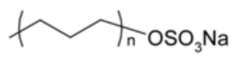
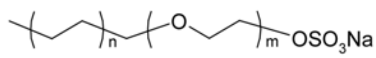
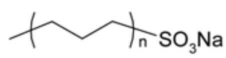
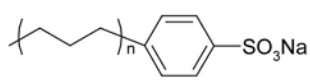
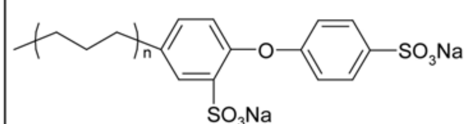
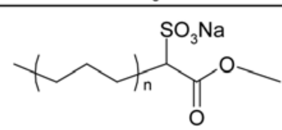
anionic surfactant class	chemical structure	tail length	# of EO	average M.W.	HLB
ethoxylated fattty acid soap		12	3	361	22
			15	865	26
alcohol sulfate		8	-	232	40
		12		288	39
alcohol ether sulfate		12	1	332	39
		12	4	464	40
		13	3	434	38
alkane sulfonate		14	-	328	11
		8		216	15
alkyl aryl sulfonate		2	-	222	13.7
		0		208	14.2
		10		455	8.2
		10		542	25.6
sulfo-carboxylic ester		14	-	340	16
		10		298	20

Table S.1. Anionic surfactants investigated (sorted by classes). The surfactant properties listed are the average of the commercially available distributed surfactant mixtures as reported by their respective manufacturers.

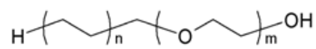
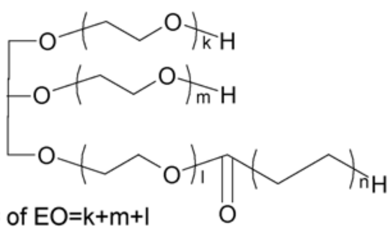
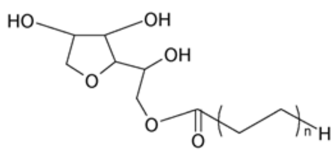
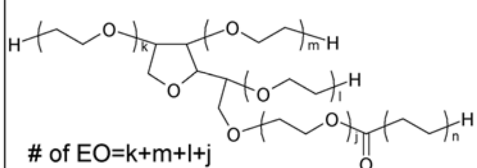
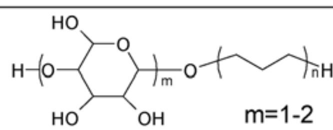
nonionic surfactant class	chemical structure	tail length	# of EO	average M.W.	HLB
ethoxylated alcohol		10	3	281	8.5
			6	425	12.4
		12	3	322	7.9
			7	484	12
		16	2	540	6.5
			10	760	11.5
			20	1110	13.2
ethoxylated glyceryl ester	 # of EO=k+m+l	18	5	1780	4.2
			20	2500	8.4
			40	3300	14.0
polysorbitan ester		12	0	346	8.6
		18		429	4.3
	 # of EO=k+m+l+j	12	20	1228	16.9
		18		1310	15
alkyl polyglucoside	 m=1-2	14	0	510	8.5
		10		440	10.5

Table S.2. Nonionic surfactants investigated (sorted by classes). The surfactant properties listed are the average of the commercially available distributed surfactant mixtures as reported by their respective manufacturers.

A.2. MWF Microemulsions Preparation and Stability Measurement

As shown in Figure S.2, ten points are uniformly selected within the formulation triangle and each point corresponds to a MWF formulation with a different oil and surfactant molar fraction. With the ten points, the triangle is divided into ten sub-regions. Denoting f_{oil}, f_{sp}, and f_{sc} as the molar fractions of oil, surfactant and co-surfactant, respectively, it holds for every formulation point in Figure S.2 that

$$f_{oil} + f_{sp} + f_{sc} = 1 \qquad \text{(S1)}$$

As a first step, a MWF concentrate of oil and surfactants was made. Given the molecular weight of oil (MW_{oil}), surfactant (MW_{sp}), and co-surfactant (MW_{sc}), the weight fraction required to make the concentrate is determined by:

$$\begin{aligned} w_{oil} &= \frac{f_{oil}MW_{oil}}{f_{oil}MW_{oil} + f_{sp}MW_{sp} + f_{sc}MW_{sc}} \times 100\% \\ w_{sp} &= \frac{f_{sp}MW_{sp}}{f_{oil}MW_{oil} + f_{sp}MW_{sp} + f_{sc}MW_{sc}} \times 100\% \\ w_{sc} &= \frac{f_{sc}MW_{sc}}{f_{oil}MW_{oil} + f_{sp}MW_{sp} + f_{sc}MW_{sc}} \times 100\% \end{aligned} \qquad \text{(S2)}$$

Since all MWF microemulsions were tested at a fixed oil molarity 0.019 mole/liter, these concentrates were diluted using ASTM I deionized water that was adjusted to pH=9.5 with sodium hydroxide to be consistent with the typical pH found in MWFs (*S1*). The weight based dilution ratio is calculated as:

$$R = \frac{w_{oil}}{MW_{oil} \times 0.019} \times 1000 \qquad \text{(S3)}$$

After dilution, the sample fluids were aged for 12-15 hours at approximately 25 ˚C before stability measurements were taken. In this paper, three metrics were used to develop an index of fluid stability: visual transparency, light transmittance, and droplet diameter. A visual inspection was first performed and a number (1, 3, or 9) was assigned according to the transparency of the samples with 9 corresponding to the completely transparent fluid and 1 corresponding to opaque or separated samples. Light transmittance and droplet size distribution were then determined using a Spectronic 20 spectrometer (Bausch & Lomb Inc., Rochester, NY)

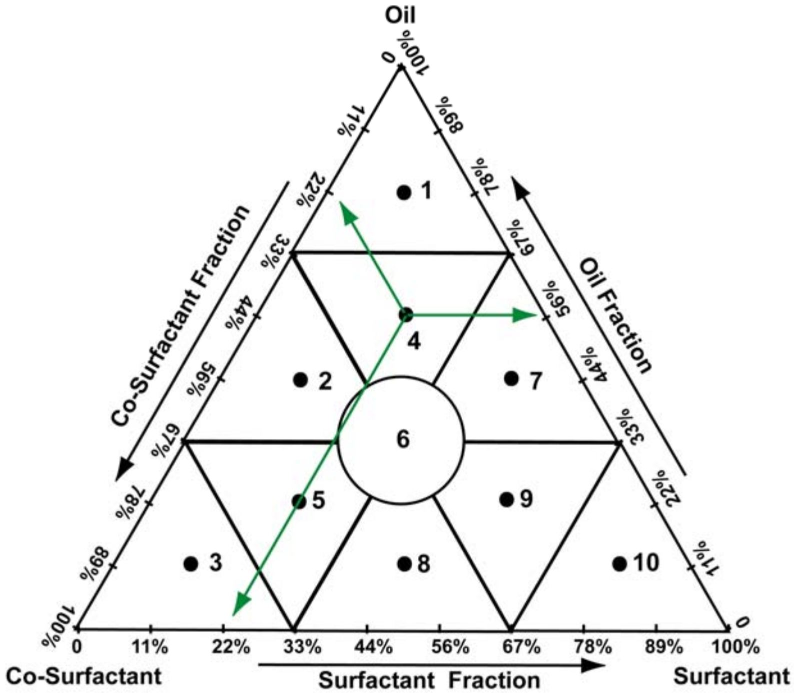


Figure S.2. Formulations diagram for a surfactant combination representing different oil/surfactant molar ratios.

and a dynamic light scattering particle sizing system NICOMP 370 (Particle Sizing Systems, Santa Barbara, CA). The results of these analyses were also discretized into numbers of 1, 3, or 9. For light transmittance, 0%-50% was assigned 9, 50%-90% was assigned 3, and 90%-100% was assigned 1. For particle size, mean droplet size of 0-100 nm was assigned 9, 100nm-500 nm was assigned 3, and >500 nm was assigned 1. The three measurements were performed again after seven days. For each formulation, an aggregate score was calculated as the sum of all the three stability metrics measured after 7 days, with a maximum of 27 and a minimum of 3.

Literature Cited

S1. Childers, J. The Chemistry of Metalworking Fluids. In *Metalworking Fluids*; Byers, J. P., Ed.; Marcel Dekker: New York, 1994.