Solubilization of Methanol and Triglycerides: Unsaturated Long-Chain Fatty Alcohol/Medium-Chain Alkanol Mixed Amphiphile Systems

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This work examines the suitability of unsaturated C_{18} fatty alcohol/1-alkanol mixed amphiphile systems as solubility enhancers for methanol in triglyceride solutions. Four fatty alcohols (all-*cis* monoene, diene and triene, and all-*trans* diene) and five alkanols (C_4-C_{12}) were investigated. Effects of the degree of unsaturation and configuration of the double bonds in the fatty alcohol tailgroup and the chainlength of the alkanol tailgroup were examined. Ternary equilibrium diagrams showed that addition of fatty alcohol/alkanol amphiphiles dramatically affect miscibility between methanol and triglyceride. Solubility, kinematic and relative viscosity, and refractive index data were analyzed to determine mechanisms responsible for the apparent solubilization effects. Under most experimental conditions, formation of large micellar aggregates of amphiphiles was unlikely, and the results were consistent with those expected for co-solvency. However, some viscosity and refractive index data showed that formation of large methanol-in-amphiphile aggregates resembling a nonaqueous microemulsion was feasible, but under limited conditions.

KEY WORDS: Alkanol, aggregates, amphiphile, co-solvency, microemulsion, solubilization, ternary phase equilibria, triglyceride, unsaturated long-chain fatty alcohol, viscosity.

Vegetable oils (triglycerides) hold an enormous potential for development as a reliable and renewable source of fuel for direct-injection compression ignition (diesel) engines. Oils from domestic field crops, such as soybean, corn, rapeseed, sunflower and cotton, have some favorable combinations of fuel characteristics with respect to petroleum-derived fuel (1). However, long-term testing (>250 h) of refined vegetable oils has frequently led to engine durability problems, including injector coking, ring carbonization and crankcase lubricant contamination. These problems were attributed to incomplete combustion of the fuel, aggravated by the relatively high viscosity of the vegetable oils. These viscosities are typically ten to fifteen times greater than that of No. 2 diesel fuel and can hinder fuel atomization and mixing with air (2-4).

Methanol has received considerable attention as a fuel extender and can be derived from a variety of base stocks, such as biomass, municipal wastes, natural gas and coal. Although methanol is not greatly soluble in triglyceride oils, its solubility increases substantially when an amphiphilic compound is added to the system (3,5,6). The increase in methanol solubility results from solubilization by the amphiphiles in the triglyceride solvent. The resulting three-component mixture forms an isotropic, thermodynamically stable solution. This technique, which has been termed "microemulsification" (2,3,5,7), can be used to formulate solutions with viscosities sufficient for use as hybrid diesel fuels.

One previous study (3) showed that medium-chain (C_4-C_{14}) alkanols are effective in solubilizing methanol in

triolein and soybean oil (SBO). Results also indicated that the viscosity of the solution is greatly influenced by chainlength (N) and degree of branching in the amphiphilic tailgroups. Similar studies (5,6) have been conducted with unsaturated long-chain (C_{18}) fatty alcohols. These studies showed that viscosity is influenced by the average degree of unsaturation of the amphiphilic tailgroup structure.

Mixed amphiphile systems have been studied as solubilizers for methanol in triglycerides. One study (8) showed that mixing the surfactants *bis*(2-ethylhexyl) sodium sulfosuccinate, triethylammonium linoleate or tetradecyl-dimethylammonium linoleate with 2-octanol was effective in solubilizing methanol in triolein. Another study (2) demonstrated that mixtures of 1-alkanols with polyoxyethylene [4] dodecyl ether (Brij-30) were effective in solubilizing methanol in SBO. The latter study also showed that candidate formulations could be prepared with viscosities within ASTM (American Society for Testing and Materials) guidelines for No. 2 diesel fuel. Both of these studies reported that nonaqueous microemulsions formed in some systems, under certain conditions.

The present work extends these studies to mixed amphiphile systems consisting of an unsaturated C_{18} fatty alcohol and a medium-length (C_4-C_{12}) straight-chain alkanol. Pseudo-ternary phase equilibria, in which the mixed-amphiphile system (S_{mix}) is treated as a single component, are examined to determine conditions that promote miscibility of various triglyceride/S_{mix}/methanol solutions. Kinematic viscosity results are used to determine the minimum concentration of methanol required to reduce viscosity within ASTM guidelines. This work examines structural variations in the alkanol tailgroup with respect to N and variations in the fatty alcohol tailgroup with respect to average degree of unsaturation and configuration of the double bonds. Methanol solubility, refractive index and relative viscosity data are also analyzed. Finally, a discussion is presented examining the mechanisms responsible for solubility and related effects of adding unsaturated long-chain fatty alcohol/alkanol mixed amphiphiles to methanol-in-triglyceride solutions.

EXPERIMENTAL PROCEDURES

Materials. SBO was selected because it has an attractive combination of fuel properties and because it currently constitutes approximately 80% of the total domestic seed oil produced annually. Refined SBO ($\varrho^{25} = 0.9226$, $n_D^{25} = 1.4715$) was obtained from Archer Daniels Midland, Inc. (Decatur, IL). The chemical properties of SBO have been described previously (1,5). Triolein (TO), 1,2,3-tri-[(Z)-9-octadecenoyl] glycerol, was selected because its physical chemistry is closely related to that of SBO (5,8). Practical grade TO (~65 wt%, $\varrho^{25} = 0.9091$, $n_D^{25} = 1.4662$) was acquired from Sigma Chemical Co. (St. Louis, MO).

Three all-*cis* and one all-*trans* C_{18} fatty alcohols were selected for study. They are as follows: oleyl alcohol, (Z)-9-octadecen-1-ol; linoleyl alcohol, (Z,Z)-9,12-octadecadien-1-ol;

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linolenyl alcohol, (Z,Z,Z)-9,12,15-octadecatrien-1-ol; and elaidolinoleyl alcohol, (E,E)-9,12-octadecadien-1-ol. Commercial grade all-*cis* fatty alcohols were used in all experiments. These alcohols typically contained 85 to 95 wt% unsaturated C_{18} fatty alcohols plus some saturated C_{16} and C_{18} fatty alcohols. Oleyl alcohol ($\sim$65 wt%) was obtained from Aldrich Chemical Co. (Milwaukee, WI). Linoleyl and linolenyl alcohol (both $\sim$54 wt%) were obtained from Sherex Chemical Co. (Dublin, OH). Elaidolinoleyl alcohol was prepared from linoleyl alcohol by an elaidinization procedure described elsewhere (9). The purities of these fatty alcohols were confirmed by gas chromatography.

Five alkanols were selected as follows: 1-butanol (99 wt%), 1-hexanol (99 wt%), 1-octanol (99 wt%), 1-decanol (98 wt%) and 1-dodecanol (98 wt%). These alkanols were obtained from Aldrich and Sigma. High-performance liquid chromatography-grade methanol (99 wt%) from EM Science (Cherry Hill, NJ) was vacuum-distilled before use. All alcohols were stored over molecular sieves.

Procedures. Miscibility conditions of several pseudo-ternary triglyceride/S_{mix}/MeOH systems were determined at 25 ± 0.1°C by the method of phase volumes. Procedures have been described elsewhere (6). The miscibility curves were determined within 0.005–0.01 volume fraction for each system. Critical mixing data (plait points) were determined at 25°C by the method described by Alders (10).

Methanol solubility studies were conducted at 25°C by procedures described elsewhere (6). The maximum solubility of methanol was determined within 0.01 volume fraction.

Kinematic viscosities were measured in calibrated Canon-Fenske (Cannon, State College, PA) viscometers. Studies were conducted at both 25 ± 0.5°C and 37.8 ±

0.1°C by submerging the viscometers in a constant temperature bath.

Refractive indices were measured at 25 ± 0.5°C with a Bausch & Lomb refractometer (Rochester, NY) connected to a constant-temperature bath.

RESULTS AND DISCUSSION

Miscibility studies. Figures 1 and 2 are ternary phase diagrams depicting phase equilibria for several SBO/S_{mix}/MeOH systems at 25°C. The data are plotted with S_{mix}, representing one component on each ternary diagram. For a given pseudo-ternary system, solutions with compositions in the region on the "S_{mix}-side" of the miscibility curve were isotropic, while those with compositions below the curve were anisotropic.

Figure 1 is a comparison of pseudo-ternary systems where S_{mix} is 10 mol% linoleyl alcohol mixed in a homologous series of 1-alkanols. With respect to the unsaturated fatty alcohol in S_{mix}, increasing the N of the alkanol tailgroup decreases the total area of the anisotropic region of the phase diagram.

The Bancroft Rule (11) states that emulsifiers that are more soluble in oil are more suitable for producing stable water-in-oil emulsions. This rule appears to apply to the methanol-in-SBO solutions in Figure 1. Increasing N for the 1-alkanol tailgroup increases the "average molar N" (N_{avg}) of the amphiphile tailgroups in S_{mix}. As a result, S_{mix} becomes more soluble in SBO and more suitable for increasing stability of methanol-in-SBO mixtures.

Another consequence of increasing N_{avg} holds that, as S_{mix} becomes more oil-soluble, the amount of solute that may be solubilized into the external phase increases with
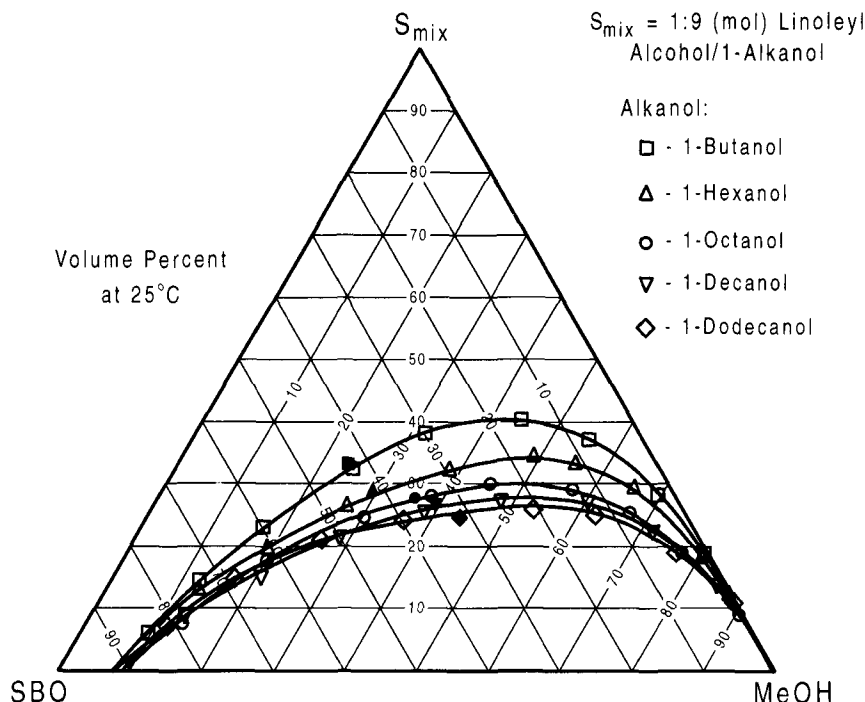

FIG. 1. Effect of alkanol chainlength on miscibility of soybean oil (SBO)/mixed amphiphile (S_{mix})/methanol (MeOH) systems at 25°C. Filled symbols denote critical mixing points.
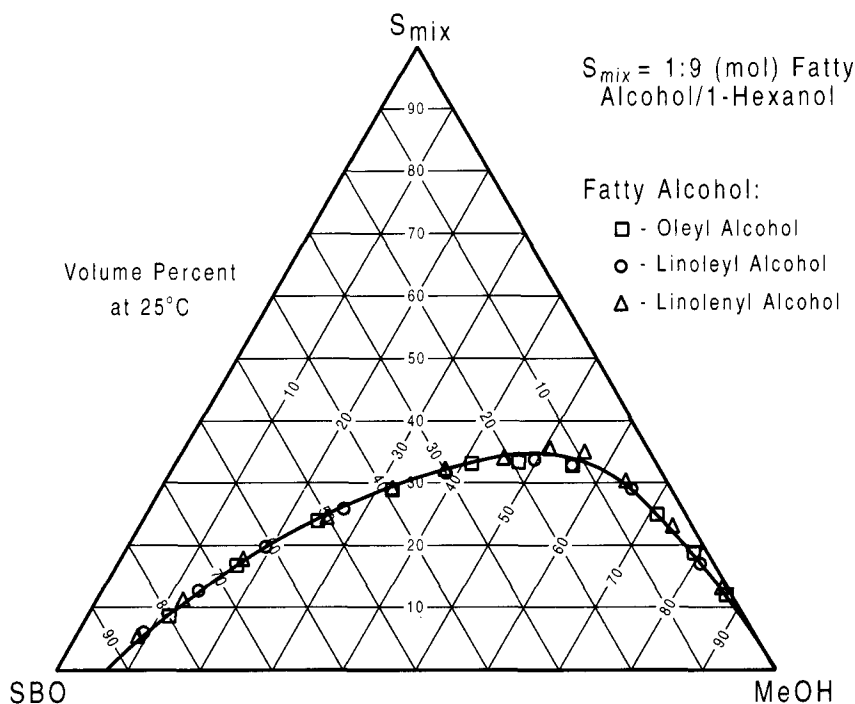
FIG. 2. Effect of average degree of unsaturation of all-*cis* fatty alcohols on miscibility of soybean oil (SBO)/mixed amphiphile (S_{mix})/methanol (MeOH) systems at 25°C.

respect to phase inversion (11). For the systems studied in this work, this phenomenon may be confirmed by examination of the critical mixing (plait) points; that is, critical mixing points indicate where phase inversion occurs on the miscibility curve. These points are plotted for each system on Figure 1 and show that increasing N_{avg} increases the concentration of methanol solubilized in SBO-external solution before phase inversion occurs.

Figure 2 is a comparison of systems where S_{mix} is 90 mol% 1-hexanol mixed with a series of all-*cis* C_{18} fatty alcohols. These results show that miscibility phase behavior is not greatly affected by increasing the degree of unsaturation in the fatty alcohol tailgroup structure. Comparisons with respect to configuration of the dienic fatty alcohol tailgroup also showed no apparent effects on miscibility phase behavior. Related studies (6) with triolein/unsaturated C_{18} fatty alcohol/methanol systems have yielded analogous results. Hence, the results from these studies were expected.

Comprehension of the miscibility conditions and phase inversion equilibria is crucial to the development of triglyceride/amphiphile/methanol-type solutions as hybrid diesel fuels. Candidate diesel fuels must be formulated to be single-phase and oil-continuous (3,12,13). Therefore, such formulations will likely have compositions in the isotropic region and near the SBO-corner of the ternary phase equilibrium diagram. This work shows that formulations with unsaturated long-chain fatty alcohol/1-alkanol mixed amphiphile systems require a minimum SBO content of 34 vol% for 1-dodecanol in S_{mix} to 44 vol% for 1-butanol, under the conditions studied.

Kinematic viscosities. Figures 3–5 are graphs depicting effects of increasing methanol concentration (V_{MeOH}) on kinematic viscosity (*v*) of various SBO/S_{mix}/MeOH solu-

tions at 37.8°C (100°F). For all experiments, methanol was added until phase separation occurred. Viscosities for isotropic solutions are presented here.

Figure 3 is a comparison of systems where S_{mix} is 20 mol% oleyl alcohol in a homologous series of 1-alkanols. These data indicate that increasing N in the alkanol tailgroup increases the viscosity, with respect to V_{MeOH}. These results were not surprising, because hydrogen bonding is likely to be a major factor in determining the
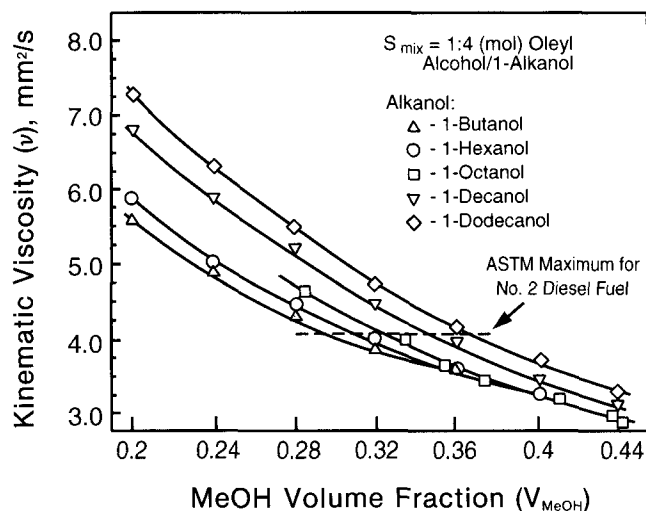

FIG. 3. Effect of alkanol chainlength on kinematic viscosity-methanol volume fraction (V_{MeOH}) curves for soybean oil (SBO)/mixed amphiphile (S_{mix})/methanol systems at 37.8°C. SBO/S_{mix} = 1:1 (vol). ASTM, American Society for Testing and Materials.
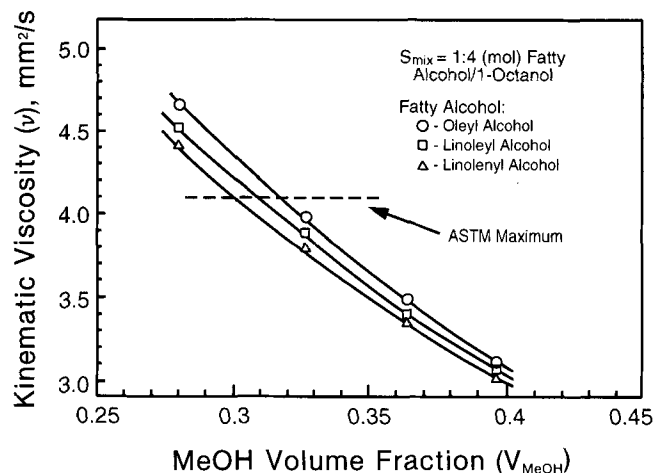
FIG. 4. Effect of average degree of unsaturation of all-*cis* fatty alcohol on kinematic viscosity–methanol volume fraction (V_{MeOH}) curves for soybean oil (SBO)/mixed amphiphile (S_{mix})/methanol systems at 37.8°C. SBO/S_{mix} = 1:1 (vol). See Figure 3 for abbreviation.

FIG. 5. Effect of average configuration of double bonds in fatty alcohol tailgroups on kinematic viscosity–methanol volume fraction (V_{MeOH}) curves for soybean oil (SBO)/mixed amphiphile (S_{mix})/methanol systems at 37.8°C. SBO/S_{mix} = 1:1 (vol). See Figure 3 for abbreviation.

overall solution viscosity. Furthermore, these results are consistent with similar studies (3) with neat 1-alkanols.

Figure 4 is a comparison of systems where S_{mix} is 80 mol% 1-octanol mixed with a series of all-*cis* C_{18} fatty alcohols. These results show that increasing the degree of unsaturation in the fatty alcohol tailgroup decreases the viscosity, with respect to V_{MeOH}. Similar comparison of systems where S_{mix} was 1:9 (mol) all-*cis* fatty alcohol/1-hexanol and 1:1 (mol) all-*cis* fatty alcohol/1-octanol yielded analogous results. These results are also consistent with those from a previous study (5) in which neat unsaturated fatty alcohols were examined. The magnitude of the viscosity effect in this work was diminished compared to those results, because a substantial portion of the amphiphilic component was alkanol.

Figure 5 is a comparison of systems where S_{mix} is 50 mol% 1-octanol mixed with configurational isomers of linoleyl alcohol. This graph shows that replacing the all-*cis* fatty alcohol with its all-*trans* isomer increases the viscosity with respect to V_{MeOH}. Comparison of systems where S_{mix} was 1:4 (mol) monoenic fatty alcohol/1-octanol, 1:1 (mol) dienic fatty alcohol/1-octanol and 1:4 (mol) dienic fatty alcohol/1-octanol yielded analogous results. Furthermore, the effects of configuration on viscosity decrease as the mole ratio of fatty alcohol to 1-alkanol in S_{mix} decreases. For example, at V_{MeOH} = 0.32 mL/mL, both 1:1 (mol) amphiphile systems showed deviations in viscosity of ~0.30 mm²/s, while both 1:4 (mol) systems showed deviations of ~0.10 mm²/s.

These results are in contrast to those from the previous study (5), which examined the neat unsaturated fatty alcohols. Under analogous conditions, that study showed no significant deviations between either monoenic or dienic configurational isomers. This work shows that replacing most of the amphiphilic conponent with 1-alkanol creates significant deviations in viscosity with respect to configuration of the fatty alcohol. Furthermore, it is not likely that interactions between SBO-fatty alcohol, methanol-fatty alcohol, SBO-alkanol or methanol-alkanol molecular pairs are causing these deviations. The only
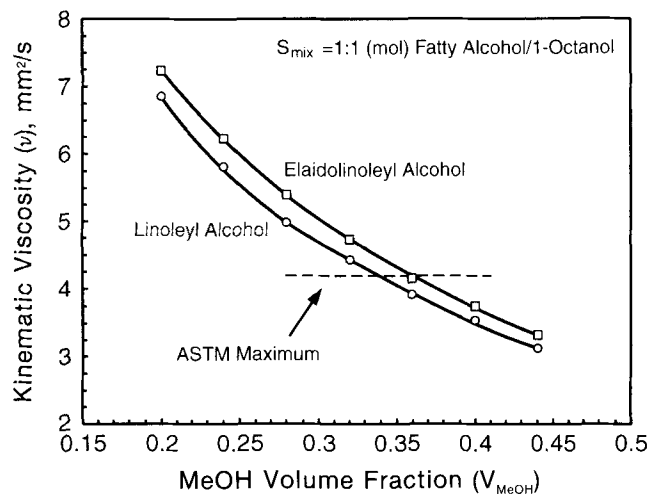
interactions that may have a significant impact on viscosity are those between the fatty alcohol and 1-alkanol tailgroups in solution. It is possible that these interactions depend on steric factors that are influenced by configuration and that these factors only manifest themselves when a sufficient concentration of alkanol is present in solution.

Studies for this work were conducted with commercial-grade fatty alcohols. These fatty alcohols were actually mixtures of long-chain fatty alcohols whose major component was either oleyl, linoleyl, elaidolinoleyl or linolenyl alcohol. There exists a relatively large degree of difference between the structures of medium-chain alkanols and unsaturated long-chain fatty alcohols. Thus, qualitative speculations based on the alkanol structure or comparisons between the alkanol and fatty alcohol structures are justified on a molecular basis. However, attempting to explain results based strictly on the fatty alcohol structure may not be practical.

Comparison with ASTM guidelines. Figures 3–5 have a horizontal reference line, which indicates the maximum allowable viscosity for No. 2 diesel fuel, 4.10 mm²/s at 40°C according to guidelines posted by ASTM (1). Table 1 shows breakthrough V_{MeOH} data for several SBO/S_{mix}/MeOH systems at 37.8°C. These data define the volume of methanol that should be added to a 1:1 (vol) SBO/S_{mix} solution to reduce viscosity to 4.10 mm²/s. Under conditions of these studies, each system is capable of solubilizing enough methanol to formulate candidate diesel fuels whose viscosities are well within ASTM guidelines.

In general, it is desirable to keep the methanol concentration in fuel formulations low because methanol tends to have a diminishing effect on other fuel properties, including cetane rating and heat of combustion (2,12). In other words, increasing the alkanol chainlength tends to make S_{mix} less desirable in formulations with SBO and methanol. For example, the 1:4 (mol) oleyl alcohol/1-butanol system broke through at V_{MeOH} = 0.295 mL/mL; while, the 1:4 (mol) oleyl alcohol/1-dodecanol system broke through at V_{MeOH} = 0.365 mL/mL. In this case, increasing N from 4 to 12 increases breakthrough V_{MeOH} by 23.7%.

TABLE 1

Breakthrough V_{MeOH} Data for Selected Systems at 37.8°C[a]

Fatty alcohol	Alkanol	Ratio[b] (mol)	V_{MeOH} (mL/mL)
Oleyl	—	—	0.427
Linoleyl	—	—	0.401
Linolenyl	—	—	0.391
—	1-Butanol	—	0.186
—	1-Hexanol	—	0.248
—	1-Octanol	—	0.293
—	1-Decanol	—	0.330
—	1-Dodecanol	—	0.354
Oleyl	1-Butanol	1:4	0.295
Oleyl	1-Hexanol	1:4	0.308
Oleyl	1-Octanol	1:4	0.322
Linoleyl	1-Octanol	1:4	0.315
Linolenyl	1-Octanol	1:4	0.306
Oleyl	1-Decanol	1:4	0.345
Oleyl	1-Dodecanol	1:4	0.365
Linoleyl	1-Octanol	1:1	0.346
Elaidolinoleyl	1-Octanol	1:1	0.366

[a]$SBO/S_{mix} = 1:1$ (vol); $v = 4.10$ mm^2/s; SBO, soybean oil; V_{MeOH}, methanol volume fraction.
[b]Fatty alcohol/alkanol in mixed amphiphile (S_{mix}).
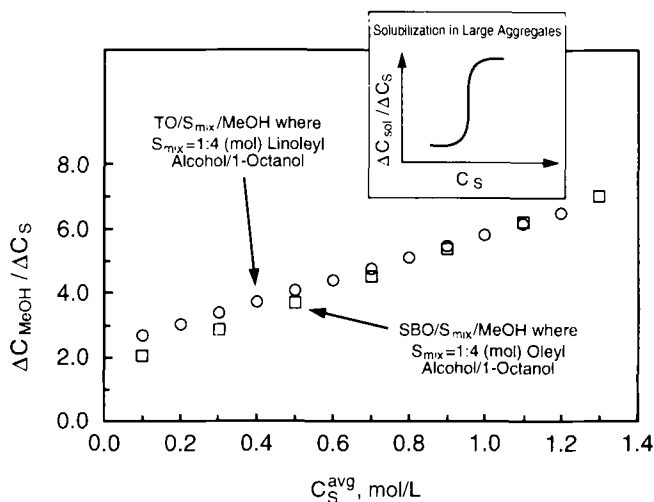

FIG. 6. Solubility of methanol in triglyceride/mixed amphiphile (S_{mix}) solutions at 25°C. Plotted as rate of increase in moles per liter methanol (ΔC_{MeOH}) with respect to moles per liter mixed amphiphile (ΔC_S) vs. average mixed amphiphile concentration (C_S^{avg}). TO = triolein; SBO = soybean oil.

On the other hand, miscibility results indicate that conditions precluding phase separation become more favorable as alkanol N increases. For the same example cited above, the former case undergoes phase separation at a V_{MeOH}-value near 0.38 mL/mL; while the latter case undergoes phase separation at a value near 0.46 mL/mL. This work shows that selection of candidate fuels may require some optimization with respect to breakthrough V_{MeOH}-data to ensure that phase separation is precluded under specified conditions.

Mechanisms. Phase equilibria and physical properties obviously are critical considerations when formulating candidate hybrid diesel fuels from triglyceride oils, unsaturated long-chain fatty alcohol/alkanol mixed amphiphiles and methanol. The following sections examine and discuss the results from this work to determine the mechanisms that control the related phenomena and the conditions that affect these mechanisms.

Phase equilibria. Figure 6 is a plot of methanol solubility data at 25°C for two systems, 1:4 (mol) linoleyl alcohol/1-octanol in TO and 1:4 (mol) oleyl alcohol/1-octanol in SBO. Methanol vs. amphiphile concentration data (C_{MeOH} vs. C_S) were collected and fitted with a second-order polynomial expression, then re-calculated to obtain data at constant intervals of C_S. Miscibility results showed that phase inversion occurs at $C_S = 1.414$ mol/L for the TO-based system, and $C_S = 1.409$ mol/L for the SBO-based system; therefore, all solubility data are for triglyceride-continuous solutions.

In general, solubilization is a phenomenon that allows dissolution of a nearly insoluble substance into a given solvent, forming a thermodynamically stable isotropic solution when a third amphiphilic compound is added (14). The primary mechanism for true solubilization results from formation of large micellar aggregates in solution (15,16). For such systems, plotting the rate of increase in C_{Sol} (solute concentration) with respect to C_S, $\Delta C_{Sol}/\Delta C_S$, should yield a curve similar to the one depicted in the inset

figure located in the upper right-hand corner of Figure 6 (15). When aggregates are present in solution, C_{Sol} increases rapidly within a narrow C_S-interval near the critical micelle concentration (CMC), causing a significant increase in $\Delta C_{Sol}/\Delta C_S$. This occurs because solutions with C_S-values less than CMC do not contain any aggregates, while those with C_S-values greater than CMC contain amphiphiles in essentially aggregated form.

The results in Figure 6 show that increasing C_S increases methanol solubility, qualitatively fitting the general definition for solubilization. However, a relatively large amount of S_{mix} is required to significantly affect methanol solubility. Furthermore, $\Delta C_{MeOH}/\Delta C_S$ increases monotonically with increasing C_S^{avg}, rather than sharply over a narrow C_S^{avg}-interval.

These solubility results are analogous to those obtained from a previous study (6) where the amphiphile was neat oleyl alcohol. That study determined that mechanisms associated with co-solvency were responsible for affecting methanol solubility. Co-solvency, a phenomenon generally associated with large C_S-values, can result from mechanisms similar to those for solubilization in large aggregates (14–16). By extension, this work shows that a mixed amphiphile system composed of an unsaturated long-chain fatty alcohol and a medium-chain alkanol also acts as a co-solvent system for enhancing the solubility of methanol in triglyceride solvent.

Physical properties. For many amphiphilic co-solvent systems, viscosity decreases as the solute concentration increases (16). Figures 3–5 show that viscosity decreases with increasing V_{MeOH} for all methanol concentrations studied. Thus, results at 37.8°C are consistent with those expected for co-solvent systems. However, this is not entirely the case for viscosity studies conducted at 25°C.

Figure 7 is a graph of kinematic viscosity data for TO/S_{mix}/MeOH at 25°C, where S_{mix} is 1:4 (mol) linoleyl alcohol/1-decanol. At lower V_{MeOH} values, the results are consistent with co-solvent phenomena. However, at larger
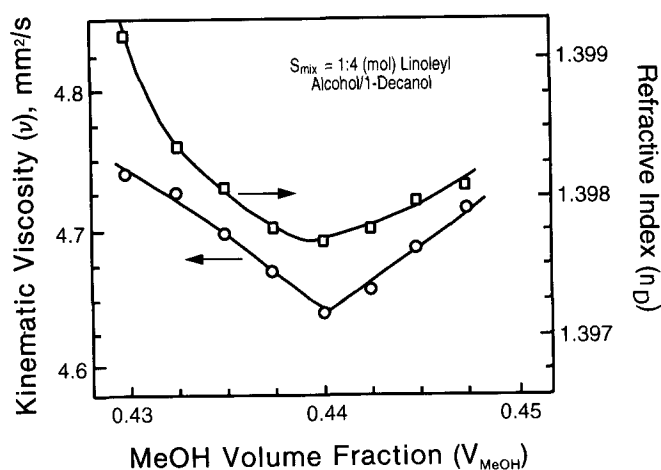
FIG. 7. Comparison of kinematic viscosity (v) and refractive index curves (n_D) for one triolein (TO)/mixed amphiphile (S_{mix})/methanol (MeOH) system at 25°C. TO/S_{mix} = 1:1 (vol). Minimum viscosity (v_{min}) = 4.638 mm²/sec at V_{MeOH} = 0.4402; minimum refractive index (n_{Dmin}) = 1.3977 at V_{MeOH} = 0.4395.

V_{MeOH} values, viscosity increases with methanol concentration. The V_{MeOH} value that corresponds to the minimum in the viscosity curve, $V_{min}(v)$, was determined by regression and was 0.4402 mL/mL.

Also shown in Figure 7 are refractive index (n_D) results for the same TO/S_{mix}/MeOH system. These data show a minimum in the curve at $V_{min}(n_D)$ = 0.4395 mL/mL, a value that is in excellent agreement with $V_{min}(v)$. Several of the systems studied exhibited similar behavior, and the results are summarized in Table 2. All data show good-to-excellent agreement between $V_{min}(v)$ and $V_{min}(n_D)$, with deviations from 0.03 to 2.51%.

Summarizing these results, significant changes in the physical property curves occur near V_{MeOH} = V_{min}. It is not likely that phase inversion from triglyceride-external to methanol-external solution is causing these changes. If this were the case, then further increasing V_{MeOH} would have the effect of diluting a suspension of triglyceride and amphiphile molecules (or perhaps triglyceride-in-amphiphile aggregates), which are significantly larger than the methanol solvent molecules. Under these cir-

cumstances, viscosity should decrease with increasing methanol concentration, regardless of the colligative nature of the system.

One feasible explanation may be the transition of the solution into one that contains large amphiphile aggregates suspended in triglyceride solvent. It is equally feasible that true solubilization exists, and that the resulting methanol-in-S_{mix} aggregates resemble a non-aqueous microemulsion. This has been discussed previously in at least two related studies (2,6), but results indicated large aggregates were feasible only under very specific conditions.

When V_{MeOH} is less than V_{min}, aggregates either do not exist in solution or they exist in pre-micellar form (dimers and trimers). In either case, the solution does not contain particles that are substantially larger than the triglyceride solvent molecules. Under these conditions, methanol is molecularly dispersed in a co-solvent mixture of amphiphiles and triglyceride, and increasing V_{MeOH} decreases the viscosity of the solution.

In general, solutions containing aggregates that are significantly larger in size than the solvent molecules are more viscous than the pure solvent (17,18). If increasing total solute concentration in a micellar solution increases the solubilized solute concentration, then the total phase volume of the aggregates increases. Under these circumstances, increasing solute concentration increases the relative viscosity of the solution. Hence, when V_{MeOH} is greater than V_{min}, formation of large methanol-in-S_{mix} aggregates suspended in triglyceride solvent is feasible.

Figure 8 is a graph of relative viscosity (η_{Rel}) data at 25°C for two systems, 1:4 (mol) oleyl alcohol/1-octanol in SBO and 1:4 (mol) oleyl alcohol/1-dodecanol in TO. The η_{Rel}s were determined as the ratio of viscosity at any given $V_{MeOH} > V_{min}(v)$ to v_{min}, where v_{min} was determined by regression analysis. The data are plotted as a function of the added phase volume fraction of methanol, ϕ_{MeOH} = V_{MeOH} − $V_{min}(v)$. Reference values of v_{min} and $V_{min}(v)$ are given in Table 2.

Einstein's law of viscosity (7), derived for a dilute suspension of noninteracting rigid spheres, is plotted through the data in Figure 8. For both sets of results, agreement is excellent at lower volume fractions, showing slight curvature at $\phi_{MeOH} > 0.005$. For comparison, Roscoe's equation for viscosity (18), derived for a high

TABLE 2

Kinematic Viscosity and Refractive Index Minima at 25°C[a]

Oil	Fatty alcohol	Alkanol[b]	SBO/S_{mix} (vol. ratio)	$V_{min}(v)$ (mL/mL)	v_{min} (mm²/s)	$V_{min}(n_D)$ (mL/mL)	$n_{D\ min}$	Dev.
TO	Oleyl	—	1:1	0.4437	5.590	0.4550	1.3993	0.0113
TO	Linoleyl	—	1:1	0.4520	5.139	0.4500	1.4023	0.0020
TO	Oleyl	1-Butanol	1:1	0.3609	5.233	0.3600	1.4030	0.0009
TO	Oleyl	1-Hexanol	1:1	0.4072	4.492	0.4100	1.3985	0.0028
SBO	Oleyl	1-Octanol	1:1	0.4120	4.392	—	—	—
TO	Oleyl	1-Octanol	1:1	0.4431	4.253	0.4425	1.3958	0.0006
TO	Oleyl	1-Octanol	2:1	0.3031	8.632	0.3030	1.4782	0.0001
TO	Oleyl	1-Decanol	1:1	0.4405	4.565	0.4485	1.3964	0.0080
TO	Linoleyl	1-Decanol	1:1	0.4402	4.638	0.4395	1.3977	0.0007
TO	Oleyl	1-Dodecanol	1:1	0.4628	4.534	0.4650	1.3956	0.0022

[a]TO, triolein; SBO, soybean oil; n_D, refractive index; $V_{min}(n_D)$, V_{MeOH} at minimum n_D; v, viscosity; V_{MeOH}, methanol volume fraction; $V_{min}(v)$, V_{MeOH} at minimum v; Dev. = [$V_{min}(v)$ − $V_{min}(n_D)$]; S_{mix}, mixed amphiphile.
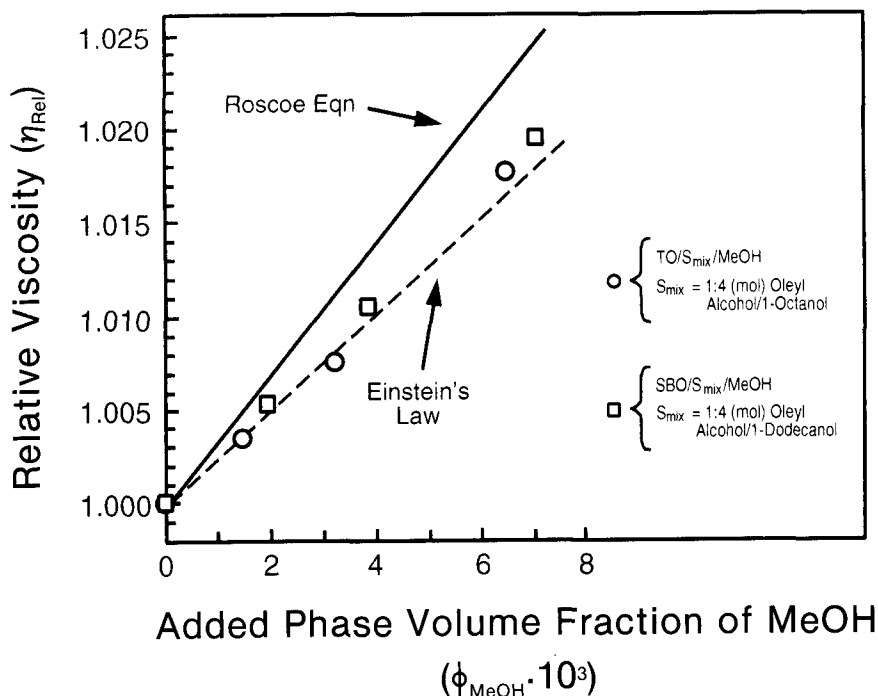[b]The 1:4 (mol) fatty alcohol/alkanol for all systems.

FIG. 8. Relative viscosities (η_{Rel}) of two triglyceride/mixed amphiphile (S_{mix})/methanol (MeOH) systems at 25°C: comparison with Einstein's law ($\eta_{Rel} = 1 + 2.5 \cdot \phi$) and Roscoe equation [$\eta_{Rel} = (1 - 1.35 \cdot \phi)^{2.5}$]. Triglyceride/$S_{mix}$ = 1:1 (vol); TO = triolein; SBO = soybean oil.

concentration of uniform rigid spheres suspended in solution, is also plotted in Figure 8.

Table 3 is a summary of results from linear least-squares analyses of η_{Rel} data for several systems studied in this work. Three systems gave slopes that agreed well with Einstein's law (values were between 2.3 and 2.7); however, the remainder of the systems deviated significantly. These deviations may be the result of any combination of effects, such as hydrogen bonding between aggregates and the continuous phase, nonrigid or polydisperse aggregate particle sizes, or nonsymmetrical shape of the aggregates in solution.

These results show that particles significant in size with respect to the solvent molecules may be present in solution and that this behavior may be an indication that the solution consists of large methanol-in-S_{mix} aggregates suspended in triglyceride solvent. However, formation of large aggregates is only feasible under limited conditions. First, temperature has an effect because results at 37.8°C indicated no aggregation could occur. Second, results at 25°C exhibited behavior consistent with aggregation only at relatively high methanol concentrations (V_{min}).

Finally, phase separation occurs when V_{MeOH} is slightly in excess of $V_{min}(v)$ for each of the systems analyzed. For

TABLE 3

Regression Analysis of Relative Viscosity Data at 25°C

Oil	Fatty alcohol	Alkanol[a]	SBO/S_{mx} (volume ratio)	Slope	Intercept	R^2[b]	σ_y[c]·10^3
TO	Oleyl	—	1:1	7.138	1.0000	0.994	2.73
TO	Linoleyl	—	1:1	4.424	1.0000	0.9999	0.107
TO	Oleyl	1-Butanol	1:1	5.911	0.9999	0.999	0.586
TO	Oleyl	1-Hexanol	1:1	3.440	0.9998	0.9994	0.327
SBO	Oleyl	1-Octanol	1:1	2.700	0.9996	0.997	0.526
TO	Oleyl	1-Octanol	1:1	5.218	1.0002	0.98	2.82
TO	Oleyl	1-Octanol	2:1	4.727	0.9999	0.9997	0.216
TO	Oleyl	1-Decanol	1:1	0.8954	0.9997	0.991	0.571
TO	Linoleyl	1-Decanol	1:1	2.3017	0.9995	0.990	0.878
TO	Oleyl	1-Dodecanol	1:1	2.626	1.0000	0.995	0.645

[a]1:4 (mol) fatty alcohol/alkanol for all systems.
[b]Square of the correlation coefficient. See Table 2 for other abbreviations.
[c]Standard error of y-estimate: $(\Sigma(y_i - y_i^{est})^2/(n - 2))^{1/2}$.

example, the system shown in Figure 7 undergoes phase separation at $V_{MeOH} = 0.4485$ mL/mL, which exceeds $V_{min}(v)$ by 0.0083 mL/mL. For the remainder of the systems listed in Table 3, phase separation occurs at V_{MeOH} values 0.004 to 0.02 mL/mL in excess of $V_{min}(v)$. Thus, it is possible that formation of large aggregates in these systems occurs as a preliminary phase transition prior to phase separation.

Comments. Formulating candidate hybrid diesel fuels by mixing triglyceride oils, nonionic amphiphiles or amphiphilic systems, and simple alcohols has frequently been referred to as microemulsification in general and patent literature. For some SBO/alkanol/MeOH systems, it has been proven that adding 1.0–1.5 vol% water will produce a microemulsion (3), and utilizing aqueous ethanol (95%) instead of methanol also produces a microemulsion (7).

This study examined the mechanisms responsible for enhancing the solubility of methanol in triglyceride oil by adding unsaturated long-chain fatty alcohol/alkanol mixed amphiphile under nonaqueous conditions. For such systems, results show that the term "microemulsions" does not adequately describe the phenomena as consistently as "co-solvency". However, some results indicated that microemulsions could form in solution, but under restrictive conditions. Nearly identical results have been obtained from similar studies with neat fatty alcohol amphiphiles (5,6). By extension, it is likely that the same mechanisms apply to systems with neat alkanol amphiphiles.

Finally, the overall goal for formulating candidate fuels from triglyceride/amphiphile/methanol solutions is to reduce to viscosity for compatibility with modern direct-injection diesel engines. In general, co-solvent systems decrease in viscosity with increasing solute (methanol) concentration, while triglyceride-external microemulsion solutions increase in viscosity with increasing solute concentration. Given these considerations, conditions promoting co-solvency may be preferable with respect to those promoting microemulsions.

REFERENCES

1. Goering, C.E., A.W. Schwab, M.J. Daugherty, E.H Pryde and A.J. Healy, *Trans. ASAE 25:*1472 (1982).
2. Schwab, A.W., M.O. Bagby and B. Freedman, *Fuel 66:*1372 (1987).
3. Schwab, A.W., and E.H. Pryde, *J. Dispersion Sci. Technol. 6:*563 (1985).
4. Ryan III, T.W., L.G. Dodge and T.J. Callahan, *J. Am. Oil. Chem. Soc. 61:*1610 (1984).
5. Dunn, R.O., A.W. Schwab and M.O. Bagby, *J. Dispersion Sci. Technol. 13:*77 (1992).
6. Dunn, R.O., A.W. Schwab and M.O. Bagby, *Ibid. 14:*1 (1993).
7. Schwab, A.W., H.C. Nielsen, D.D. Brooks and E.H. Pryde, *Ibid. 4:*1 (1983).
8. Schwab, A.W., and E.H. Pryde, in *Phenomena in Mixed Surfactant Systems, ACS Symposium Series 311,* edited by J.F. Scamehorn, American Chemical Society, Washington, D.C., 1986, pp. 283–294.
9. McCutchon, M.A., R.T. O'Connor, E.F. DuPre, L.A. Goldblatt and W.G. Bickford, *J. Am. Oil Chem. Soc. 36:*450 (1959).
10. Alders, L., *Liquid-Liquid Extraction: Theory, and Laboratory Experiments,* Elsevier Publishing Co., New York, 1955, p. 20.
11. Rosen, M.J., *Surfactants and Interfacial Phenomena,* 2nd Edn., John Wiley & Sons, New York, 1989, pp. 304–336.
12. Schwab, A.W., and E.H. Pryde, U.S. Patent No. 4,557,734 (1985).
13. Schwab, A.W., and E.H. Pryde, U.S. Patent No. 4,526,586 (1985).
14. Mackay, R.A., in *Nonionic Surfactants: Physical Chemistry Surfactant Science Series Vol. 23,* edited by M.J. Schick, Marcel Dekker, Inc., New York, 1987, pp. 297–368.
15. Mukerjee, P., in *Solution Chemistry of Surfactants Vol. 1,* edited by K.L. Mittal, Plenum Press, New York, 1979, pp. 153–174.
16. McBain, M.E.L., and E. Hutchinson, *Solubilization and Related Phenomena,* Academic Press, New York, 1955, pp. 179–194.
17. Ito, K., and Y. Yamashita, *J. Colloid Sci. 19:*152 (1964).
18. Roscoe, R., *Brit. J. Appl. Phys. 3:*267 (1952).