Aggregation of Unsaturated Long-Chain Fatty Alcohols in Nonaqueous Systems[1]

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ABSTRACT: Aggregation and related phenomena in nonaqueous binary and ternary solutions containing unsaturated long-chain fatty alcohol amphiphiles have been studied. Six C_{18} fatty alcohols were studied—oleyl alcohol (9*Z*-octadecen-1-ol), elaidyl alcohol (9*E*-octadecen-1-ol), linoleyl alcohol (9*Z*, 12*Z*-octadecadien-1-ol), elaidolinoleyl alcohol (9*E*, 12*E*-octadecadien-1-ol), linolenyl alcohol (9*Z*, 12*Z*, 15*Z*-octadecatrien-1-ol) and elaidolinolenyl alcohol (9*E*, 12*E*, 15*E*-octadecatrien-1-ol). Equivalent conductivity and photon correlation spectroscopy confirmed that unsaturated long-chain fatty alcohols form large and polydisperse aggregates in methanol. Critical micelle concentration (CMC) results showed that the degree of unsaturation and configuration of the double bonds in the fatty alcohol significantly influences aggregation. Aggregation of oleyl alcohol in a series of straight and branched medium-chainlength (C_3–C_8) alkanol solvents was studied. For shorter-chained alkanols (C_1–C_4), decreasing solvent dielectric constant decreases the CMC; however, for longer-chained alkanols (C_4–C_8), no significant effects occurred on the CMC. The effect of solubilized soybean oil on the viscosity of long-chain fatty alcohol/methanol solutions was also analyzed. Relative viscosity results were consistent with those expected for microemulsions. Although preliminary in nature, these results generally support the notion that soybean oil is solubilized by incorporation into large soybean oil-in-fatty alcohol aggregates in methanol solvent, resembling a nonaqueous detergentless microemulsion.
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KEY WORDS: Aggregate, alkanol, conductivity, configuration, critical micelle concentration, degree of unsaturation, microemulsion, nonaqueous solvent, solubilization, tailgroup coiling, triglyceride, unsaturated long-chain fatty alcohol, viscosity.

Vegetable (triglyceride) oils have recently gained attention as "environmentally friendly" and renewable resources for development of nonfood-grade industrial products. These products have enormous potential to extend or replace similar petrochemical-based products and yield equivalent or superior performance. Examples of products currently under development include soybean oil-based inks, diesel fuel from soybean, sunflower or rapeseed oils, cutting oils and lubricants, cleaning oils, fragrance oils, pesticides and other agricultural emulsions, spray coatings and pharmaceutical mixtures. Products of this nature generally require emulsification or microemulsification with water or polar organic liquids. Consequently, commercial development of triglyceride oil-based products will require a thorough comprehension of the interfacial and related phenomena between oil and polar phases, and the effects that surfactants and other additives have on the physical properties of such systems.

The work presented here was derived within the framework of studies with hybrid diesel fuel candidates, formulated by solubilizing short-chain alcohols in triglyceride oils under nonaqueous conditions. Previous studies emphasizing oil-external solutions showed that methanol solubility improved substantially when long-chain unsaturated fatty alcohols were added (1,2). Under most conditions, results were more consistent with co-solvency than formation of methanol-in-amphiphile aggregates. Analogous conclusions have been drawn from studies with medium-chain alkanols and fatty alcohol/alkanol mixtures as solubilizers (3,4).

The present work focuses on another key in understanding the nature of nonaqueous triglyceride/unsaturated long-chain fatty alcohol/methanol solutions. That is, this work complements other studies by examining the colloidal properties of fatty alcohols in polar liquid solvents, first in binary solution, then with solubilized triglyceride oil present in ternary solution. Electrical conductivity and photon correlation spectroscopy (PCS) data were analyzed for evidence of aggregation of the fatty alcohols in methanol solvent. Effects of the degree of unsaturation and configuration of the double bonds in the amphiphilic tailgroup are examined. Phase behavior of the fatty alcohols in a series of straight and branched medium-chain (C_3–C_8) alkanol solvents was also studied. Finally, viscosity results were analyzed in a preliminary effort to examine solubilization of soybean oil in nonaqueous methanol solutions that contain unsaturated long-chain fatty alcohol aggregates.

EXPERIMENTAL PROCEDURES

Materials. Commercial- and technical-grade fatty alcohols were used in conductivity and viscosity experiments. These

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alcohols were actually mixtures of all-*cis* monoenic, dienic and trienic C_{18} fatty alcohols (82–90 wt%), with the remainder composed primarily of saturated C_{16} and C_{18} fatty alcohols. For purposes of discussion in this work, the mixture whose primary component was monoenic all-*cis* C_{18} fatty alcohol will be referred to as "oleyl alcohol" and have a nominal degree of unsaturation equal to one. By convention, all-*cis* dienic and trienic fatty alcohols will be "linoleyl alcohol" and "linolenyl alcohol," with nominal degrees of unsaturation equal to two and three, respectively.

Oleyl alcohol (~70 wt% 9Z-octadecen-1-ol) was from Aldrich Chemical Co. (Milwaukee, WI). This fatty alcohol mixture also contained ~2.7 wt% saturated C_{14} and ~6.0 wt% unsaturated C_{16} fatty alcohol. Linoleyl alcohol was nonconjugated safflower oil alcohols (~78 wt% 9Z, 12Z-octadecadien-1-ol), provided by Dr. A.W. Schwab (deceased, U.S. Department of Agriculture), and Unadol 40 (~48 wt% 9Z, 12Z-octadecadien-1-ol), provided by Witco (Sherex) Chemical Co. (New York, NY). Linolenyl alcohol was Unadol 90 (~50 wt% 9Z, 12Z, 15Z-octadecatrien-1-ol) from Witco (Sherex). The second most abundant fatty alcohol present in both Unadol 40 and Unadol 90 was monoenic 9Z-octadecen-1-ol. In some studies, 1-octadecanol (99 wt%) from Aldrich was used for comparison of unsaturated and saturated fatty alcohols. Compositions of all fatty alcohol mixtures were confirmed by gas chromatography.

Corresponding all-*trans* isomeric mixtures of the C_{18} fatty alcohols were obtained by elaidinization of oleyl alcohol, Unadol 40 and Unadol 90. The elaidinization procedure has been outlined elsewhere (5). Confirmed by gas chromatography, the average conversion rate for the predominating fatty alcohol was ~75%, and the total all-*trans* C_{18} fatty alcohol composition was in the range of 75–80 wt%.

PCS experiments were conducted with high-purity (99 wt%) 9Z, 12Z-octadecadien-1-ol and 9*E*, 12*E*-octadecadien-1-ol from Sigma Chemical Co. (St. Louis, MO).

Refined soybean oil ($\rho^{25} = 0.9226$, $n_D^{25} = 1.4715$) was supplied by Archer Daniels Midland, Inc. (Decatur, IL). The average fatty acid weight composition was 11.8% palmitic, 3.1% stearic, 23.3% oleic, 55.5% linoleic and 6.3% linolenic. The acid value was 0.20.

Straight and branched medium-chain alkanols were obtained as follows: 1-propanol and 2-hexanol from Aldrich; 2-propanol, 2-butanol, 1-heptanol and 1-octanol from Sigma; 1-butanol, 1-pentanol and 2-pentanol from EM Science (Cherry Hill, NJ); and 1-hexanol from Union Carbide (Danbury, CT). All alkanols were 99+ wt% in purity except 2-pentanol, which was 98 wt%. Methanol (99+ wt%) was from Aldrich and EM Science, and was redistilled and filtered before use. All alcohols were stored over 4Å molecular sieves from Union Carbide.

Methods. Conductivities were measured at 25.0°C with a portable Lectro Mho-Meter, Mark V (Lab-Line, Melrose Park, IL). Samples were equilibrated at 25 ± 0.5°C through careful control of the laboratory room temperature. Methanol solutions were bubbled under low-pressure N_2–gas purge to prevent CO_2 accumulation. Viscosities were measured at 37.8 ± 0.05°C with calibrated Cannon-Fenske viscometers (Cannon, State College, PA). The viscometers were immersed and equilibrated in a constant-temperature bath. PCS measurements were conducted extramurally by E. Gulari and coworkers (University of Michigan, Ann Arbor, MI). Equipment and methodology have been described elsewhere (6,7). The samples were carefully centrifuged and filtered (0.2 μm) before analysis.

RESULTS AND DISCUSSION

Aggregation in methanol solvent. Figure 1 is a plot of equivalent conductivity data for linoleyl alcohol in nonaqueous methanol solution at 25°C. A sharp break in the titration curve occurs near a value of 0.3020 on the abscissa. These results are consistent with those for surfactant solutions that exhibit micellar aggregation phenomena (8–13). Accordingly, the break point corresponds to the minimum fatty alcohol concentration that supports aggregation to form micelles. This point, referred to as the critical micelle concentration (CMC), was inferred for linoleyl alcohol in methanol to be 0.0912 mol/L.

The source of conductivity for nominally nonionic fatty alcohols can likely be attributed to the presence of small concentrations of impurities, such as free fatty acids. Acid values of oleyl, linoleyl and linolenyl alcohols were 4.3, 1.7 and 0.7 mg KOH/g sample, respectively. Speculatively, micellar aggregation of the fatty alcohols allows solubilization of the fatty acids, hence the sharp break in the conductivity curve.

PCS results for both 9Z, 12Z-octadecadien-1-ol and 9*E*, 12*E*-octadecadien-1-ol in methanol solvent are posted in Table 1. The results indicate that under the conditions studied, the aggregates are large (~1,000 Å) and relatively polydisperse in size distribution.

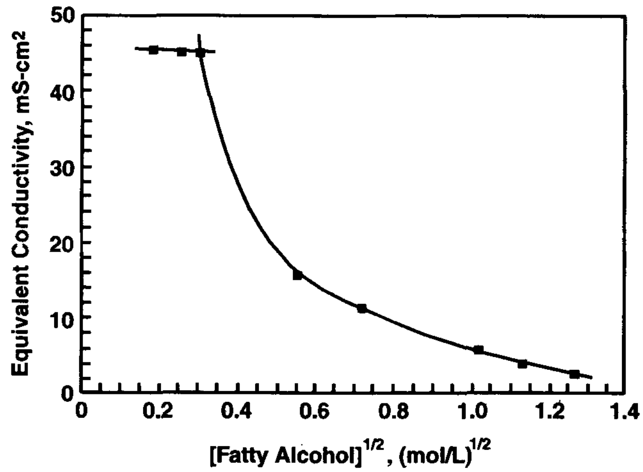

FIG. 1. Equivalent conductivity results for linoleyl alcohol in methanol at 25°C. For this fatty alcohol, critical micelle concentration = 0.0912 mol/L. Linoleyl alcohol was nonconjugated safflower alcohols (~78% 9Z, 12Z-octadecadien-1-ol).

TABLE 1
Photon Correlation Spectroscopy of High Purity (99 wt%) Dienic Fatty Alcohols in Methanol at 25°C[a]

Alcohol	Con'c (mol/L)	Particle diameter (Å) 1 Exp[b]	Particle diameter (Å) Cumulants[c]	Q[d]
9*Z*, 12*Z*-Octadecadien-1-ol	0.341	1203	1019	0.250
9*E*, 12*E*-Octadecadien-1-ol	0.341	855	776	0.173

[a] Solvent data: $n_D = 1.329$, $\mu = 5.85$ cP; angle (θ) = 90°; wavelength (λ) = 514.5 nm.
[b] First exponential autocorrection function (rigid, compact monodisperse particles).
[c] Method of cumulants, or deconvolution of sum over all exponential contributions to autocorrelation function (polydisperse particles).
[d] Polydispersity index.

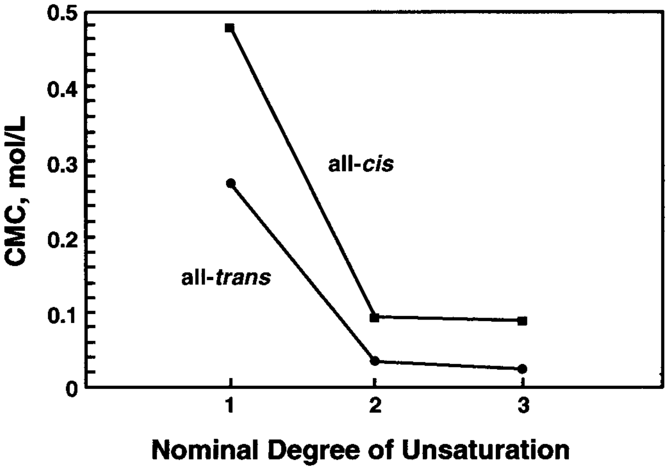

FIG. 2. Critical micelle concentrations (CMCs) of unsaturated long-chain fatty alcohols in methanol at 25°C: effects of degree of unsaturation and configuration of double bonds in amphiphilic tailgroup. All-*cis* alcohols: oleyl alcohol (~70% 9*Z*-octadecen-1-ol), linoleyl alcohol [nonconjugated safflower alcohols (~78% 9*Z*, 12*Z*-octadecadien-1-ol)] and linolenyl alcohol [Unadol 90 (~50% 9*Z*, 12*Z*, 15*Z*-octadecatrien-1-ol)]. All-*trans* alcohols: elaidinized oleyl alcohol, elaidinized Unadol 40 (~48% 9*Z*, 12*Z*-octadecadien-1-ol) and elaidinized Unadol 90. Unadols from Witco (Sherex) Chemical Co. (New York, NY).

In either aqueous and nonaqueous media, spherical micellar aggregates are generally characterized by smaller diameters (20–150 Å) and more uniform size distribution (12,14–21). Consider the criterion that one dimension of a spherical micellar core cannot exceed the length of two fully extended tailgroup chains (11). If the fully extended chain-length of a C_{18} fatty alcohol tailgroup is estimated to be ~16Å, then comparison with the results in Table 1 indicates that the aggregates are assuredly not spherical in geometry. Hence, under the conditions of these studies, the dienic C_{18} fatty alcohol aggregates are likely to be disk-like or rod-like in geometry (15,22).

Finally, a few observations regarding the nature of the solvent can be noted. The number of hydrogen-bonding centers in the structure of the solvent molecules greatly influences aggregation of nonionic amphiphiles. Some reports suggest that linear hydrogen bonding with respect to only one center on the solvent molecular structure does not appear to support aggregation (10,23). Thus, solvents with multiple hydrogen-bonding centers, such as formamide or ethylene glycol, tend to lend themselves to micellar aggregation more readily. However, the results in this work suggest that solvents such as methanol (as well as alkanols, which are discussed later) do lend themselves to formation of long-chain fatty alcohol aggregates, under specified conditions.

Effect of fatty alcohol tailgroup structure. The results in Figure 1 and Table 1 provide evidence of aggregation of unsaturated long-chain fatty alcohols in nonaqueous methanol solution. Furthermore, the CMC of a given fatty alcohol may be inferred from its corresponding equivalent conductivity titration curve. This was done for each of the six unsaturated fatty alcohols, and the CMC data are graphed as a function of the "nominal" degree of unsaturation in Figure 2. For a given commercial-grade fatty alcohol, it is recognized that the nominal degree of unsaturation does not necessarily correspond to its actual degree; however, some generalized conclusions, based on the fatty alcohol tailgroup structure, may be drawn.

First, the CMC of any given all-*trans* fatty alcohol is less than that of its corresponding all-*cis* isomer. Analogous results have been observed for aqueous solutions that contain surfactants with unsaturated tailgroup structures (10). It is reasonable to expect that this class of surfactant will exhibit similar behavior in solution with a polar solvent. Therefore, this observation was not unexpected.

When aggregates are present in polar solvents, the aggregated amphiphilic tailgroups orient themselves toward the interior of the aggregates. For aqueous systems, long-chain tailgroups (C_{16} and longer) of nonaggregated amphiphiles self-associate, tending to coil with themselves (10). In methanol solvent, it is not unreasonable to expect long-chain nonaggregated fatty alcohol tailgroups to exhibit analogous behavior.

For unsaturated C_{18} fatty alcohols, the all-*trans* tailgroups tend to be more rigid than their corresponding all-*cis* isomers. The increase in rigidity (or decrease in coiling) decreases their solubility in methanol; therefore, their propensity to form aggregates increases. Thus, all-*trans* long-chain amphiphiles tend to have lower CMCs than their all-*cis* counterparts.

A second observation drawn from Figure 2 holds that the CMC decreases with increasing degree of unsaturation in the fatty alcohol tailgroup. Upon first glance, this result appears intriguing because analogous studies with aqueous media showed that increasing the degree of unsaturation increases the CMC (10).

Increasing the degree of unsaturation will have at least two effects on aggregation of long-chain fatty alcohols in methanol. First, lipophilic forces between the amphiphilic tailgroups are reduced, causing the CMC to increase. In the present study, CMCs for oleyl alcohol and 1-octadecanol are 0.476 and 0.00436 mol/L, respectively. Thus, the effect of increasing degree of unsaturation from zero to one (nominal) in this example is analogous to aqueous systems.

The second effect of increasing the degree of unsaturation is a corresponding increase in rigidity in the fatty alcohol tailgroup, caused by replacing a saturated carbon-carbon bond with a nonrotating double bond. Reiterating an earlier point, increasing tailgroup rigidity reduces its coiling and decreases the CMC. The results in Figure 2 show that increasing the nominal degree from one to two decreases the CMC by a factor between three and four. The same general effect is observed when the nominal degree is increased to three; however, the magnitude of the reduction of the CMC is significantly smaller. Under the conditions of these studies, reduced tailgroup coiling appears to predominate over reduced lipophilic interaction when the degree of unsaturation increases for an unsaturated tailgroup structure.

Aggregation in medium-chain alkanols. Figure 3 is a plot of equivalent conductivity titration data for oleyl alcohol in 1-propanol at 25°C. Figure 4 is a similar plot for oleyl alcohol in 2-hexanol. Both graphs show breaks in the data at one distinct amphiphile concentration. The CMCs are 0.0961 mol/L in 1-propanol and 0.0676 mol/L in 2-hexanol. Similarly, CMCs were determined for oleyl alcohol in each of the alkanol solvents studied in this work.

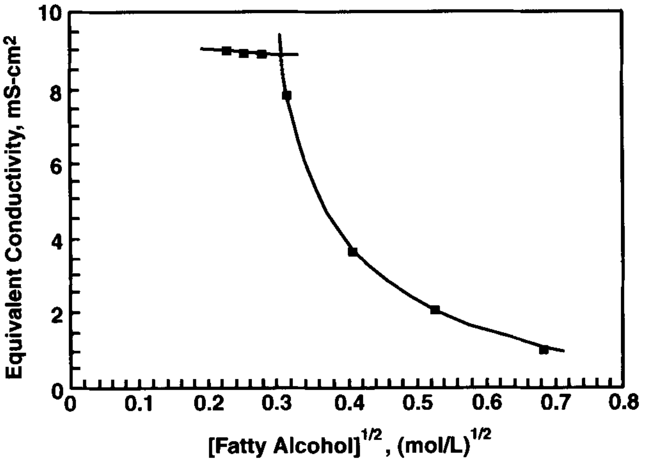

FIG. 3. Equivalent conductivity results for oleyl alcohol (~70% 9Z-octadecen-1-ol) in 1-propanol at 25°C. Critical micelle concentration = 0.0961 mol/L.

Straight-chain alkanols. The nature of the solvent with respect to its dielectric constant can greatly influence aggregation of amphiphiles in solution. Studies with nonionic surfactants have shown that CMC increases and average aggregation number decreases when the solvent dielectric constant decreases (11,23). Becher *et al.* (24, 25) showed that adding ethanol or dioxane to aqueous solutions of polyoxyethylene [23] dodecyl ether destroys micelles, eventually reaching a composition where no micelles are present in solution. Deguchi *et al.* (26) observed similar results when mixing aqueous polyoxyethylene [7] dodecyl ether solutions with methanol, ethanol, 2-propanol, 1-propanol, dioxane, propylene glycol or ethylene glycol. Mehrota *et al.* (8) showed that nonaqueous solutions of rare earth metal caproate (C_6) soaps and methanol, ethanol, propanol, butanol or pentanol behaved in an analogous fashion. The conditions of this study suggested that the dissociation of the metal soaps in alkanol was small, allowing the soap to behave essentially as a nonionic surfactant. In each of these studies, results were attributed to increasing relative solubility of the amphiphilic tailgroup in the lower dielectric solvent, which decreases the driving forces for micellization.

The CMC results for oleyl alcohol in a series of straight-chain alkanols have been graphed as a function of alkanol chainlength in Figure 5. These data show that the CMC decreases with increasing chainlength; that is, decreasing solvent dielectric constant decreases the CMC. This contradicts the results from studies previously cited.

The C_{18} fatty alcohols studied in this work had long tailgroups compared to the C_6 and C_{12} chainlength surfactants in

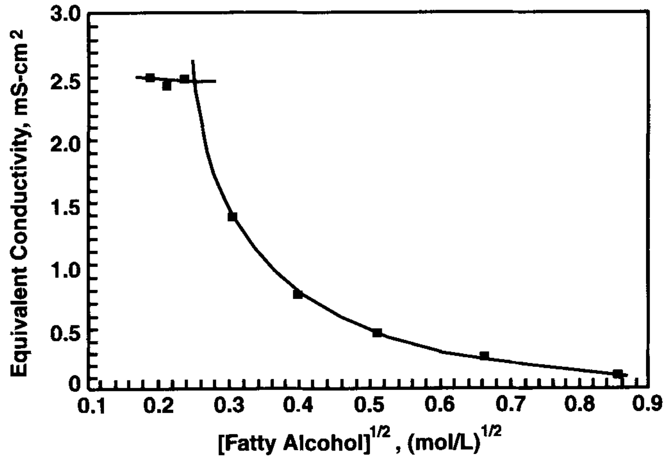

FIG. 4. Equivalent conductivity results for oleyl alcohol (~70% 9Z-octadecen-1-ol) in 2-hexanol at 25°C. Critical micelle concentration = 0.0676 mol/L.

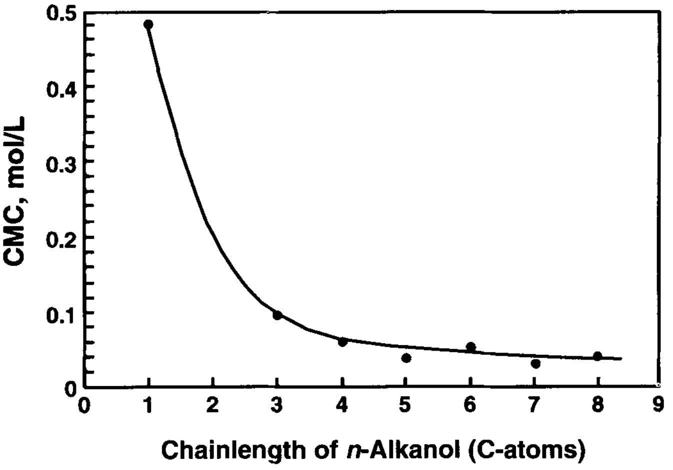

FIG. 5. Critical micelle concentration (CMC) of oleyl alcohol (~70% 9Z-octadecen-1-ol) in a series of straight-chain alkanol solvents at 25°C: effect of alkanol chainlength (number of C-atoms).

the comparison studies. Reviewing previous discussions, tailgroups of nonaggregated C_{18} amphiphiles are likely to coil (that is, self-associate) in polar solvents. Given the conditions of the conductivity studies in this work, it is conceivable that the degree of coiling in the fatty alcohol tailgroups plays a significant role in determination of the overall driving forces for aggregation.

Consider a solution of noncoiled amphiphiles in a given solvent. With respect to the tailgroup structure, aggregation depends on the strength of lipophilic forces between the tailgroups in solution. Decreasing solvent dielectric decreases resistance to dissolution, thereby weakening lipophilic forces between the tailgroups. Thus, decreasing solvent dielectric should result in decreasing the driving forces for aggregation and increasing the CMC.

Suppose the amphiphilic tailgroups experience a significant degree of coiling. The normally expected resistance to dissolution is partially abated, resulting in a reduction in the driving forces for aggregation and an increase in CMC, relative to a solution of noncoiled amphiphiles. Under these conditions, decreasing solvent dielectric would have the following two effects: (i) the expected decrease in resistance to dissolution; and (ii) a reduction in the degree of tailgroup coiling. The latter effect reduces the "negative contribution" from tailgroup coiling to the overall driving forces for aggregation. If this reduction is significant, then under specific conditions it is feasible that the combination of the two effects yields a net increase in the overall driving forces for aggregation. If this is the case, then decreasing solvent dielectric would decrease the CMC.

The effect of solvent dielectric on tailgroup coiling should be more pronounced when the degree of coiling itself is greater. Hence, the effects on CMC should be greater between smaller-chained alkanol solvents. The results in Figure 5 reflect this trend. On the other hand, the degree of tailgroup coiling in longer-chained alkanol solvents is essentially nil. Under these conditions, the CMC should increase with decreasing solvent dielectric. Although the results in Figure 5 do not reflect this trend, it is apparent that CMC is less dependent on solvent dielectric for alkanol chainlengths of C_4 and longer. It is possible that the CMC eventually increases when alkanol chainlengths are greater than C_8.

Finally, it is feasible that the fatty alcohols form "reverse" micellar aggregates in alkanol solvents. The reverse aggregates would have low aggregation numbers (10,13), an indication that the driving forces are relatively small. Furthermore, these driving forces should not depend greatly on tailgroup coiling in the solution. Analogous to "normal" micellar solutions (with no significant degree of tailgroup coiling), increasing alkanol chainlength decreases the driving forces for reverse micellization. Therefore, reducing solvent dielectric in reverse micellar solutions should increase the CMC, regardless of amphiphilic tailgroup length. Again, the CMC results in Figure 5 do not show this trend. If reverse micellization of long-chain fatty alcohols occurs in alkanol solvent, it apparently occurs in alkanols with lower dielectrics (and longer chains) than those studied in this work. This point may be taken up in subsequent studies, perhaps with techniques such as PCS to examine longer-chained alkanols.

Branched-chain alkanols. The CMC results for oleyl alcohol in four pairs of straight and branched medium-chain (C_3–C_6) alkanol solvents are given in Table 2. With respect to alkanol chainlength, small branching variations have a diminished effect on the CMC of oleyl alcohol. These results are in good agreement with those from studies of aqueous potassium tetradecanoate (C_{14}) solutions mixed with C_2–C_7 alkanols (11). That work attributed the results to the slight effect that small branching variations have on solvent dielectric of alkanols.

Preliminary examination of solubilization of soybean oil in nonaqueous fatty alcohol/methanol solutions. Earlier studies (2,3) have demonstrated that soybean oil is essentially insoluble in methanol. These same studies showed that adding unsaturated long-chain fatty alcohol decreases the interfacial tension between oil and methanol phases and significantly enhances the solubility of the oil in methanol. With regard to conductivity and PCS results, addressed earlier in this work, the following preliminary conclusion can be made: If a sufficient concentration of unsaturated long-chain fatty alcohol is present in nonaqueous methanol solution, then solubilization of soybean oil results from its incorporation into fatty alcohol aggregates.

At this point, it should be noted that some controversy exists among many researchers whether and how to differentiate between solutions that contain micellar aggregates and microemulsions. This work considers a microemulsion to be a thermodynamically stable dispersion of optically isotropic fluid microstructures consisting of aggregated amphiphiles and solubilized solutes. Consequently, if aggregation of the amphiphiles is the primary mechanism of soybean oil solubilization, then the corresponding solutions in this work are microemulsions.

Confirmation of the existence of microemulsions can be made by detailed analysis of the physical properties of soybean oil/fatty alcohol/methanol solutions. As an initial and qualitative step, the effects of solubilized soybean oil on viscosity of unsaturated long-chain fatty alcohol/methanol solutions were analyzed.

TABLE 2
Critical Micelle Concentration (CMC) Data from Equivalent Conductivities for Oleyl Alcohol (~70 wt%) in 1- and 2-Alkanol Solvents

Alkanol	CMC (mol/L)
1-Propanol	0.0961
2-Propanol	0.102
1-Butanol	0.0590
2-Butanol	0.0778
1-Pentanol	0.0380
2-Pentanol	0.0361
1-Hexanol	0.0520
2-Hexanol	0.0676

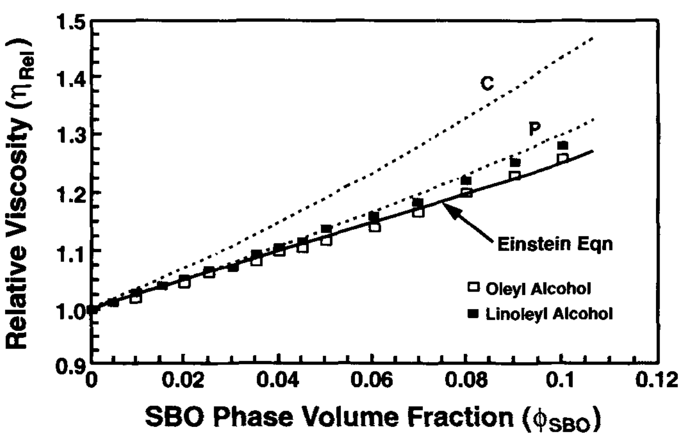

FIG. 6. Relative viscosity (η_{Rel}) of soybean oil/unsaturated long-chain fatty alcohol/methanol solutions at 37.8°C (100°F): effect of increasing soybean oil phase volume fraction (ϕ_{SBO}) in methanol-external solution. Initial fatty alcohol concentration was 1.58 mol/L. Oleyl alcohol was ~70% 9Z-octadecen-1-ol and linoleyl alcohol (Unadol 40) was ~48% 9Z, 12Z-octadecadien-1-ol. Company source as in Figure 2.

Figure 6 is a graph of relative viscosity (η_{Rel}) results for two ternary systems at 37.8°C, one each for oleyl alcohol and linoleyl alcohol. Initial fatty alcohol concentration was 1.58 mol/L. For a given solution, η_{Rel} was determined by taking the ratio of its viscosity to that of a fatty alcohol/methanol solution with no added soybean oil. Soybean oil is nearly insoluble in methanol; hence, the phase volume fraction of solubilized soybean oil was approximated as the total volume fraction of soybean oil (ϕ_{SBO}) in the solution.

Linear least-squares analysis of the data (excluding $\phi_{SBO} = 0$) yielded the following:

$$\eta_{Rel} = 1.000 + 2.396\ (\phi_{SBO}) \qquad [1]$$

for oleyl alcohol, and

$$\eta_{Rel} = 1.000 + 2.670\ (\phi_{SBO}) \qquad [2]$$

for linoleyl alcohol. For Equation 1, the standard error of the Y-estimate (σ_y) was 0.0560, and the square of the correlation coefficient (R^2) was 0.9951. For Equation 2, $\sigma_y = 0.0029$, and $R^2 = 0.9961$. Both data curves begin to exhibit slight nonlinearity at ϕ_{SBO} in the range 0.07–0.08.

The viscosity of microemulsions has been studied rigorously. In general, a solution that contains a dispersion of microscopically small aggregates significantly larger in size than the solvent molecules is more viscous than the "pure" solvent (27–29). Increasing the total phase volume of the aggregates (either by increasing the average size or the total number of the aggregates) increases the viscosity of the solution. For this reason, η_{Rel} data have been successfully modeled as a function of phase volume fraction of the aggregates.

For microemulsions, increasing the solubilized solute concentration typically increases the average aggregation number and the solute/amphiphile concentration ratio within the aggregates (21,30,31). This increases the total aggregate phase volume fraction, which increases η_{Rel}. If no significant change in the concentration of aggregated amphiphiles occurs, then η_{Rel} is essentially dependent on the solubilized solute concentration (2,3,32). Under these conditions, η_{Rel} data may be modeled as a function of the solute phase volume fraction in equations analogous to those depicting the dependence of viscosity on the total phase volume fraction of the aggregates in solution. Three models are discussed below.

Einstein's law of viscosity (27,28) was derived for a dilute suspension of noninteracting, rigid and uniform spheres:

$$\eta_{Rel} = 1 + 2.5\ (\phi) \qquad [3]$$

where ϕ is the solubilized solute phase volume fraction. This equation is plotted as a solid line through the experimental data in Figure 6. Dashed line P represents the following expression derived by Roscoe (27) for an arbitrary concentration of polydisperse spheres:

$$\eta_{Rel} = (1 - \phi)^{-2.5} \qquad [4]$$

Dashed line C represents the following equation derived by Roscoe (27) and Brinkmann for a highly concentrated suspension of uniform spheres:

$$\eta_{Rel} = [1 - 1.35(\phi)]^{-2.5} \qquad [5]$$

Spherical aggregates are predominating at smaller phase volume fractions (21,29,32); therefore, η_{Rel} vs. ϕ results are generally modeled on the basis of Equations 3–5 only at lower phase volume fractions.

The oleyl alcohol data are in good agreement with Einstein's law over the entire range of soybean oil concentrations. With respect to the raw data, Equation 3 gave $\sigma_y = 0.0217$ and $R^2 = 0.9950$. Correspondingly, Equation 4 gave $\sigma_y = 0.787$ and $R^2 = 0.9336$. Hence, under the conditions of these studies, viscosity results for this system are more consistent with those predicted for a dilute suspension of uniform spheres than polydisperse spheres.

On the other hand, the linoleyl alcohol data are in good agreement with Equation 4 over the entire range of soybean oil concentrations. With respect to raw data, Equation 4 gave $\sigma_y = 0.0293$ and $R^2 = 0.9923$; whereas Einstein's law gave $\sigma_y = 0.0553$ and $R^2 = 0.9726$. Hence, under the conditions of these studies, the viscosity results are more consistent with those expected for suspension of polydisperse spheres than a dilute suspension of uniform spheres.

Previously in this work, analysis of conductivity and PCS results for binary solutions (at 25°C) showed that the fatty alcohol aggregates were likely to be polydisperse and nonspherical in methanol solvent. Within the boundaries of those studies, solubilization of soybean oil in the aggregates is not likely to change either of these conditions. With respect to polydispersity, the viscosity results in Figure 6 for linoleyl alcohol are more consistent with this condition than those for oleyl alcohol. Roscoe (27) suggested that Equation 5 works equally well with spherical and nonspherical aggregates; that is, η_{Rel} of a concentrated suspension of aggregates depends primarily on interactions between aggregates rather than geometry. However, neither of the systems in Figure 6 agrees well with Equation 5. Thus, under the conditions of these viscosity studies, two observations may be made. First, the results are more consistent with those for spherical aggregates than nonspherical ones. Second, interactions between aggregates do not significantly affect viscosity, regardless of geometry or size distribution of the aggregates.

Increasing the temperature of microemulsion solutions can decrease the average size of the aggregates under certain conditions (10). It is also known that decreasing the average particle size of aggregates makes them more uniform and spherical in solution (10,21,22,32). Hence, with respect to particle size and geometry, one reasonable explanation for the contrasting viscosity and conductivity/PCS results may have to do with the increase in temperature (to 37.8°C) for the viscosity studies.

Qualitatively, the viscosity results in Figure 6 exhibit good agreement with established theories for microemulsions. Under the conditions of these studies, the results represent partial evidence supporting the notion that soybean oil is solubilized in unsaturated long-chain fatty alcohol/methanol solutions by formation of oil-fatty alcohol aggregates, resembling a nonaqueous detergentless microemulsion.

Equivalent conductivity and PCS results indicated that unsaturated C_{18} fatty alcohols form large (~1,000 Å), polydisperse aggregates in nonaqueous methanol solution at 25°C. Variations in the fatty alcohol tailgroup structure may significantly influence the CMC of the solution. Increasing the degree of unsaturation or substituting all-*trans* for all-*cis* double bonds in the amphiphilic tailgroup decreases CMC, under the conditions studied. These results were attributed to the effect of tailgroup structure on the degree of coiling of nonaggregated fatty alcohol tailgroups, which may significantly influence the driving forces for aggregation.

Conductivity results showed that aggregation of unsaturated long-chain fatty alcohols occurs in straight and branched medium-chain alkanol solvents. For the short-chain alkanols (C_4 or less), reducing the solvent dielectric constant decreases the CMC. These results were attributed to the effect of solvent dielectric on the degree of tailgroup coiling, which may allow a net increase in the overall driving forces for aggregation.

With respect to miscibility and interfacial tension studies in prior works, and to conductivity and PCS studies in this work, a preliminary conclusion concerning the incorporation of soybean oil into soybean oil-in-fatty alcohol aggregates in methanol solution was made. An initial step toward confirmation of this notion was offered by analysis of the effects of alcohol/methanol solutions at 37.8°C. The results showed good agreement with equations derived for a dilute suspension of uniform spheres (Einstein's law) or a suspension of polydisperse spheres. The results did not agree well with the Roscoe/Brinkmann equation, indicating that interaction between aggregates in solution was not significant under the conditions studied. In general, the viscosity results were consistent with established theories for microemulsions. This evidence represents partial support for the notion that soybean oil is solubilized by formation of soybean oil-unsaturated long-chain fatty alcohol aggregates in methanol solution, resembling a nonaqueous detergentless microemulsion.

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