Effect of Secondary Alcohol Ethoxylates on Behavior of Triolein-Water-Surfactant Systems

Teeradetch Tungsubutra and **Clarence A. Miller***
Department of Chemical Engineering, Rice University, Houston, Texas 77251-1892

Study of the equilibrium phase behavior of systems containing water, triolein and secondary alcohol ethoxylates showed that a D or microemulsion phase, which solubilized significant amounts of triolein, formed at temperatures as low as 25°C when the surfactant was a suitable mixture of TERGITOL 15-S-3 and 15-S-5 (Union Carbide, Charleston, WV) with average ethylene oxide numbers of 3 and 5, respectively. In previous work with pure C_{12} linear ethoxylates and triolein, the D phase had formed only at temperatures above about 55°C. Based on the earlier studies, formation of the D phase would be expected to improve soil removal from synthetic fabrics by a solubilization–emulsification mechanism. When sufficient oleyl alcohol was mixed with triolein, the D phase was observed at 25°C with Tergitol 15-S-5 alone. Observation of dynamic behavior in this system for triolein–oleyl alcohol drops injected into surfactant–water mixtures revealed that intermediate phases frequently formed near the drop surfaces and that considerable spontaneous emulsification of triolein occurred for appropriate drop compositions. Experiments with drops initially attached to individual polyester fibers confirmed that little oil remained on the fibers when emulsification was extensive. This mechanism involving spontaneous emulsification provides a means for soil removal different from that found previously in other systems, where the soil was solubilized into an intermediate phase, and this phase was emulsified by externally imposed agitation.

KEY WORDS: Detergency, emulsification, secondary alcohol ethoxylates, solubilization.

Nonpolar liquid soils, such as hydrocarbons (mineral or motor oils) and triglycerides (cooking oils), are not as easily removed from polyester-cotton and polyester fabrics as from 100% cotton fabrics during washing processes. The main reason is the greater adhesion of these oils to the less polar synthetic fabrics than to cotton, which reduces the ability of surfactant solutions to spread along the fabric and displace the oils by the well-known rollup mechanism.

A promising means for removing nonpolar liquid soils from synthetic fabrics is a solubilization–emulsification mechanism in which oil is incorporated into a new phase, which forms during the washing process at the interface between oil and surfactant solution. If this intermediate phase has properties such as low interfacial tensions with the adjacent liquids, which facilitate emulsification, it can be dispersed by agitation into the washing bath. For instance, videomicroscopy observations (1,2) have shown that an intermediate microemulsion phase forms when *n*-hexadecane, a model hydrocarbon soil, is brought into contact with dilute mixtures of a pure nonionic surfactant and water near the system's phase inversion temperature (PIT), where hydrophilic and lipophilic properties are balanced. Washing experiments demonstrated that *n*-hexadecane removal from polyester-cotton fabric was greatest near the PIT in such systems (2). Subsequently, various groups have confirmed this result and have also shown that the removal of *n*-hexadecane from polyester-cotton fabric is greatest near an appropriately defined PIT for pure nonionic surfactants with lipophilic additives, for commercial nonionic surfactants that are mixtures of many individual compounds, and for anionic–nonionic surfactant mixtures (3–8). In all these systems, the PIT is well above the surfactant's cloud point temperature, often so far above it that the surfactant-water mixture present in the initial washing bath is a dilute dispersion of the lamellar liquid crystalline phase in water. This work with hydrocarbon soils, as well as studies of the solubilization–emulsification mechanism for other soils, has recently been reviewed (9).

To date, only limited success has been achieved in removing triolein, a model liquid triglyceride, by this mechanism. Videomicroscopy experiments were performed in which three pure nonionic surfactants, the linear alcohol ethoxylates $C_{12}E_3$, $C_{12}E_4$ and $C_{12}E_5$, were contacted with pure triolein at various temperatures (10). Only for the last of these was an intermediate microemulsion phase formed, and in this case the PIT occurred at a rather high temperature (about 65°C). Triolein removal from polyester-cotton fabric was excellent near the PIT in this system. However, it was considerably less at other temperatures for $C_{12}E_5$ and at all temperatures for the other two surfactants.

It appears that microemulsions are formed less readily with triolein than with *n*-hexadecane and similar hydrocarbons because the large triolein molecules have difficulty penetrating the hydrocarbon chain portion of the surfactant films present at triolein-water interfaces. For films of the surfactants mentioned in the preceding paragraph, the hydrocarbon chains are long, straight and of uniform length. Apparently, rather high temperatures are required before thermal motion can induce sufficient disorder to permit significant amounts of triolein to be solubilized in such films.

One might suppose that if the films were less ordered, *e.g.*, if the hydrocarbon chains were of nonuniform length and/or branched, solubilization of triolein would be facilitated. This concept was supported by a study where a short-chain alcohol, tertiary amyl alcohol (TAA), was added to $C_{12}E_4$ (11). With suitable amounts of TAA present, microemulsions were observed in this system between about 45 and 55°C, both as equilibrium phases and as intermediate phases formed during experiments in which rather concentrated mixtures of the surfactant and alcohol in water were contacted with triolein. However, addition of TAA did not improve triolein detergency because, when dilute mixtures of surfactant and alcohol were used, as would be the case in current practice, most of the TAA partitioned into the water and so was not present in the surfactant films to facilitate solubilization of triolein. However, this approach with TAA or another short-chain additive might be effective should washing be carried out in the future with concentrated surfactant solutions, as some have proposed.

In this paper we describe another approach to forming less-ordered surfactant films. In this case, the linear alcohol

---

*To whom correspondence should be addressed at Department of Chemical Engineering, Rice University, P.O. Box 1892, Houston, TX 77251-1892.

ethoxylates used previously are replaced by secondary alcohol ethoxylates. The latter are double-chain surfactants with chains of various lengths. The total number of carbon atoms in the two chains is nearly the same for all the molecules present, but the position of the ethoxylated alcohol group varies, yielding different species with chains of different lengths. Equilibrium phase behavior results are described below for systems containing these surfactants and triolein. They demonstrate that microemulsions can be formed at temperatures near 30°C with an appropriate choice of surfactant.

Dynamic contacting experiments, including some with drops of triolein-oleyl alcohol mixtures on single polyester fibers, immersed in surfactant solutions, showed that spontaneous emulsification can be effective in dispersing oily soils into the washing bath. This mechanism has not been observed in the previous studies mentioned above (2,3,7–10), where emulsification was produced by externally imposed agitation.

EXPERIMENTAL PROCEDURES

Materials. Secondary alcohol ethoxylates of the TERGITOL 15-S series were obtained from Union Carbide (Charleston, WV) and used as received. Their average hydrocarbon chainlength was 11–15. The products with average ethylene oxide (EO) numbers of 3, 5 and 7 were used in this work. Triolein and oleyl alcohol were obtained from Sigma (St. Louis, MO) and had reported purities of 99%. Water used for solution preparation was deionized and distilled.

Methods. Solutions for phase behavior studies were prepared in Teflon-capped, 13-mm-i.d., flat-bottomed test tubes and mixed for 20 s by Vortex mixing. All surfactant solutions were blanketed with nitrogen.

The polarized light screening system described previously (12) was used for determining macroscopic phase behavior. Liquid crystalline phases were easily distinguished by the birefringence displayed with polarized light.

The oil drop contacting technique described previously (7,13) was used with our videomicroscopy system to observe the dynamic behavior of small, individual drops of oily soils immersed in a large quantity of surfactant solution. Samples of the surfactant solutions to be studied were introduced into rectangular optical glass capillaries (Vitrodynamics Inc., Rockaway, NJ) by capillary action. The capillaries were 50 mm long and 4 mm wide and had an optical path length of 400 μm. A thin hypodermic needle (0.21 mm o.d., Hamilton Co., Whittier, CA) was used to inject individual oil drops into the solution. This procedure gave good control of drop size. Drops about 20–100 μm in diameter were injected. The samples were maintained at constant temperature in a thermal stage especially modified for these experiments (7,13).

A new fiber-contacting experimental technique was developed to observe the dynamic behavior of oil drops attached to single fibers immersed in a surfactant solution. Samples of polyester cloth were obtained from Shell Development Company (Houston, TX). An individual thread (approximately 0.25 mm in diameter) was pulled from the fabric. It consisted of many individual polyester fibers, each approximately 10 μm in diameter. The thread was tied to a rubber ring (0.62 cm diameter of rubber material, 3.17 cm o.d. of ring), and a small syringe was used to place oil drops on the thread. A 35 × 10 mm polystyrene culture dish (Corning, Corning, NY) was filled with surfactant solution and placed on the microscope stage. The rubber ring was then immersed in the solution. Oil drops that adhered to single fibers extending out from the thread were monitored with the videomicroscopy system.

Interfacial tensions were measured with a University of Texas Model 300 spinning drop tensiometer (Austin, TX).

RESULTS

Phase behavior and interfacial tension. Figure 1 shows a partial phase diagram for mixtures of triolein. TERGITOL 15-S-5 (average EO number of 5) and water. The sequence of multiphase regions, found to occur with increasing temperature, is the same as that observed previously for systems containing water, pure linear alcohol ethoxylates and mixtures of either triolein and *n*-hexadecane (10) or of triolein and oleyl alcohol at moderate alcohol contents (14). At temperatures above the D′ + O two-phase region, two three-phase regions. W + D′ + O and W + D + O, which contain both excess water (W) and excess oil (O), were seen. They were separated by the W + D + D′ + O four-phase region. The D or microemulsion phase appeared at higher temperatures than the D′ or sponge phase. As indicated previously, excellent detergency results have been reported for conditions when the microemulsion forms as an intermediate phase, *e.g.*, near the PIT in water-nonionic surfactant-*n*-hexadecane systems. An important factor contributing to this effectiveness is the high solubilization of the hydrocarbon in the microemulsion (D) phase. Although the structures of the D and D′ phases are related, both having continuous surfactant layers, only the D phase contains substantial amounts of oil. The D′ phase, more prominent in liquid

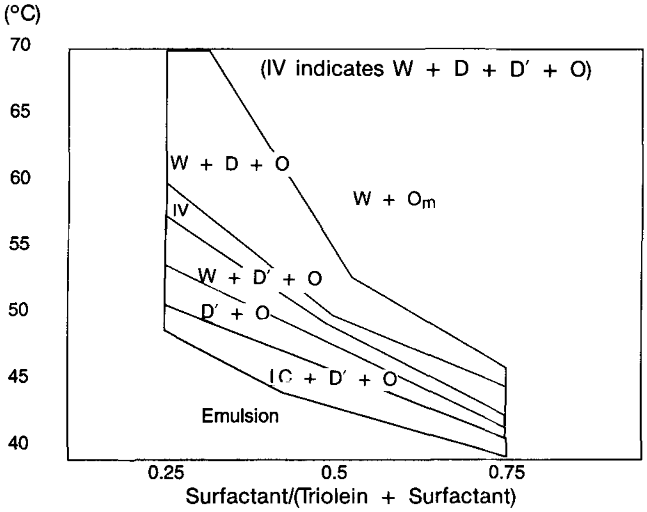

FIG. 1. Phase behavior as a function of temperature and composition for TERGITOL 15-S-5–triolein–water samples (Union Carbide, Charleston, WV). Each sample contained 60% water. All the compositions were prepared on a volume basis. W = water, D = microemulsion phase, D′ = sponge phase, LC = lamellar liquid crystal, O = oil phase, O$_m$ = oil-continuous microemulsion.

TABLE 1

Compositions in Volume Fractions of Four Coexisting Phases of the $C_{12}E_4$-Water-Triolein-*n*-Hexadecane System at 39.2°C[a]

	Component			
Phase	Triolein	n-C_{16}	$C_{12}E_4$	Water
O	0.45	0.49	0.056	0.00
D	0.16	0.24	0.24	0.36
D′	0.00	0.026	0.15	0.82
W	0.00	0.00	0.00	1.00

[a] Abbreviations: O, oil; D, microemulsion; D′, sponge; W, water.

triglyceride than in hydrocarbon systems (10,15), has little oil in its continuous surfactant bilayers. A comparison of D and D′ phase compositions in the four-phase region of the $C_{12}E_4$-water-triolein-*n*-hexadecane system at 39.2°C is given in Table 1 (10).

The phase diagram of Figure 1 shows that all phase transitions shift to higher temperatures as S, the ratio of surfactant content to the sum of oil and surfactant contents, decreases. Because the TERGITOL surfactant is not a single, pure component, its EO number represents the average number of EO groups for the various species present. The more oil present in a system at fixed surfactant content, the more the lipophilic components of the surfactant can partition into the oil phase. This partitioning causes the composition of the surfactant films, which is the most important factor in determining phase transitions, to become more hydrophilic. Thus, the observed increase in transition temperatures under these conditions is expected. For the sample with S = 0.25, the transition to the W + O_m region, where O_m denotes an oil-continuous microemulsion, was not seen even when the temperature was raised above 75°C. This behavior suggests that the surfactant films in this sample were sufficiently hydrophilic to prevent transition to an oil-continuous microemulsion from occurring even at these high temperatures.

The four-phase region provides proof of the existence of both D and D′ phases and is also the lowest temperature at which the D phase occurs in Figure 1. This region was seen at about 46°C for the sample with S = 0.75. Because the D phase with its higher solubilization capability is the preferred intermediate phase for detergency applications, we conclude that the temperatures required for good triolein removal with this surfactant are higher than desired for warm- and cold-water washing. Preliminary experiments with the TERGITOL 15-S-3 surfactant showed some of the multiphase regions of interest at about 5°C. Accordingly, we chose to investigate mixtures of the 15-S-5 and 15-S-3 surfactants, which should exhibit the phase transitions of Figure 1 at intermediate temperatures.

The partial phase diagram for a 1:1 mixture of these two surfactants is shown in Figure 2 for samples that contained 66.7% water by volume. Though present over a temperature range of less than 1°C, the four-phase region was detected in all samples at temperatures ranging from 30 to 41.1°C. As before, all phase transition temperatures decreased with increasing values of S. Additional samples with S = 0.6 and 0.7 were equilibrated at 30°C. As shown in Figure 2, the former sample is in the W + D′ + O region, and the latter is in the W + D + O region at this temperature. The phases in both samples were separated, and interfacial tensions were measured. The results are shown in Table 2. The interfacial tension between D and O phases had a low value, *i.e.*, less than 0.01 mN/m, indicating high solubilization of oil in the D phase. A low interfacial tension (about 0.06 dyne/cm) was also found between the water and D phases, an indication that the latter could be readily emulsified in water by the agitation present during a washing process.

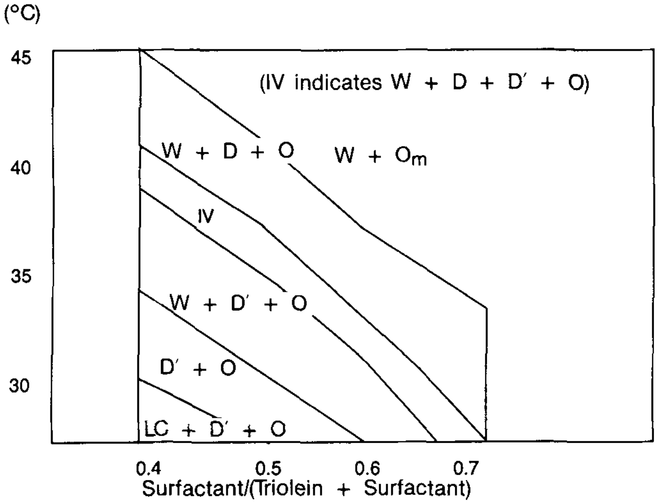

FIG. 2. Phase diagram of surfactant-triolein-water systems which contained a 1:1 mixture of TERGITOL 15-S-3 and 15-S-5. Each sample contained 66.7% water. All the compositions were prepared on a volume basis. Abbreviations and company source as in Figure 1.

One significant observation was that, for the samples with S ⩾ 0.5, the transition from W + D + O to W + O_m with increasing temperature occurred by disappearance of the top (triolein) phase. These observations confirm the ability of the D phase to solubilize significant quantities of triolein. That is, the D phase for the sample with equal weights of surfactant and triolein can solubilize all the triolein present at the transition temperature. This solubilization is much higher than would be expected in the D′ and L_α phases, based on earlier studies of triolein systems (10). On the other hand, when S < 0.5, the same transition occurred through the disappearance of the middle or D phase. The high solubility of surfactant in triolein was likely responsible for this behavior.

TABLE 2

Preequilibrated Interfacial Tension Measurements Water-Triolein-Surfactant Systems, at 30°C[a]

Phase	Interfacial tension (dyne/cm or mN/m)
D and Oil	0.008
D and Water	0.06
D′ and Oil	0.035
D′ and Water	0.03

[a] Surfactant solution contains 15-S-5:15-S-3 = 1, 66.7% water. See Table 1 for abbreviations.

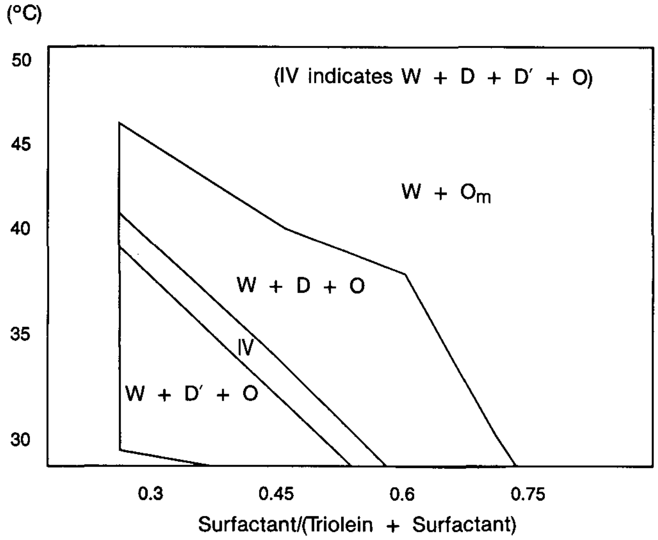

FIG. 3. Phase diagram of surfactant–triolein–water systems which contained a 2:1 mixture of TERGITOL 15-S-3 and 15-S-5. Each sample contained 66.7% water. All the compositions were prepared on a volume basis. Abbreviations and company source as in Figure 1.

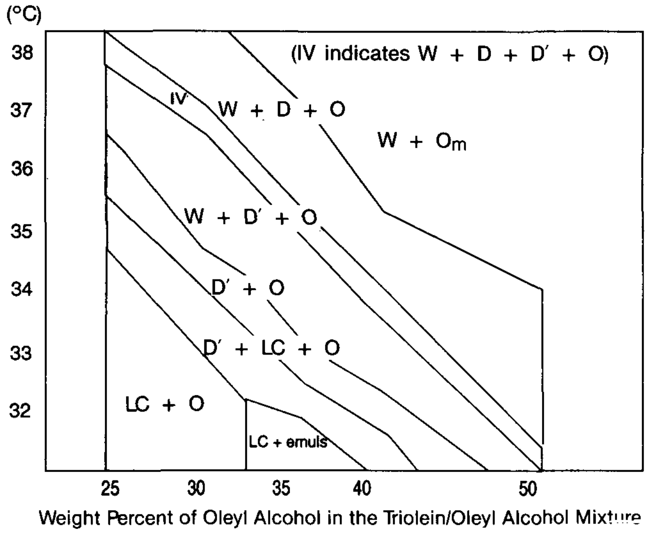

FIG. 4. Phase behavior as a function of temperature and of the wt% oleyl alcohol in the oil phase, which consisted of triolein–oleyl alcohol mixture. The system contained water, surfactant (15-S-5) and oil in the ratios 6:3:1. All the compositions were prepared on a weight basis. Abbreviations as in Figure 1; emuls, emulsion.

A surfactant mixture with a 15-S-3:15-S-5 ratio of 2:1 was also studied. Two different water contents were used, 54.5 and 66.7% by volume. The results for the latter are shown in Figure 3. Transition temperatures were slightly lower (about 2°C) than for the former, presumably because more of the most hydrophilic species in the 15-S-5 surfactant partitioned into the water, leaving slightly more lipophilic surfactant films. The 2:1 surfactant mixture is more lipophilic than the 1:1 mixture of Figure 2 and, hence, exhibits lower transition temperatures. Indeed, for samples with more surfactant than oil, multiphase regions that contain the D phase occur at temperatures below 30°C. The transition from W + D + O to W + O_m for $S \geqslant 0.5$ again showed disappearance of the triolein phase, an indication of significant solubilization, as indicated above.

Long-chain fatty acids are frequently formed in liquid triglyceride-water systems due to hydrolysis. Experiments with the 15-S-5 surfactant and with mixtures of oleyl alcohol and triolein as oil phase were conducted to investigate the effect of a long-chain polar compound on phase behavior. The effect of oleyl alcohol should be similar to that of oleic acid. The water-to-surfactant-to-oil ratios were 6:3:1 in these experiments. Figure 4 shows that increasing amounts of oleyl alcohol in the oil phase shift the phase transition temperatures to lower values. The reductions are not as dramatic as in the hexadecane–oleyl alcohol system with pure linear alcohol ethoxylates (16) and, indeed, are somewhat less than reported previously for pure $C_{12}E_6$ with mixed oils of triolein and oleyl alcohol (14). The sequence of phases seen with increasing temperature in Figure 4 is the same as in Figures 1–3, as might be expected. The temperature range of the W + D + D′ + O four-phase region was about 1°C. All the transitions from W + D + O to W + O_m in all the samples occurred through disappearance of the upper (oil) phase. This behavior is expected, based on the results presented above, because all the samples had S = 0.75.

Oil drop contacting experiments. Contacting experiments were conducted to observe intermediate phase formation and other aspects of dynamic behavior when drops of triolein and triolein–oleyl alcohol mixtures were injected into aqueous solutions of secondary alcohol ethoxylate surfactants.

A series of experiments was conducted with solutions of TERGITOL 15-S-7, which was below its cloud point at the experimental temperature of 22°C. Little activity was seen when the drops were of pure triolein or a 50:50 mixture by weight of triolein and oleyl alcohol. This behavior is the same as seen previously in other systems for rather hydrophilic conditions (13,14). In contrast, intermediate phase formation was observed for drops containing at least 75% oleyl alcohol. When surfactant concentration in the aqueous solution was 0.1 wt%, some swelling of the drop was observed, followed by formation of an intermediate D′ phase. Later, the lamellar liquid crystalline phase L_α developed as myelinic figures growing outward from the D′ phase. With higher surfactant concentrations (up to 5 wt%), the D′ phase sometimes formed immediately on contact and, in a few instances, so did the L_α phase. Drops of pure oleyl alcohol were converted completely into the new phases. Drops containing some triolein were not completely solubilized, drop volume at the end of the experiment being slightly less than the volume of triolein initially present. This behavior is not surprising in view of the ability of the D′ phase to incorporate significant quantities of oleyl alcohol but not triolein, as discussed above.

Contacting experiments with the more lipophilic surfactant TERGITOL 15-S-5 were also conducted at room temperature (22°C) and at 30°C. Mixtures of this surfactant and water formed dispersions of the L_α phase at these temperatures with particles having diameters of about 5–15 μm. The results of these experiments are summarized in Table 3 for a surfactant concentration of 2 wt%. Little activity was seen for pure triolein drops, indicating

TABLE 3

Oil Drop Contacting Experiment Results with 2 wt% 15-S-5

Oil drop composition triolein/oleyl alcohol (all by weight)	Dynamic Behavior	
	22°C	30°C
100:0	No activity	No activity
75:25	No activity	Formation of D′ phase (no significant solubilization)
50:50	Formation of D′[a] phase (no significant solubilization)	Swelling of the oil drop, formation of two interemediate phases (significant solubilization)
25:75	Swelling of the oil drop, formation of two intermediate phases (significant solubilization)	Swelling of the oil drop until very low contrast between surfactant solution and the oil drop
0:100	Swelling of the oil drop until very low contrast between surfactant solution and the oil drop	Swelling of the oil drop until very low contrast between surfactant solution and the oil drop

[a] D′, sponge.

that the surfactant was too hydrophilic at these temperatures. This conclusion is consistent with the phase behavior shown in Figure 1 and with the relatively high interfacial tensions of this surfactant with triolein, which were about 0.3 and 0.2 mN/m at 22 and 30°C, respectively. These tensions are about the same as found previously for $C_{12}E_4$ with triolein at 30°C (10).

At 22°C, formation of an intermediate liquid phase occurred after some time for drops of a 50:50 mixture by weight of triolein and oleyl alcohol (Fig. 5). However, drop size did not decrease significantly during the experiment, the low solubilization indicating that the new phase was the D′ phase. Similar behavior was observed at 30°C for drops containing 25 wt% oleyl alcohol, as indicated in Table 3. It was not possible to measure dynamic interfacial tensions for conditions where intermediate phases formed. The reason is that knowledge of the densities of the oil drop, which was likely rather different from its initial value, and of the intermediate phase itself, which was unknown, would be required to calculate interfacial tensions from the spinning drop data.

Rather different behavior was observed at 30°C for drops of the 50:50 mixture. As at the lower temperature, some swelling of the injected drop was observed, followed by formation of the D′ phase (Fig. 6b). Later, spontaneous emulsification generated many small drops near the surface of the original oil drop (Fig. 6c). Many of the drops escaped into the aqueous phase; others coalesced to form a somewhat larger drop (Fig. 6d). The original drop continued to decrease in volume and ultimately disappeared. Figure 6e shows the remaining drop, believed to be triolein-rich, which has a diameter approximately half that of the original drop shortly ater injection. By assuming that the remaining drop is nearly all triolein, we reached the conservative conclusion that at least 75% of the triolein has disappeared, primarily by emulsification into the aqueous phase. In fact, all the oil was emulsified, and only the D′ phase remained at the end of the experiment in a few cases when smaller oil drops were injected.

Similar behavior was seen for drops of the 50:50 mixture injected into 5 wt% $C_{12}E_4$ in water at 30°C, which was also a dispersion of the lamellar phase in water. In this case, spontaneous emulsification began inside the drop before the intermediate phase was seen outside it. Again, the original drop was eventually entirely consumed. One difference was that myelinic figures were seen growing from the intermediate phase near the end of the experiment.

As indicated in Table 3, drops of pure oleyl alcohol at both temperatures rapidly swelled as they took up the aqueous solution until the contrast between the phases became poor. Similar behavior was observed at 30°C for drops containing 75 wt% oleyl alcohol.

Contacting experiments with oil drops on polyester fibers. The experiments with 50:50 and 25:75 mixtures of triolein and oleyl alcohol at 22°C were repeated but with oil drops attached to individual polyester fibers, some 10 μm in diameter, by using the technique described previously. The behavior observed was similar to that described above in the absence of the fibers. Figures 7b and 7c for the 25:75 mixture show intermediate phase formation and spontaneous emulsification similar to those of Figures 6b and 6c. Of particular interest is Figure 7d, which shows that at the end of this experiment only a few small drops of the emulsified oil remained on the fiber, the original phase having completely disappeared, as in Figure 6, and the D′ phase having been detached from the fiber.

DISCUSSION

The phase-behavior studies with pure triolein demonstrate that while the D′ phase having low triolein solubilization is prominent, the D or microemulsion phase which solubilizes significant amounts of triolein, can be formed at temperatures as low as 25°C with an appropriate choice of secondary alcohol ethoxylate surfactant. In contrast, the D phase was seen in a previous study of the pure C_{12} linear ethoxylates and triolein only at temperatures above about 55°C (10). The improved solubilization for the secondary alcohol ethoxylates is likely the result of a more disordered hydrocarbon chain region of the surfactant

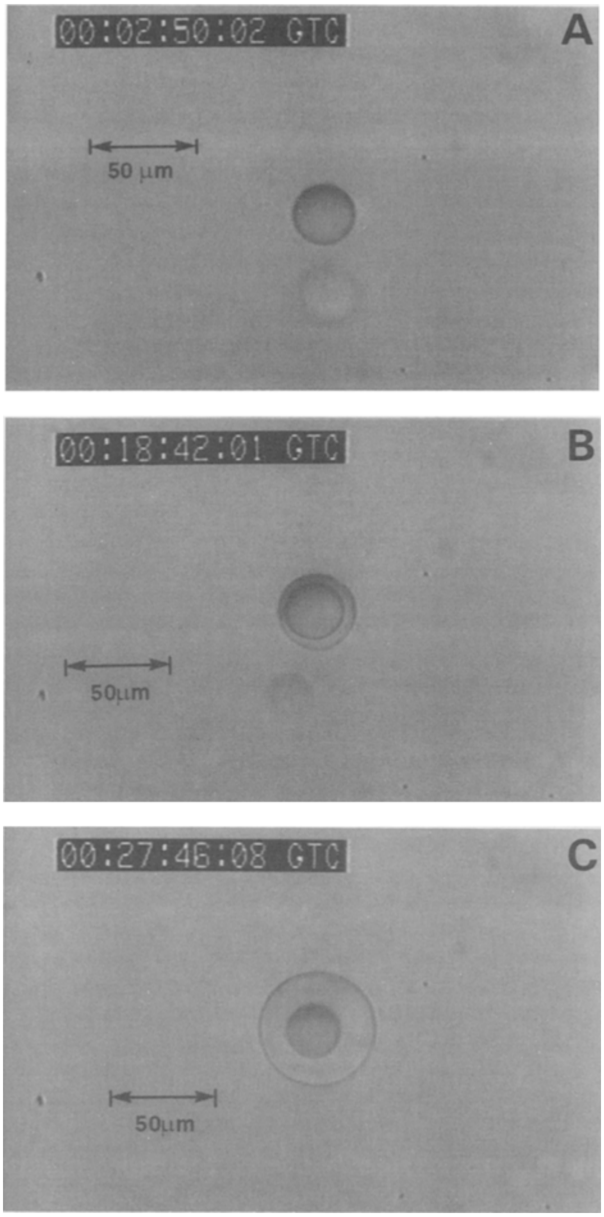

FIG. 5. Sequence of video frames where an oil drop containing 50 wt% oleyl alcohol and 50 wt% triolein was injected into a 2 wt% 15-S-5 surfactant solution at 22°C: (top panel) approximately 3 min after injection; (middle panel) about 16 min later-intermediate D′ phase has formed; (bottom panel) almost half an hour after the injection-growth of D′ phase but no significant reduction in drop size.

films, which is more favorable for incorporation of the large triolein molecules than the ordered films of the linear ethoxylates.

While the D phase is clearly a microemulsion, in that it contains significant amounts of both water and triolein, its microstructure is unknown and an interesting topic for future research. Similarly, experiments are desirable to determine whether the D′ phase retains the sponge-like microstructure over its entire range of existence in these systems.

The contacting experiments also confirm the widespread occurrence of the D′ phase and the need to have rather lipophilic conditions to form the D phase. TERGITOL 15-S-7, which has a cloud point of about 37°C, is evidently too hydrophilic to form the D phase at 22°C, no matter how much oleyl alcohol is present with triolein in the injected oil drops. As surfactant diffuses into alcohol-rich drops in this system, surfactant-alcohol films form, and water is taken up to form an oil-continuous microemulsion O_m. As the films become richer in surfactant, and hence more hydrophilic, an intermediate D′ or sponge phase begins to develop, which incorporates oleyl alcohol but little triolein. Continuing diffusion of surfactant into the bilayers of the D′ phase causes them, in turn, to transform into the lamellar phase L_α, which is known to be more hydrophilic than the sponge phase. Little change in diameter of the original drop is observed, and alcohol losses apparently are roughly balanced by surfactant and water gains. Similar behavior was observed previously for drops, containing a 50:50 mixture of triolein and oleyl alcohol, injected into a dilute solution of pure $C_{12}E_6$ at 35–40°C, *i.e.*, about 10–15° below its cloud point (14).

For TERGITOL 15-S-5, the behavior, shown in Figure 5 for a 50:50 drop at 22°C, is similar except that no lamellar phase grows from the D′ phase. In this case, the surfactant is less hydrophilic and already present as the lamellar phase near the transition temperature to the D′ (or L_3) phase in the initial surfactant–water mixture. Thus, bilayers in the D′ intermediate phase apparently never become sufficiently hydrophilic to form the lamellar phase. Because relatively little of the original triolein is solubilized, this behavior would not be expected to be favorable for detergency.

The behavior shown in Figure 6 for a 50:50 drop at 30°C is especially interesting. Here, too, the first intermediate phase is apparently D′ because its presence produces no significant change in drop diameter. But, in this case, it appears that the drop continues transformation from the O_m into the D phase as it takes up surfactant and water and as it loses alcohol to the D′ phase, once the latter begins to form. Evidently, the D phase becomes sufficiently hydrophilic that it can no longer solubilize all the triolein present, and drops of a triolein-rich oil form spontaneously. As shown in Figures 6 and 7, only a small drop of this oil remains at the end of the experiment, the remainder having been dispersed into the aqueous phase.

It appears that this behavior, which differs from solubilization–emulsification phenomena our group has observed in other systems (1,2,10,13) in that the emulsification is spontaneous, would be favorable for detergency. However, spontaneous emulsification is not always desirable. For nonionic surfactant–hydrocarbon systems above the PIT, extensive spontaneous emulsification of water in the oil phase was observed (1,2), but detergency was nevertheless poor. A key difference for the present situation is that emulsification is accompanied by a reduction in soil volume and indeed by eventual disappearance of the original drop. Moreover, the emulsified drops coalesced readily and generated flow that enhanced the rate of the overall process.

Behavior similar to that of Figure 6 was observed for drops containing 75 wt% oleyl alcohol that were injected into dilute solutions of $C_{12}E_6$ at 40°C (14). Recent review of the videotapes of these experiments indicates that the above interpretation more accurately reflects the observed

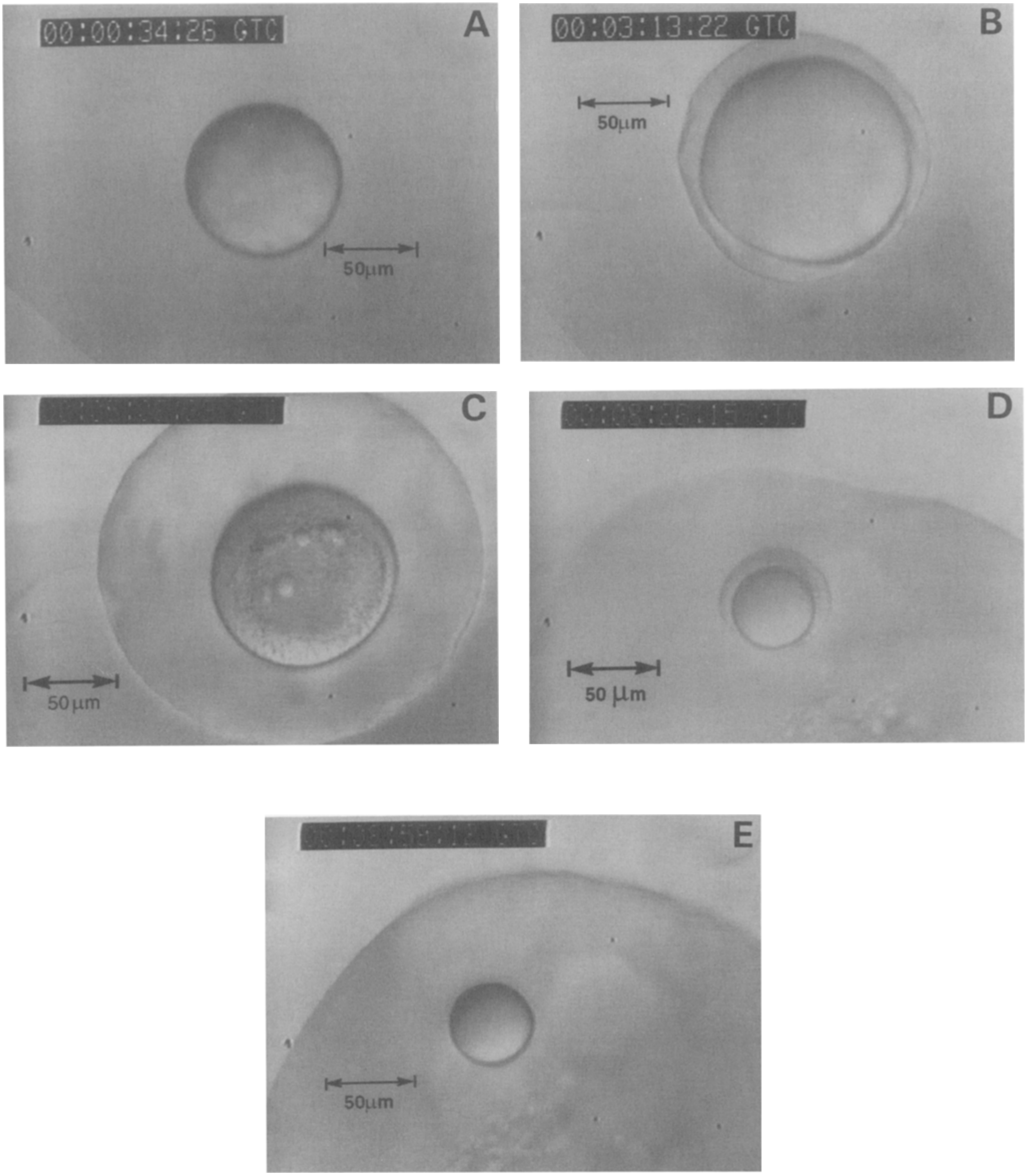

FIG. 6. Sequence of video frames where an oil drop containing 50 wt% oleyl alcohol and 50 wt% triolein was injected into a 2 wt% 15-Sponge-5 surfactant solution at 30°C: (a) shortly after injection; (b) approximately 3 min later—some swelling has occurred and intermediate sponge phase has formed; (c) 2 min later—some emulsification on the surface of the original oil drop; (d) about 8.5 min after injection—many emulsion drops have coalesced while the original oil has nearly disappeared. (e) Shortly after the previous frame—the only remaining phases are the two intermediate phases.

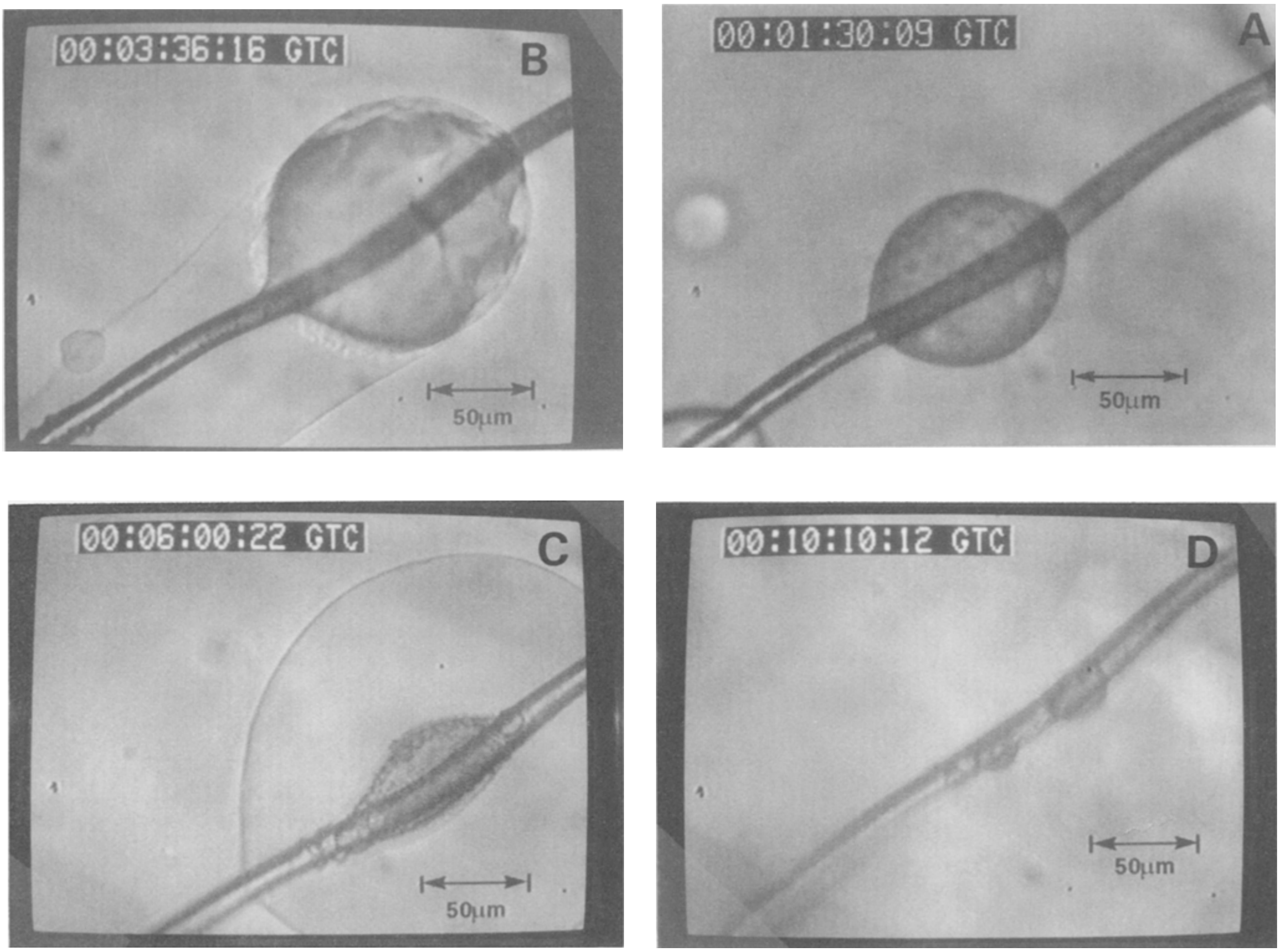

FIG. 7. Sequence of video frames where an oil drop containing 75 wt% oleyl alcohol and 25 wt% triolein attached to a polyester fiber was immersed into a 2 wt% 15-S-5 solution at room temperature (22°C): (a) initial configuration of the drop; (b) about 2 min later—an intermediate sponge phase has formed; (c) approximately 2.5 min later—emulsification and behavior similar to that of Figure 6c; (d) about 4 min later—the first intermediate phase separated from the fiber, only small drops of emulsified phase remain.

behavior than that given in the original paper. The lamellar phase formed near the end of the experiment as myelinic figures growing from the D′ phase, so that the overall behavior was much like that described above for pure $C_{12}E_4$ at 30°C with drops containing 50 wt% oleyl alcohol.

It is not clear whether the behavior observed in the contacting experiments under lipophilic conditions, *i.e.*, drops with 75 wt% oleyl alcohol at 30°C in Table 3, would be favorable for detergency. As the original drop continues to swell under these conditions, and its composition becomes more similar to that of the aqueous phase, interfacial tension should decrease and promote emulsification for washing processes where there is considerable mixing. This behavior should favor soil removal. On the other hand, the results for both hydrocarbons and triolein with linear ethoxylates suggest that detergency is poor for highly lipophilic conditions (2,7,8,10).

The phase-behavior and interfacial-tension results presented above suggest that contacting experiments for triolein drops near 30°C with a 1:1 mixture of TERGITOL 15-S-5 and 15-S-3 would be interesting because the D phase should be formed. We were not successful in observing dynamic behavior for these conditions with our technique. The surfactant-water mixture was a dispersion of the L_3 or L_2 phase in water, in contrast to 15-S-5 alone, which was a dispersion of the lamellar liquid crystal. In our experiments, with no external mixing, little coalescence of the L_3 or L_2 drops with the larger injected oil drops occurred. Because vigorous mixing does take place during washing, it may well be that coalescence does occur and that the 1:1 surfactant mixture is effective for detergency of pure triolein, as the phase behavior suggests, even though little activity was observed in our experiments.

ACKNOWLEDGMENTS

This research was supported by a grant from the National Science Foundation. Suggestions and comments during the work by Kirk Raney were very helpful.

REFERENCES

1. Benton, W.J., K.H. Raney and C.A. Miller, *J. Colloid Interface Sci. 110*:363 (1986).
2. Raney, K.H., W.J. Benton and C.A. Miller, *Ibid. 117*:282 (1987).
3. Raney, K.H., and C.A. Miller, *Ibid. 119*:539 (1987).
4. Solans, C., N. Azemar, J. Parra and J. Calbet, *Proc. CESIO 2nd World Surfactants Congress*, Paris, 1988, Vol. 2, p. 42ff.
5. Schambil, F., and M.J. Schwuger, *Colloid Polym. Sci. 265*:1009 (1987).
6. Raney, K.H., *INFORM 1*:284 (1990).
7. Mori, F., J.C. Lim and C.A. Miller, *Prog. Colloid Polym. Sci. 82*:114 (1990).
8. Raney, K.H., *J. Am. Oil Chem. Soc. 68*:525 (1991).
9. Miller, C.A., and K.H. Raney, *Colloids Surfaces 74*:169 (1993).
10. Mori, F., J.C. Lim, O.G. Raney, C.M. Elsik and C.A. Miller, *Ibid. 40*:323 (1989).
11. Lim, J.C., C.A. Miller and C. Yang, *Ibid. 66*:45 (1992).
12. Benton, W.J., and C.A. Miller, *J. Phys. Chem. 87*:4981 (1983).
13. Lim, J.C., and C.A. Miller, *Langmuir 7*:021 (1991).
14. Tungsubutra, T., and C.A. Miller, in *Organized Solutions*, edited by S. Friberg, and B. Lindman, Marcel Dekker, New York, 1992, Chapter 7, pp. 91–106.
15. Kuneida, H., H. Asaoka and K. Shinoda, *J. Phys. Chem. 92*:185 (1988).
16. Raney, K.H., and H.L. Benson, *J. Am. Oil Chem. Soc. 67*:722 (1990).

[Received August 6, 1993; accepted October 22, 1993]