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Rates of Solubilization of Triolein/Fatty Acid Mixtures by Nonionic Surfactant Solutions

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Spontaneously-generated convection and rapid initial solubilization were observed when drops containing mixtures of triolein and oleic acid were injected into aqueous solutions of nonionic surfactants. For drops having oleic acid contents between 15% and 25% by weight, solubilization rates were at least an order of magnitude greater than those found for pure triolein, and drop volumes decreased by amounts ranging from 45% to 70% in less than 5 min with no external stirring. With the assumption that the end of the rapid solubilization period occurred because most of the oleic acid had been solubilized, it could be shown that about two thirds by volume of the material solubilized was triolein. At later times the solubilization rate was about the same as that for pure triolein with the same surfactant solutions. A similar effect was observed during the first minute or two after contact for a hydrocarbon/oleic acid mixture. Spontaneously-generated convection and rapid initial solubilization of triolein occurred for only a few seconds when the experiment was conducted at pH 9 or 10. When oleic acid was replaced by lauric acid at neutral pH, there was no convection and no significant enhancement of the rate of triolein solubilization. In this case an intermediate phase containing relatively little triolein developed between the oil and aqueous phases.

Introduction

Recently we presented data on rates of solubilization of pure triolein by nonionic surfactant solutions and found that they were controlled by phenomena occurring at the oil−water interface.[1] Minimal solubilization rates were found at 30 and 35 °C for 2 wt % solutions of the pure linear alcohol ethoxylate $C_{14}E_6$ and of a mixture of $C_{12}E_6$ and *n*-dodecanol having about the same cloud point temperature (40 °C). In contrast, solubilization at a significant rate was found at 35 °C for a 2 wt % solution of the commercial secondary alcohol ethoxylate Tergitol 15-S-7, whose cloud point temperature is 37 °C. Higher triolein solubilization rates were also observed when a short-chain alcohol was added to the surfactant solution. Increased flexibility of surfactant films at the oil−water interface was considered to be a significant factor promoting more rapid solubilization for both the change to Tergitol 15-S-7 and the addition of alcohols. However, both with the surfactants alone and with added alcohol the rates were considerably lower than would be obtained by multiplying the rates of solubilization of *n*-hexadecane in the same solutions by the corresponding ratios of the equilibrium solubilization capacities of triolein and *n*-hexadecane.

In practical applications triolein and other liquid triglycerides are rarely pure but contain fatty acids formed by hydrolysis of the ester bonds. As a result, we have extended our work to include triolein/fatty acid mixtures.

Solubilization rates of pure, solid fatty acids in surfactant solutions have been measured at temperatures low enough that no intermediate phase formation occurs

at the interface.[2,3] At higher temperatures, i.e., above a "penetration temperature" which depends on both fatty acid and surfactant, the lamellar liquid crystal forms as an intermediate phase, usually as myelinic figures. Many of the experiments reported below utilize oleic acid, which forms from hydrolysis of triolein. We have verified that oleic acid does exhibit an intermediate lamellar phase when contacted with typical nonionic surfactant solutions at temperatures of interest here.

As we show below, addition of suitable amounts of oleic acid to triolein causes a large increase in the initial solubilization rate of triolein over that found with pure triolein for the same nonionic surfactant solutions. The increase ranges from severalfold to an order of magnitude or more. The presence of oleic acid in the surfactant film at the oil−water interface reduces interfacial tension and perhaps also generates a local interfacial tension gradient driving flow from the oil phase into micelles with which it is temporarily fused. However, when lauric acid, which has a straight hydrocarbon chain, is present instead of oleic acid, little rapid initial solubilization of triolein is seen. The difference in the two cases stems from a difference in phase behavior.

Experimental Section

Tergitol 15-S-7 is a mixture of species with the alcohol group located at various positions along a chain of 11−15 carbon atoms and with an average ethylene oxide number of 7. It was supplied by Union Carbide. The pure linear alcohol ethoxylates $C_{12}E_6$ and $C_{12}E_8$ were obtained from Nikko Chemical. Triolein with a purity of 99% was purchased from Sigma, as were oleyl alcohol, oleic acid, *n*-pentanol, and n-hexanol. Lauric acid (98%) was obtained from Aldrich Chemical, isopropanol and isobutanol were obtained from J. T. Baker, *n*-butanol was obtained from

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1997.

(1) Chen, B.-H.; Miller, C. A.; Garrett, P. *Colloids Surf.* **1997**, *128*, 129.

(2) Chan, A. F.; Evans, D. F.; Cussler, E. L. *AICHE J.* **1976**, *22*, 1006.
(3) Shaeiwitz, J. A.; Chan, A. F.; Evans, D. F.; Cussler, E. L. *J. Colloid Interface Sci.* **1981**, *84*, 471.

Fluka, and *n*-hexadecane was obtained from Humphrey Chemical.

Solubilization rates were measured using the basic oil drop contacting procedure described previously.[1,4] A thin hypodermic needle was used to inject small oil drops, typically 50−100 μm in diameter, into a rectangular glass capillary cell having a thickness of 400 μm and filled with the aqueous surfactant solution of interest. The cell was placed in a Mettler thermal stage modified for use in these experiments. The dynamic behavior was observed and recorded using videomicroscopy. While the earlier work[4] was mainly concerned with observing intermediate phase formation in rather lipophilic systems, the emphasis here was on obtaining quantitative information on variation of the drop size with time in the absence of intermediate phases. For measuring drop diameter as a function of time, the videomicroscopy system was equipped with a JV 6000 video-micrometer.

In some systems contacting experiments were conducted with the same glass capillary cells oriented vertically and placed in a thermal stage.[5] The lower half of the cell was filled with surfactant solution, the bottom of the cell was sealed, and oil was carefully injected into the upper half of the cell using a syringe in such a way as to minimize mixing. With this procedure the behavior at the interface could be carefully observed.

Equilibrium solubilization capacities were determined by adding small increments of oil to a micellar solution in an environmental room maintained at 30 °C and observing whether the turbidity disappeared over periods of up to 5 days. Light transmittance was measured with a PC 800 colorimeter which was connected to a fiber optic probe inserted into the solution.

Interfacial tensions were measured using a spinning drop device developed by workers at the University of Texas[6] and used extensively by various groups studying enhanced oil recovery.

Results

1. Triolein/Oleic Acid Drops at Neutral pH. For a spherical drop with radius $R(t)$, the volumetric rate of solubilization per unit area $[-A^{-1}(dV/dt)]$ is easily shown to be given by $(-dR/dt)$. Figure 1 shows the variation of R with time for a drop containing 85 wt % triolein and 15 wt % oleic acid injected into a 2 wt % solution of the commercial secondary alcohol ethoxylate Tergitol 15-S-7 at 35 °C and neutral pH. As mentioned previously, this surfactant is a mixture of species, each with two hydrocarbon chains having a total of 11−15 carbon atoms but with different lengths of the two chains for different species. It was chosen because it was able to solubilize pure triolein much faster than pure linear alcohol ethoxylates.[1] Particularly striking in Figure 1 is the rapid initial decrease in drop size $(-dR/dt)$, having a value of about 2.1 μm/min. The volume of the drop decreased by about 46% in 5 min, a process accompanied by vigorous spontaneously generated convection. Later in the experiment the solubilization rate decreased by an order of magnitude, eventually reaching a constant value of 0.20 μm/min, about the same as found previously for pure triolein and the same surfactant solution at the same temperature.[1]

Similar experiments with this surfactant and with drops of the same composition showed that the initial rate of solubilization did not depend on drop size. It was approximately proportional to surfactant concentration (Figure 2) but relatively insensitive to temperature (Figure 3) and to the addition of short-chain alcohols (Figure 4). Solubilization rates plotted in Figures 2−4 are averages of at least two experiments. Some variation for repeat experiments was observed, but the rate for any individual
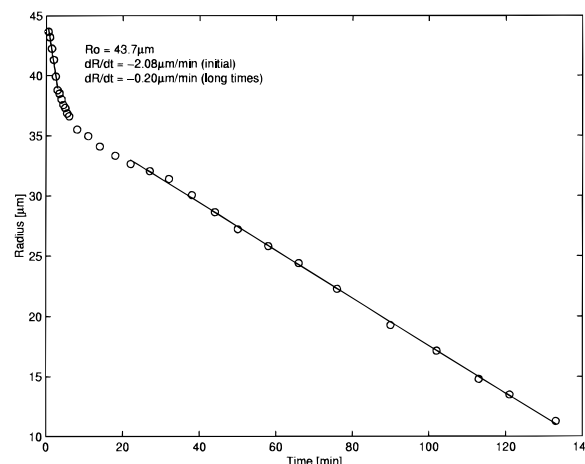
(4) Lim, J. C.; Miller, C. A. *Langmuir* **1991**, *7*, 2021.
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(6) Cayias, J. L.; Schechter, R. S.; Wade, W. H. Adsorption at Interfaces. *ACS Symp. Ser.* **1975**, *8*, 234.

Figure 1. Variation with time of radius of drop containing 85/15 triolein/oleic acid (by weight) injected into 2 wt % Tergitol 15-S-7 at 35 °C.

experiment rarely deviated from the average by more than 10%. The asymptotic solubilization rates at long times shown in these figures were much lower and comparable to those found previously for pure triolein.[1] Accordingly, they increased with increasing temperature and with addition of butanol, pentanol, and hexanol. Finally, Figures 2−4 show that the reduction in drop volume during the initial period of rapid solubilization decreased slightly as surfactant concentration increased from 1 to 4 wt % but was little influenced by temperature or by addition of alcohol.

A solution of 2 wt % Tergitol 15-S-7 and the same mixture of triolein and oleic acid were contacted using the vertical-stage microscope at 35 °C in order to observe more clearly behavior near the interface during the initial solubilization process. Although spontaneously-generated convection developed, as in the drop experiments, no intermediate phase was observed at the interface, in contrast to the behavior reported below for drops containing much larger amounts of oleic acid.

Interfacial tension was also measured at 30 °C for the same surfactant solution and oil compositions. As shown in Figure 5, tension fell during the first few minutes of the experiment to about 0.045 mN/m, remained nearly constant for some time, and then rose slowly, reaching a value greater than 0.2 mN/m at the end of the experiment. This latter value is of the same order of magnitude as that reported previously at the same temperature for another nonionic surfactant and pure triolein.[5] It should be noted that the results in Figures 1 and 5 cannot be compared directly at a given time owing to differences in drop size and shape in the two experiments.

The initial solubilization process appears to be only slightly affected by nonionic surfactant structure. When Tergitol 15-S-7 was replaced by the pure linear alcohol ethoxylate $C_{12}E_6$ for the experiment shown in Figure 1, behavior during the first 5 min of the experiment was similar although the solubilization rate was a little higher (2.8 vs 2.1 μm/min). The fractions of the initial drop volume solubilized during this time, 44% for $C_{12}E_6$ and 46% for Tergitol 15-S-7, agreed within experimental error. However, no further solubilization occurred for the $C_{12}E_6$ solution after this time, which is consistent with the negligible solubilization rate found with this surfactant solution for pure triolein at 35 °C.[1] Addition of 0.3 wt % *n*-hexanol had little effect on the initial solubilization rate or the amount solubilized by $C_{12}E_6$ but yielded an asymptotic solubilization rate of 0.15 μm/min, again about the same as found previously for pure triolein.[1]
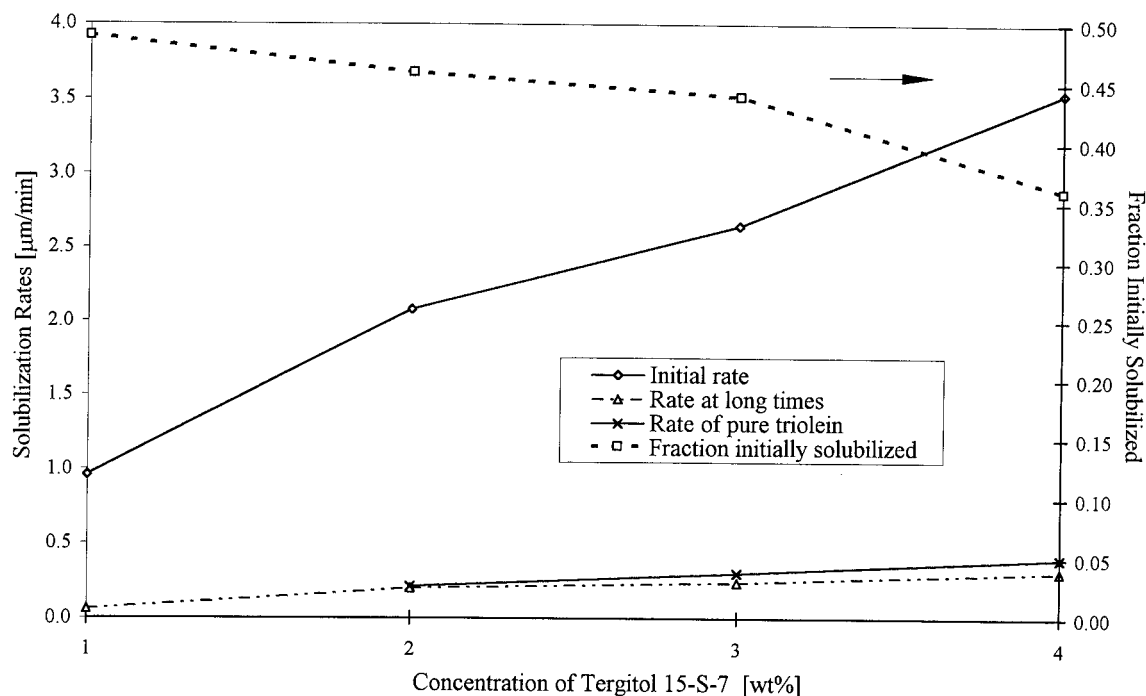
Figure 2. Initial and final solubilization rates and amount of initial solubilization as a function of surfactant concentration for the system of Figure 1.
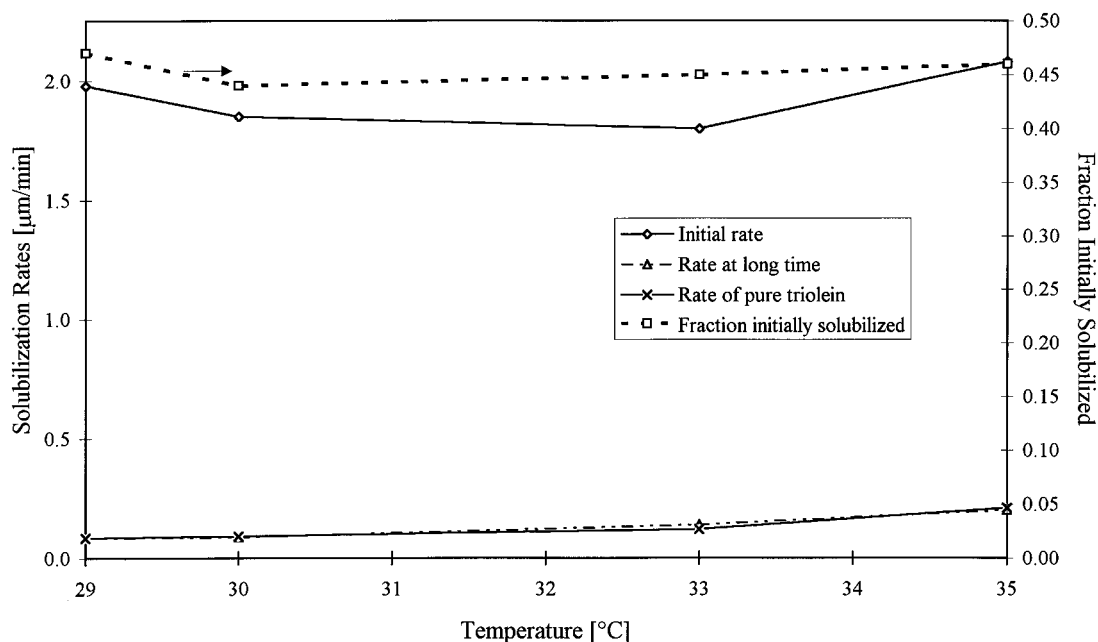
Figure 3. Initial and final solubilization rates and amount of initial solubilization as a function of temperature for the system of Figure 1.

The initial rate of solubilization $(-dR/dt)$ by 2 wt % solutions of Tergitol 15-S-7 was about the same at 35 °C for drops having oleic acid contents of 15, 20, and 25 wt % (Figure 6). However, the amount solubilized during this time was greater when more oleic acid was present intially. The variation of interfacial tension with time for a drop containing 25 wt % oleic acid was similar to that shown in Figure 5 except that the minimun interfacial tension was lower—about 0.005 mN/m.

For an oil with 40 wt % oleic acid, myelinic figures could be observed growing from the surface of the drop; i.e., an intermediate lamellar liquid crystalline phase was formed. The percentage decrease in drop volume during the initial solubilization stage was about 70% and thus about the same as that for drops containing 25 wt % oleic acid. For drops containing 50 wt % oleic acid no initial shrinkage occurred. Indeed, the drops actually increased in size before beginning to shrink, and myelinic figures were again observed.

Spontaneously-generated convection and rapid drop shrinkage were observed in the first minute or two after a drop containing 88 wt % n-hexadecane and 12 wt % oleic acid contacted a solution of 2 wt % $C_{12}E_8$ at 25 °C. The drop volume decreased by about 35% during this time. The initial value of $(-dR/dt)$ was about 6.8 μm/min, more than three times greater that that shown in Figure 1 for a triolein/oleic acid mixture. Subsequently, neither significant convection nor further drop shrinkage was
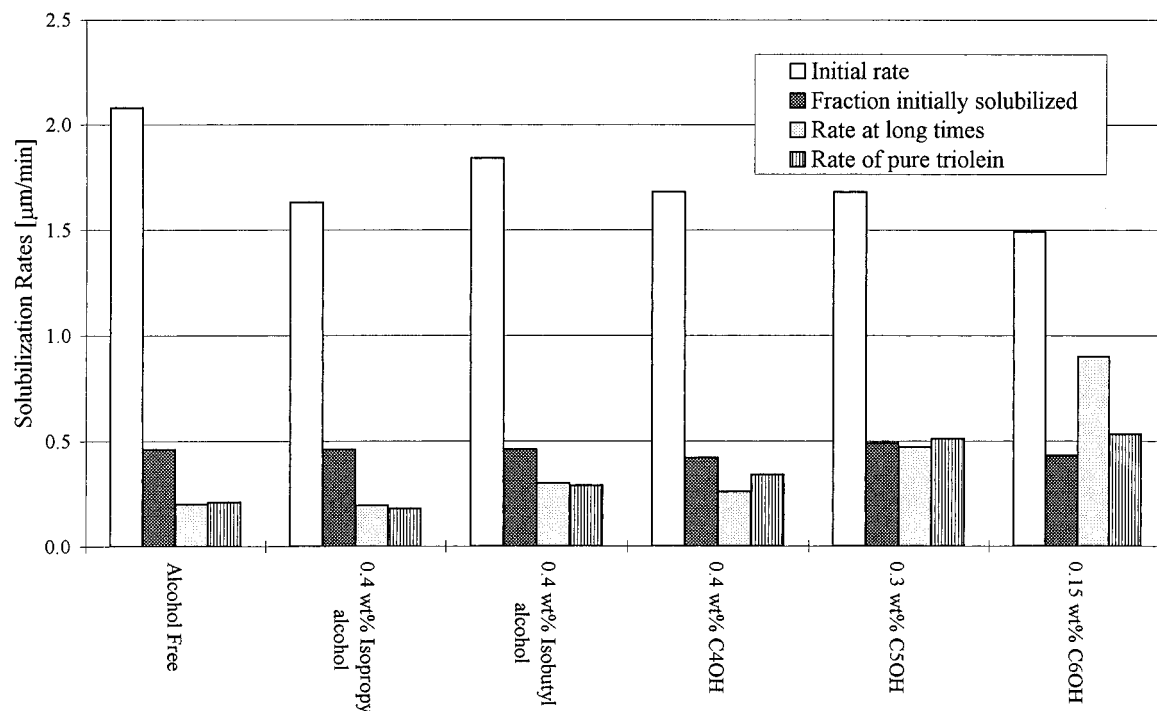
Figure 4. Effect of added short-chain alcohols on initial and final solubilization rates and amount of initial solubilization for the system of Figure 1. The cloud points of all the solutions are between 36 and 38 °C.
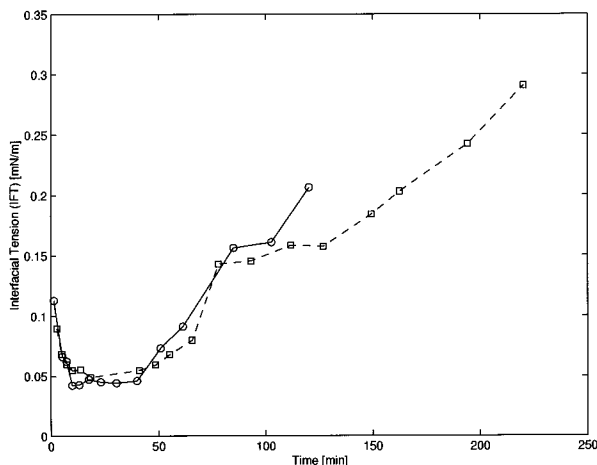

Figure 5. Interfacial tension as a function of time for the system of Figure 1 at 30 °C.

observed. The PIT for this system is about 43 °C.[7] Above the PIT, behavior is very different in such systems as the drop swells, and eventually an intermediate lamellar liquid crystalline phase develops at the drop surface.[4]

2. Triolein/Oleic Acid Drops at Alkaline Conditions. The experiment of Figure 1 was repeated with the surfactant solution buffered to pH 10 by a mixture of $NaHCO_3$ and Na_2CO_3. The temperature was maintained at 30 °C because addition of the salts had reduced the cloud point temperature from its inital value of 37 °C to a value below 35 °C. As shown in Figure 7, the drop size remained nearly constant for some time and then decreased at a rate of about 0.11 μm/min, which is close to the value of 0.09 found for pure triolein at this temperature.[1] Interfacial tension fell very rapidly to about 0.003 mN/m and then rose almost immediately to about 1 mN/m (Figure 8).

Addition of 0.4 and 0.8 wt % *n*-butanol to the surfactant solution failed to restore the initial rapid solubilization

although the asymptotic solubilization rates for long times increased, as would be expected from the results for pure triolein.[1] Similarly, no rapid initial solubilization was seen when another buffer solution at pH 9 was used.

A vertical cell experiment was also performed for this system. Initially, very distinct roll cells produced by vigorous Marangoni flow were observed as well as extensive spontaneous emulsification in the aqueous phase (Figure 9a). After only 45 s, the convection stopped and the emulsion was pushed away from the oil phase by a distance which increased with time (Figure 9b). Discussion of this behavior is given below.

It is perhaps worth noting that no measurable solubilization occurred when drops containing 75 and 85 wt % triolein and 25 and 15 wt % oleic acid, respectively, were injected into various surfactant-free solutions with pH values between 9 and 13.

3. Drops of Triolein Mixed with Other Long-Chain Polar Compounds. Drops of triolein/oleyl alcohol mixtures containing 15 and 25 wt % of the alcohol were injected into 2 wt % solutions of Tergitol 15-S-7 at neutral pH and at temperatures between 29 and 35 °C. Initial rapid solubilization was observed, the rates and amounts of solubilization were similar to the corresponding results presented above for mixtures of triolein and oleic acid.

In contrast, much less initial solubilization occurred when oleic acid was replaced by lauric (dodecanoic) acid, as shown in Figure 10 for a drop containing 15 wt % acid. The initial solubilization rate was about half that seen for the corresponding oleic acid system (Figure 1), and only 18% by volume of the drop was solubilized. The vertical cell experiment for this system showed no significant convection at any time. Evidently, an intermediate phase formed immediately at the surface of contact. After a minute or two it became visible, and its thickness was proportional to the square root of time; i.e., its growth was diffusion controlled (Figures 11 and 12).

Addition of small amounts of short-chain alcohols to the surfactant solution did not improve significantly the
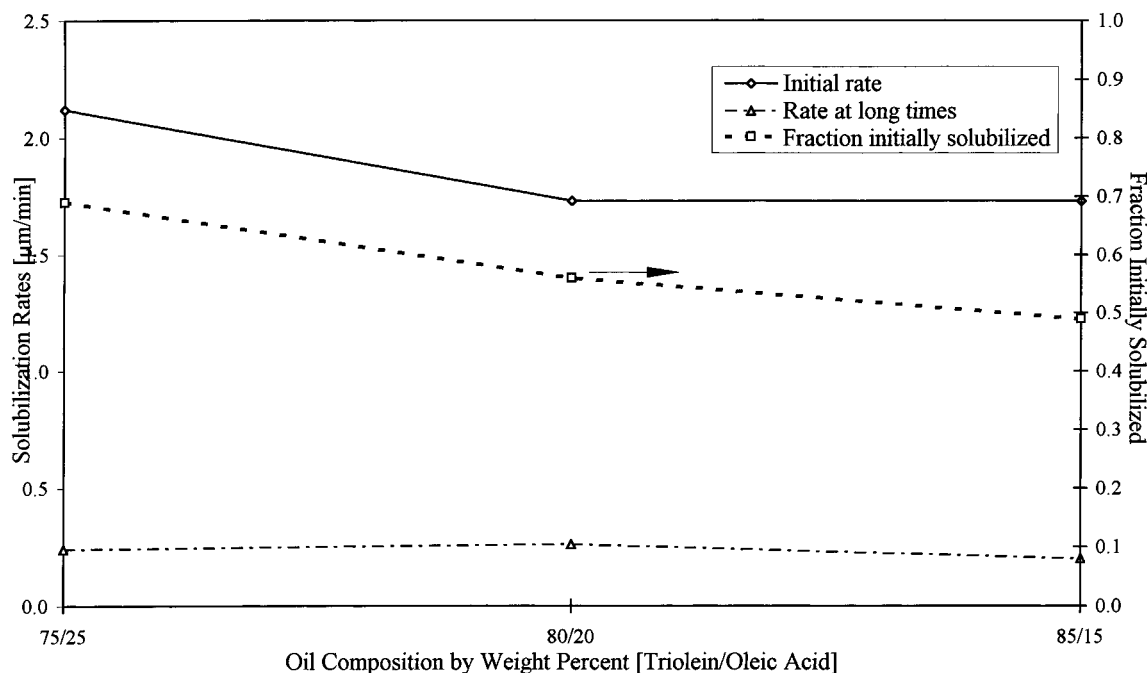
(7) Raney, K. H.; Benson, H. L. *J. Am. Oil Chem. Soc.* **1990**, *67*, 722.

Figure 6. Initial and final solubilization rates and amount of initial solubilization as a function of oleic acid concentration in triolein drops for 2 wt % Tergitol 15-S-7 solutions at 35 °C.
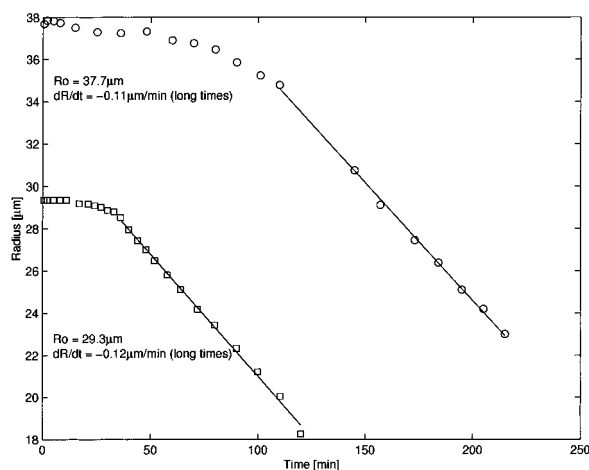

Figure 7. Variation with time of radius of drop containing 85/15 triolein/oleic acid (by weight) injected into 2 wt % Tergitol 15-S-7 at pH 10 and 30 °C.
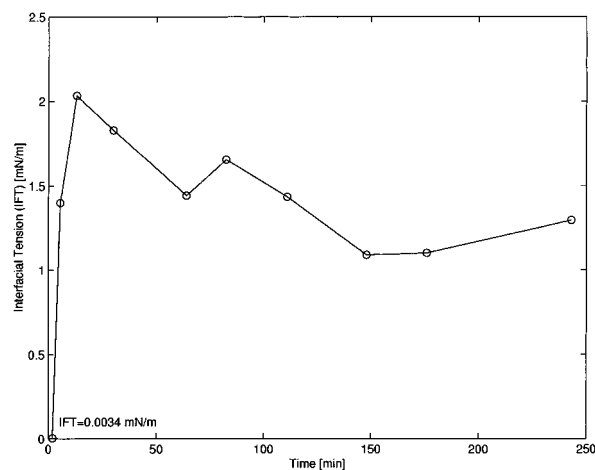

Figure 8. Interfacial tension as a function of time for the system of Figure 7 at pH 10 and 30 °C.

Discussion

rate or amount of initial solubilization (Figure 13). If anything, the amount solubilized decreased slightly. However, solubilization rates at long times increased when alcohol was added, as found in previous experiments for pure triolein.[1]

At pH 9 and 10 no initial rapid solubilization was observed (Figure 14), the same as reported above for triolein/oleic acid mixtures. Addition of 0.8 wt % n-butanol to the surfactant solution did not restore the initial rapid solubilization.

Drops containing mixtures of triolein and capric (decanoic) acid exhibited behavior similar to that for triolein and lauric acid shown in Figures 10 and 14. That is, a small amount of initial solubilization was seen at neutral pH, but none was seen at pH 10.

Experiments were also conducted with drops containing 85 wt % triolein and mixtures of oleic and lauric acid at neutral pH. As shown in Figure 15, both the initial rate of solubilization and the percentage decrease in drop volume during this time became smaller as the amount of lauric acid increased.

1. Initial Rapid Solubilization at Neutral pH. As indicated above, the solubilization rates at times long after initial contact for the triolein/oleic acid drops at neutral pH are about the same as those found previously for pure triolein.[1] Accordingly, it seems reasonable to assume that virtually all the oleic acid is solubilized during the initial rapid decrease in drop size. Using this assumption, one finds that, for 2 wt % Tergitol 15-S-7 and triolein/oleic acid drops with initial acid contents of 15−25 wt %, about twice as much triolein as acid (by volume) is solubilized during the first few minutes following contact. Moreover, the initial rate of solubilization of triolein is nearly seven times that of pure triolein for the same conditions and, in fact, slightly greater than the solubilization rate of pure n-hexadecane reported previously.[1] For 2 wt % $C_{12}E_6$ at 35 °C the initial ratio of triolein to acid solubilized is again about 2. However, the increase in solubilization rates is even more striking because such a solution exhibits an initial solubilization rate comparable to that of Tergitol 15-S-7 when oleic acid is present but a negligible solubilization rate for pure triolein.
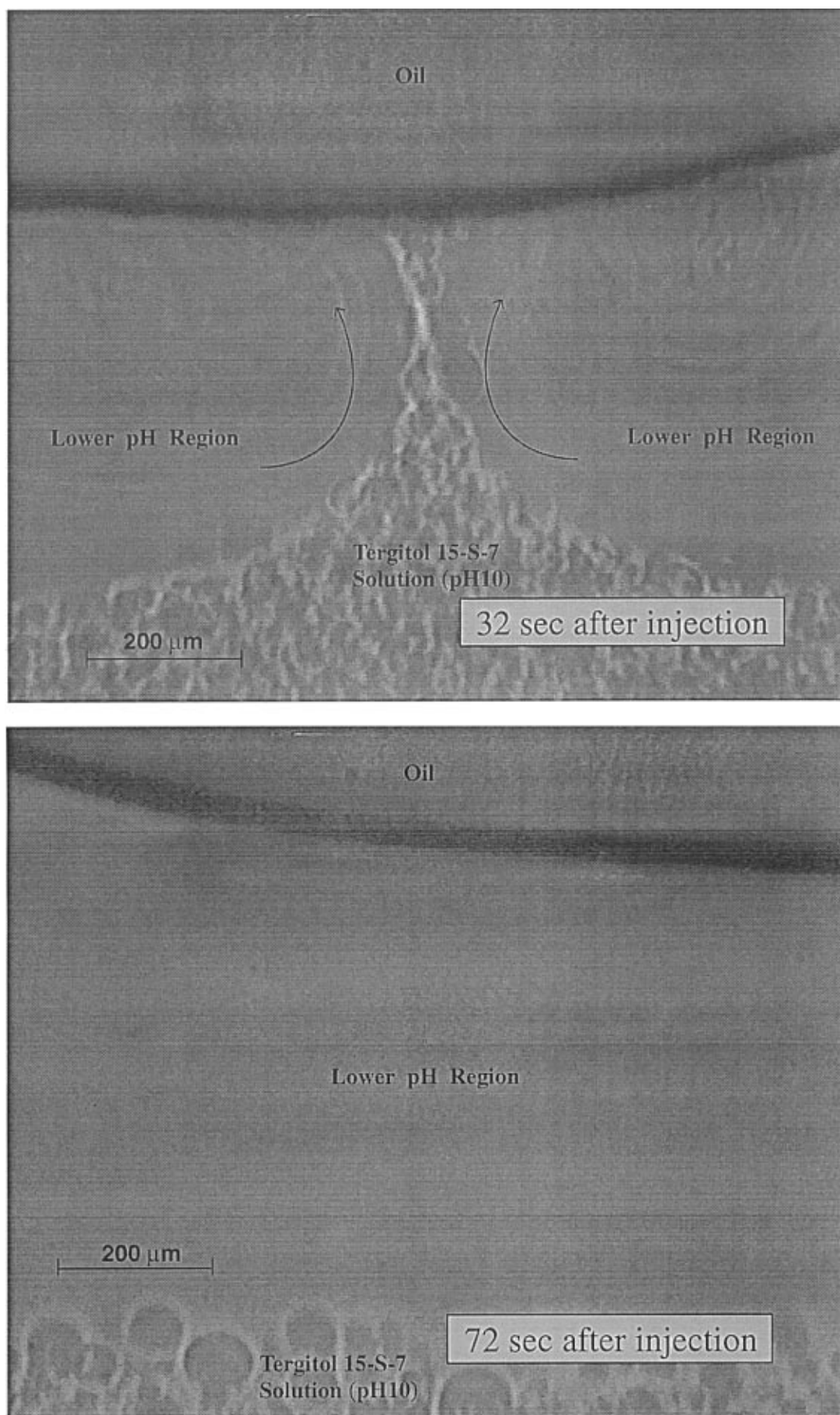
Figure 9. Video frames from vertical cell contacting experiment for the system of Figure 7. (a, top) Vigorous Marangoni flow and spontaneous emulsification at 32 s after injection. (b, bottom) Flow is minimal at 72 s after injection.
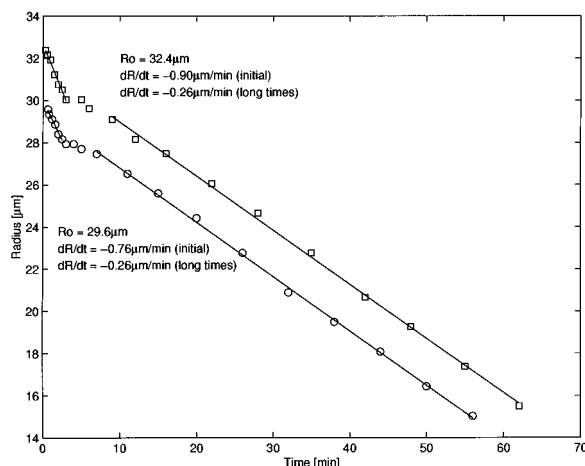
Figure 10. Variation with time of radius of drop containing 85/15 triolein/lauric acid (by weight) injected into 2 wt % Tergitol 15-S-7 at 35 °C.

Various experiments reported above provide insight on how oleic acid causes such a large increase in the solubilization rate of triolein. Figure 2 shows that the initial solubilization rate is proportional to the bulk surfactant concentration. The same behavior was found previously for pure hydrocarbons and triolein and was interpreted as indicating that, for a given oil and surfactant, the rate-limiting step was "adsorption" of micelles by the oil drop.[1,8,9] The high solubilization rates seen here suggest that adsorption is much faster when oleic acid is present in the surfactant film at the surface of the oil drop than when the film consists entirely of nonionic surfactant.

This conclusion is plausible, since oleic acid lowers the cloud point of the surfactant; i.e., it reduces the repulsive interaction between micelles and presumably also between a micelle and an oil−water interface. Indeed, since spontaneously-generated Marangoni flow was present in our experiments but could not be varied systematically, one cannot rule out the possibility that adsorption became so fast that the rate of mass transfer of surfactant from the bulk fluid to the interface was an important factor influencing the solubilization rate. The mass transfer rate would be proportional to the bulk surfactant concentration in these experiments if adsorption were very fast.

Figure 2 also shows that the ratio of triolein to oleic acid solubilized decreased somewhat with increasing surfactant concentration. For a micelle being emitted from the drop, oleic acid is already present in the interfacial film while triolein must enter from the bulk oil phase. Probably less triolein has time to enter each micelle when the emission rate is more rapid at high surfactant concentrations.

Figure 4 shows that addition of small quantities of short-chain alcohols did not strongly affect the initial rapid solubilization rate. It has been suggested that "adsorption" of surfactant may result from dissociation of micelles located very near the interface.[8] If controlled by this mechanism of adsorption, the solubilization rate should increase with decreasing micelle dissociation time τ_2. Experiments for other surfactants have shown that τ_2 decreases when short-chain alcohols are added.[10] Since no increase in initial solubilization rate was seen here, one can conclude that it is not significantly affected by micelle dissociation. However, the final solubilization
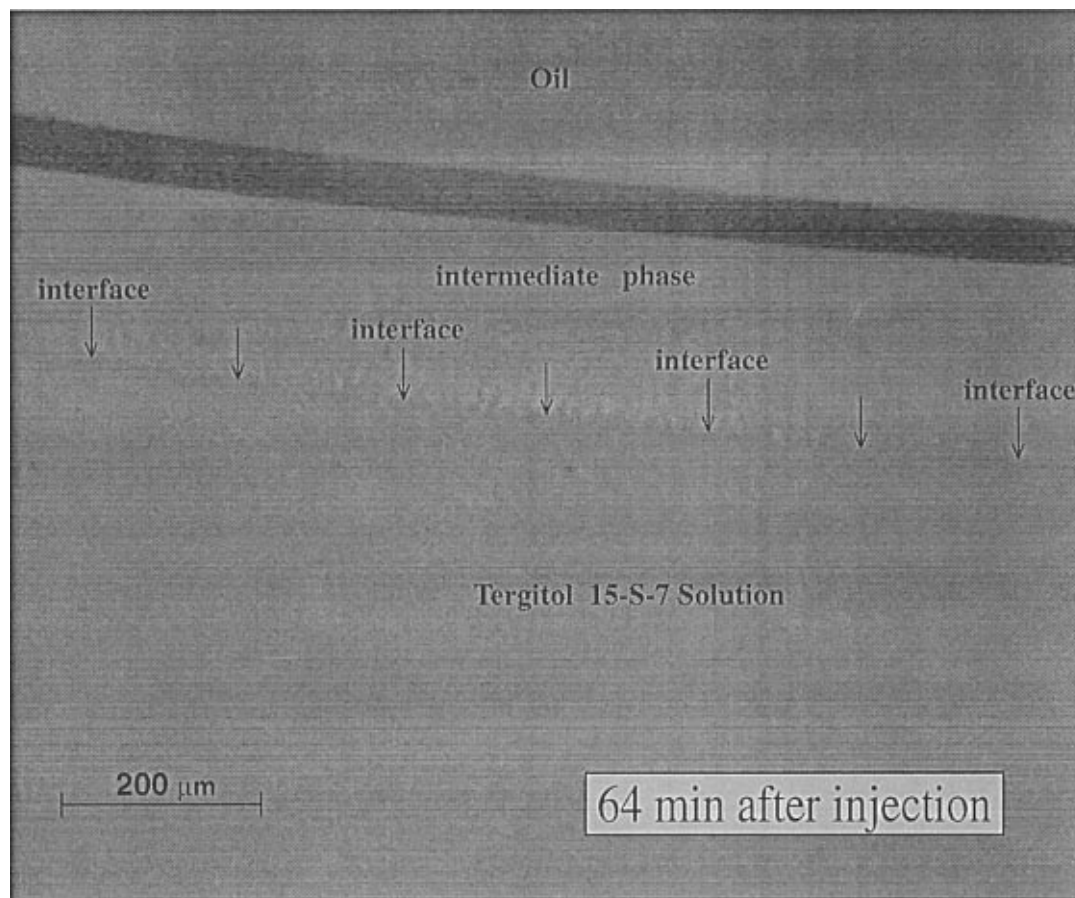

Figure 11. Video frame from vertical cell contacting experiment showing development of intermediate phase in the system of Figure 10.
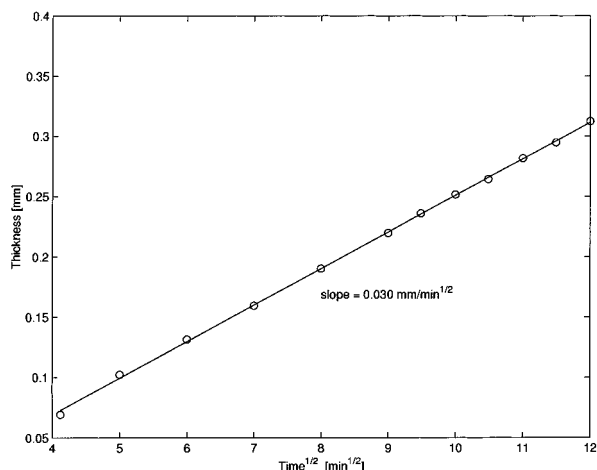
Figure 12. Thickness of intermediate phase for the experiment of Figure 11 as a function of $t^{1/2}$.

rates of Figure 4 when the drops are nearly pure triolein do increase upon addition of alcohols (see also ref 1) and thus may be influenced by micelle dissociation.

As indicated previously, the solubilization rate $(-dR/dt)$ obtained from Figure 1 for a given time cannot be compared directly with interfacial tension at the same time in Figure 5 because of differences in the experiments. However, the trends seen in the two curves are revealing. That interfacial tension passes through a minimum as the oleic acid content of the surfactant film decreases during the experiment suggests that the film shifts from an initial lipophilic state to a final hydrophilic state with the minimum occurring when hydrophilic and lipophilic properties are balanced. Initial rapid solubilization occurs when the film is lipophilic and perhaps when it is nearly balanced as well, while the slower solubilization at long times corresponds to a situation where nearly all the oleic acid has been solubilized into the bulk aqueous solution. The interfacial tensions of 0.22−0.25 mN/m in Figure 5 after 100−200 min are comparable to the steady state

tension of about 0.4 mN/m attained after about 300 min for the same surfactant solution and pure triolein.[1] That they are slightly lower in the present case indicates that a small amount of oleic acid remains in the film.

Donegan and Ward[11] found that the solubilization rates of several pure straight-chain hydrocarbons in solutions of a pure nonionic surfactant were proportional to the respective equilibrium solubilization capacities. We showed previously that a similar relationship did not hold for triolein and n-hexadecane.[1] Equilibrium solubilization also appears to shed little light on the rapid initial solubilization process seen here. In the first place, the solubilization rate does not change greatly while the oleic acid content of the drop falls from its initial value to some small value during the first few minutes of an experiment such as that of Figure 1. Moreover, limited equilibrium solubilization data presented in Table 1 do not seem to correlate with initial solubilization rates. For example, the table shows that a 2 wt % solution of Tergitol 15-S-7 can solubilize an order of magnitude more of a triolein/oleic acid mixture containing 15 wt % acid than can pure $C_{12}E_6$, but the initial solubilization rates are comparable. Also equilibrium solubilization changes little for 2 wt % Tergitol 15-S-7 when oleic acid is replaced by lauric acid, according to the table, but the initial solubilization rate drops by more than a factor of 2 (compare Figures 1 and 10).

The discussion to this point indicates that rapid initial solubilization occurs when the film at the drop interface is rich in oleic acid and hence much more lipophilic than when it contains surfactant alone. Moreover, micelle dissociation is unimportant, so that micelles are apparently incorporated at least temporarily into the interface during the adsorption step. Finally, equilibrium solubilization does not seem to play a significant role. Evidently dynamic mechanisms are operative which enable triolein to be solubilized quite rapidly along with oleic acid. We will discuss adsorption of micelles by the drop and emission of micelles containing solubilized material separately.

One might imagine that a micelle upon "adsorption" is
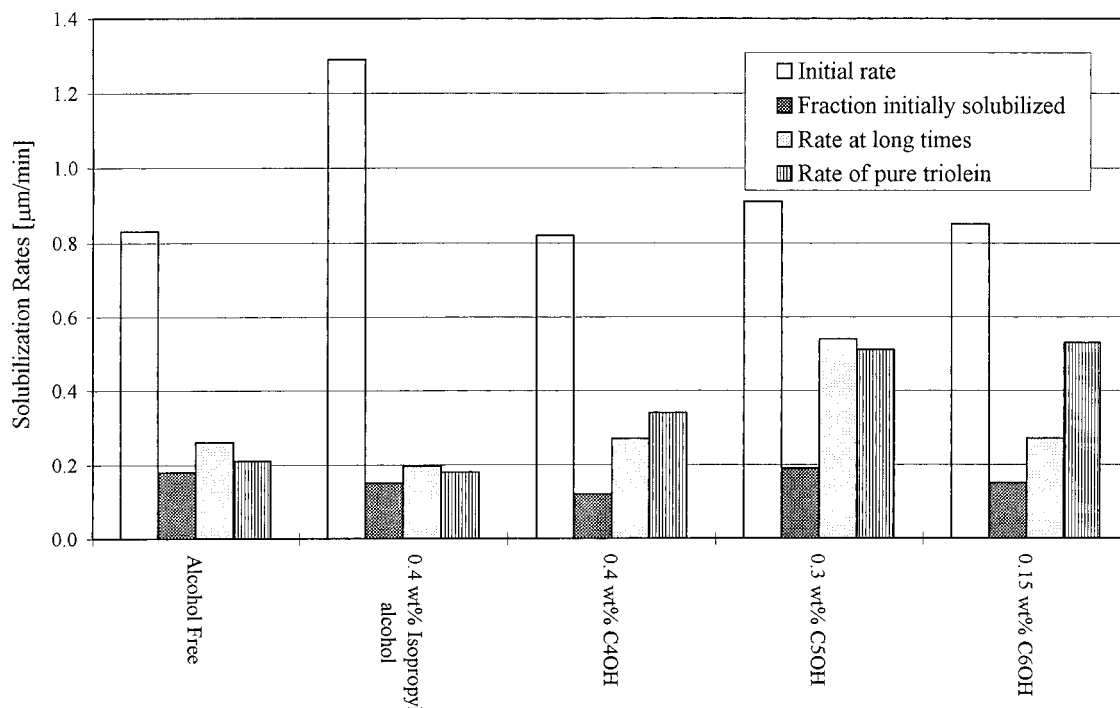

Figure 13. Effect of added short-chain alcohols on initial and final solubilization rates and amount of initial solubilization for the system of Figure 10. The cloud points of all the solutions are between 36 and 38 °C.
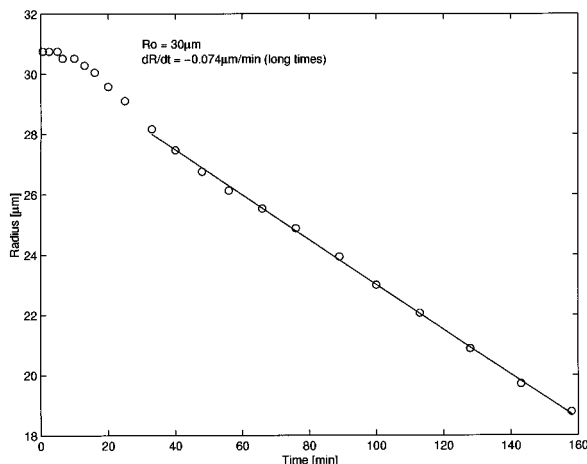
Figure 14. Variation with time of radius of drop containing 85/15 triolein/lauric acid (by weight) injected into 2 wt % Tergitol 15-S-7 at pH 10 and 30 °C.

transiently joined to the interface. As shown in Figure 16, a neck must develop between the micelle and the drop for their partial fusion to occur. As this neck has the opposite curvature in the plane of the diagram of Figure 16 from that of the micelle, the molecules from the micelle incorporated into the surfactant film in the neck region have an energetically less favorable configuration. The more flexible the micelle surface, i.e., the lower its bending modulus, the less energy required for this process, a possible reason that the rate of solubilization of pure triolein was found to increase with increasing flexibility.[1] We note that temporary connection of a bulk phase and a droplet in a microemulsion during solubilization was suggested previously by Plucinski and Nitsch[12,13] to explain their results on solubilization rates of metal ions and amino acids by water-in-oil microemulsions. Implications for emulsion stability of formation of such a neck between drops have been discussed by Kabalnov and Wennerström.[14]

Like the micelle, the drop interface must be deformed locally as the neck develops. If the film contains surfactant

alone, energy must also be supplied for this process, as the water-in-oil configuration at the neck is unfavorable. However, when the film is more lipophilic, as when it is rich in oleic acid, the water-in-oil configuration is favorable and energy may even be released during neck formation. Of course, reversing the curvature of some part of the micelle surface is also a part of neck formation and requires energy as before. Nevertheless, the net result is that temporary fusion of micelle and drop occurs more readily when oleic acid is present than for pure triolein and facilitates solubilization.

Let us next consider the mechanism of emission from the interface of micelles containing solubilized oil. The much lower interfacial tension with oleic acid present (about 0.04 and 0.4 mN/m for the 85/15 mixture and pure triolein, respectively) would be expected to promote larger fluctuations in interfacial shape which should facilitate micelle emission. However, this effect seems not to be dominant because the minimum tension is nearly an order of magnitude lower for the 75/25 than for the 85/15 mixture with little difference in the solubilization rate.

One possible mechanism for the high initial solubilization rate is the interfacial tension gradient which exists between the low-tension interface of the drop (A of Figure 16) and the higher tension interface of an acid-free micelle (B of Figure 16) which has just become connected to the drop. Such a gradient produces flow from the drop into the micelle, i.e., from A to B, until the latter breaks off and returns to the aqueous solution, behavior which clearly promotes greater solubilization. The same mechanism could account for the even faster initial solubilization reported above for a drop containing *n*-hexadecane and oleic acid, which should have a lower interfacial tension than the triolein/oleic acid drop. As suggested previously,[1] an oppositely directed interfacial tension gradient could generate flow from micelle to drop, i.e., from B to A, when a nonionic surfactant solution containing solubilized *n*-hexadecane contacted a pure triolein drop. In this case the triolein drop was, in contrast to the situation here, observed to actually increase in volume until it had incorporated a significant amount of *n*-hexadecane, which
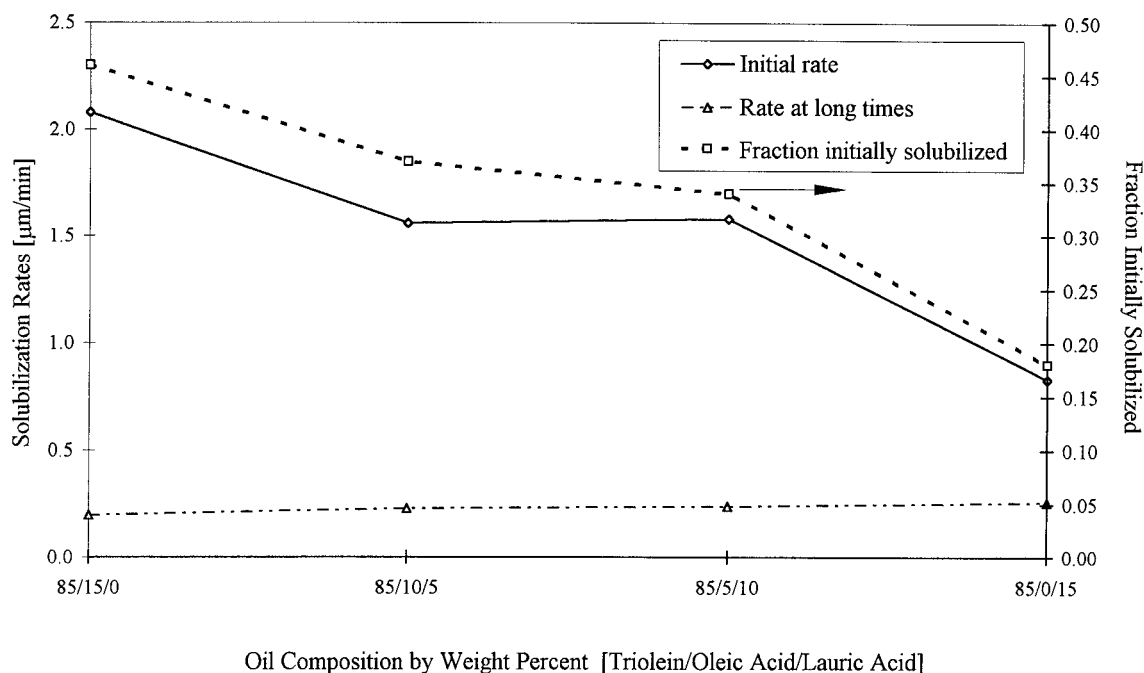

Oil Composition by Weight Percent [Triolein/Oleic Acid/Lauric Acid]

Figure 15. Initial and final solubilization rates and amount of initial solubilization for drops containing triolein and mixtures of oleic and lauric acid.

Table 1. Equilibrium Solubilization Capacities (wt %) of Triolein/Fatty Acid and Triolein/Fatty Alcohol Mixtures in Surfactant Solutions at 30 °C

	2% Tergitol 15-S-7			2% $C_{12}E_6$	
		+0.15% C_6OH	+0.30% C_5OH		+0.30% C_6OH
triolein	0.24−0.30	0.40−0.46	0.38−0.41		0.25−0.30
TO/OAc[a] = 85/15	0.50−0.55	0.60−0.65	0.60−0.65	0.04−0.07	0.70−0.75
TO/OAc = 80/20	0.65−0.70	<0.06[b]			
TO/OAc = 75/25	0.17−0.20[b]	<0.06[b]	0.12−0.15[b]		0.80−0.85
TO/OAc/LA = 85/10/5	0.47−0.51	<0.06[b]			
TO/LA = 85/15	0.55−0.60	<0.04[b]	0.17−0.20[b]		0.60−0.65
TO/LA = 75/25	0.12−0.14[b]	<0.04[b]			
TO/OA = 85/15	0.41−0.49	0.55−0.60			
TO/OA = 75/25	0.21−0.25[b]	<0.04[b]			

[a] TO, triolein; OAc, oleic acid; LA, lauric acid; OA, oleyl alcohol. [b] Sample reached cloud point first.
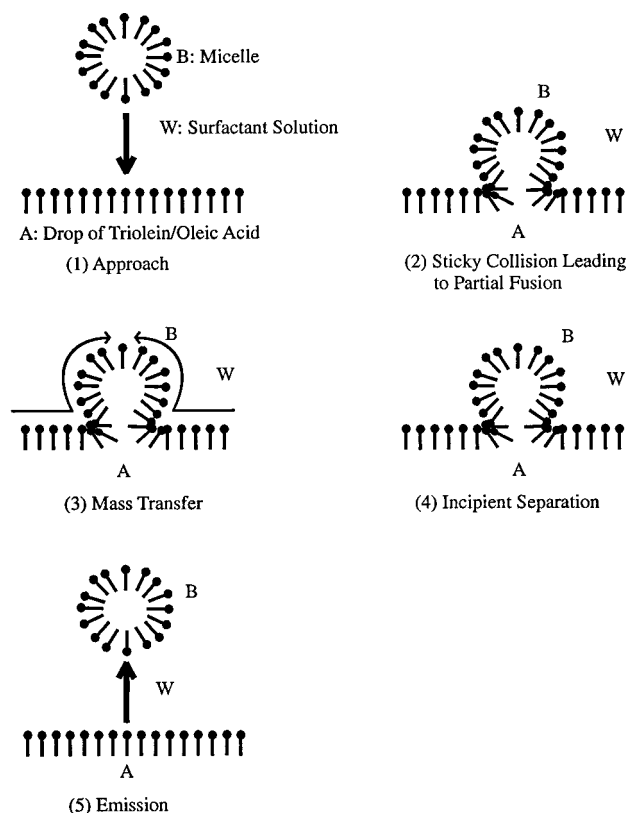

Figure 16. Schematic diagram of solubilization resulting from micelle collision with interface. Adapted from ref 12 with addition of Marangoni flow promoting solubilization.

presumably reduced the interfacial tension gradient to a much smaller value.

2. Effects of pH and Acid Type. Figure 7 shows that rapid initial solubilization does not occur when the surfactant solution is buffered at pH 10, a result that is initially surprising since sodium oleate is much more soluble in water than oleic acid. As Figure 8 shows, an interfacial tension minimum occurs at pH 10 but much more quickly than at neutral pH (Figure 5). Because some acid at the interface is almost immediately converted to the more hydrophilic soap, the surfactant film becomes hydrophilic before much of the oleic acid can be solubilized.

As a result, little rapid solubilization, which apparently requires the drop interface to be somewhat lipophilic, takes place. In particular, the rapid increase in tension as the interface becomes more hydrophilic (Figure 8) largely or completely eliminates the local tension gradient promoting solubilization which is discussed above and illustrated in Figure 16.

The vigorous Marangoni convection observed during the first 45 s for the vertical cell experiment at pH 10 (Figure 9a) and the low interfacial tensions seen at short times in Figure 8 raise the question of whether substantial inital shrinkage occurred for the drop experiment of Figure 7 during the first few seconds following contact before the video system could be focused on a particular drop. In most cases it took 15−20 s for a suitable drop to be located and brought into focus so that its diameter could be measured. However, in one experiment for the conditions of Figure 7 when the drop was injected with a micropipet using a scheme similar to that described by Deshikan and Papadopoulos,[15] drop diameter was measured within 1 s after detachment from the micropipet. No shrinkage was observed after this time. This observation confirms the conclusion that the amount of initial solubilization is small at pH 10.

The existence of Marangoni convection such as that shown in Figure 9a for situations where a mixture of a nonpolar oil and a fatty acid contacts an alkaline surfactant solution is not surprising though previous studies[16,17] have used hydrocarbons instead of triglycerides as the nonpolar oil. The spontaneous emulsification in the aqueous phase seen in Figure 9a is probably produced by local supersaturation. Under these conditions micelles containing a mixture of fatty acid and soap as well as solubilized triolein diffuse away from the interface, where the pH is lower than that in the bulk aqueous phase. When the micelles reach the bulk surfactant solution, the higher pH there converts more of the acid to soap, making the micelles too hydrophilic to solubilize all the triolein present. As a result, spontaneous emulsification of triolein occurs. A similar mechanism was presumably responsible for spontaneous emulsification of oil in the aqueous phase observed when a mixture of *n*-decane, oleic acid, and 2-pentanol was contacted with an aqueous solution of NaCl and NaOH in the vertical-stage microscope for conditions when the oleic acid/sodium oleate mixture formed was expected to be preferentially soluble in water.[16]

As indicated in Figure 9b, the Marangoni flow for the triolein/oleic acid mixture cannot be maintained when the thickness of the lower pH region near the interface becomes

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sufficiently large. Both the lower gradient in pH and the enhanced viscosity of the emulsion may contribute to this behavior.

Calculations similar to those described at the beginning of this section for triolein/oleic acid mixtures indicate that only 20−25% as much triolein as lauric acid (by volume) is solubilized by 2 wt % Tergitol 15-S-7 during the first few minutes after drop injection. Since the total initial solubilization rate ($-dR/dt$) is only about four or five times that of pure triolein in this case, one finds that the initial triolein solubilization rate is comparable to that for pure triolein. These results suggest that the intermediate phase shown in Figure 11 solubilizes relatively little triolein. For 2:1 and 1:2 mixtures of oleic and lauric acid the volumetric ratios of triolein to acid solubilized during initial drop shrinkage are about 1.5 and 1.2, respectively, and the initial rates of triolein solubilization are about four times that of pure triolein. Thus, both the ratio and the initial rate are intermediate between those found for pure oleic acid and pure triolein.

The intermediate phase shown in Figure 11 for a triolein/lauric acid mixture did not exhibit birefringence, myelinic figures, or other evidence that it was liquid crystalline in nature. Perhaps lauric acid reduced the cloud point temperature of the surfactant solution to a value below the experimental temperature, and a surfactant-rich L_1 phase developed. In any case the intermediate phase evidently had a low content of triolein, as indicated above. No intermediate phase was seen in the vertical cell experiments for the system of Figure 1, which did exhibit rapid initial solubilization.

Summary

Rapid initial solubilization accompanied by vigorous Marangoni flow occurs when drops of triolein/oleic acid are injected into nonionic surfactant solutions. In the systems studied the volumetric ratio of triolein to oleic acid solubilized during this period is about 2. This behavior continues until most of the oleic acid has been solubilized, after which the solubilization rate becomes that seen for pure triolein. Similar behavior was seen for *n*-hexadecane/oleic acid and triolein/oleyl alcohol drops. One possible mechanism for the rapid solubilization is local Marangoni flow from the drop, which has a low tension, into a micelle temporarily attached to the drop which has a higher tension.

The rapid solubilization was not seen at high pH except during the first few seconds after contact, possibly because conversion of acid to soap increased interfacial tension, eliminating the local Marangoni flow from drop to micelle. Similarly, the initial solubilization rate of triolein was not significantly enhanced when lauric acid was used instead of oleic acid because an intermediate phase containing little triolein was formed.