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RATES OF SOLUBILIZATION OF TRIOLEIN AND TRIOLEIN/FATTY ACID MIXTURES AND DISSOLUTION PROCESSES OF NEAT SURFACTANTS

by

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A THESIS SUBMITTED
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DOCTOR OF PHILOSOPHY

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Abstract

Rates Of Solubilization Of Triolein And Triolein/Fatty Acid Mixtures And Dissolution Processes Of Neat Surfactants

by

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Videomicroscopy was used to measure rates of solubilization of triolein drops injected into thin, rectangular glass cells containing solutions of nonionic surfactants and their mixtures with alcohols at various temperatures. In most cases the solubilization rate per unit area was independent of time and of initial drop size. This indicates that processes occurring at the interface control the rate of solubilization. The solubilization rate can be increased by increasing the flexibility of the surfactant films either by adding short-chain alcohols or by using a surfactant mixture with a thinner and less ordered hydrocarbon chain region.

Videomicroscopy was also used to investigate the mechanisms and rates of dissolution of neat, liquid nonionic surfactants in water. A microinjection technique was used to produce drops of pure C_{12}E_5 and C_{12}E_6, which dissolved rapidly at temperatures below their cloud points. The results indicated that the process was diffusion controlled. Estimates of effective binary diffusion coefficients in the intermediate liquid crystalline phase(s) which formed were obtained by combining their measured growth rates in one-
dimensional experiments where neat surfactant contacted water with measured dissolution times of surfactant drops.

Drops of the commercial nonionic surfactants Neodol 25-7 and Tergitol 15-S-7 required considerable time for complete dissolution at temperatures just below their cloud points. Considerable spontaneous emulsification of water in the surfactant drops was also observed. Moreover, the final small drops frequently became elongated and sometimes formed conical projections that emitted jets. Similar behavior was seen for the model system C_{12}E_{6}/n-decanol/water and occurs because the more hydrophilic component dissolves more rapidly.

At 30°C a compact mass of viscous myelinic figures developed when a drop of C_{12}E_{3} was injected into water. However, complete dissolution occurred when 5 wt% of small SDS crystals was added to the drop. Here too considerable spontaneous emulsification, elongation, and some jetting were observed. Complete dissolution also occurred when C_{12}E_{4} drops were injected into dilute SDS solutions. However, dissolution was much slower when the SDS concentration was large enough that hexagonal and cubic intermediate phases formed in addition to the lamellar phase which was seen in all cases.
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Chapter 1: Introduction

Surfactants have long been known to human beings for their applications in many aspects of life, for example, washing and cleaning processes. Soaps, salts of naturally occurring fatty acids, were the form of surfactants most widely known to mankind in early days. Surfactants perform important functions in cleaning, such as loosening, emulsifying and holding soil in suspension until it can be rinsed away. Surfactants can also provide alkalinity, which is useful in removing acidic soils. Soaps and detergents are essential to personal and public health. Through their ability to loosen and remove soil from a surface, they contribute to good personal hygiene; reduce the presence of germs that cause infectious diseases; extend the useful life of clothes.

Soap has been known for at least 2,300 years. The Phoenicians prepared it from goat's tallow and wood ashes in 600 BC. Soap was widely known in the Roman Empire, whether the Romans learned its use and manufacture from ancient Mediterranean peoples or from the Celts. The Celts produced their soap from animal fats and plant ashes [Britannica, 1997]. Large-scale commercial soapmaking did not occur until 1791 when a French chemist, Nicholas Leblanc, presented a process for making soda ash, or sodium carbonate, from common salt. Soda ash is the alkali obtained from ashes that combines with fat to form soap [SDA, 1994].

Surfactants also play an important role in biological systems. Cellular membrane lipids are principally of two types, phospholipids and sterols (generally cholesterol). Phospholipids are a type of surfactant and are the primary components to make up the cell
membranes. Bile salts are another type of surfactant that plays a major role in digestive process of lipids in intestine. Bile salts in digestion act to emulsify lipid-soluble groups and also to increase the solubility of lipids in water. The existence of surfactants in the lung is also very important to lives. Without a very thin layer of surfactant film in air sacs (alveoli) of the lung, the air sacs would collapse and we could not breathe to survive. The disease of a lack of surfactant, a pulmonary substance that prevents the alveoli from collapsing after the infant's first breaths, is called *Idiopathic Respiratory Distress Syndrome* or *Hyaline Membrane Disease*. It is a very common complication in infants, especially in premature newborns, and was formerly the leading cause of death in premature infants [Britannica, 1997].

Surface-active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as *lyophobic* group, with a group that has strong attraction with solvent, known as *lyophilic* group [Rosen, 1989]. In general, a surfactant molecule has a hydrophilic head and one or two hydrophobic tails. The tail, usually a long hydrocarbon or fluorocarbon chain, acts to reduce solubility in water while the polar head, often ionizable, has the opposite effect. These unique amphiphilic structures and properties give surfactants many applications. Surfactant molecules can accumulate along the air-liquid and liquid-liquid interfaces and thus reduce both surface tensions and interfacial tensions at the same time. In addition, surfactant molecules can form aggregates, called micelles, in aqueous solution to achieve segregation of their lipophilic parts from water. In nonpolar media, the structures of aggregates are similar but reversed, with the hydrophilic heads in the interior region.
surrounded by an outer region having hydrophobic groups and nonpolar solvent. The shape of micelles is important in determining various properties of a surfactant solution, such as its viscosity and its capacity to solubilize water-insoluble material. The major types of micelles appear to be small spherical, elongated cylindrical (rod-like), lamellar (disk-like), and vesicles. In addition to forming these small aggregates, surfactant molecules can also arrange themselves as large bilayer sheets, which can assemble into liquid crystalline phases, or form microemulsions which are often encountered in many processes with use of surfactants, such as in detergency and enhanced oil recovery (EOR).

Turkey-red oil, the first synthetic surfactant other than soaps, was produced by neutralization of sulfated castor oil with base and has been used mainly in dyeing industry since about 1830. Most synthetic surfactants were first invented by German companies in the beginning of this century in response to a World War I-related shortage of fats for making soap. Alkyl naphthalene sulfonate, the first synthetic detergent and a soap replacement was developed in 1916. By 1953, sales of detergents in the U.S. had surpassed those of soap[SDA, 1994]. Today, detergent surfactants are made from a variety of petrochemicals and oleochemicals.

1.1 Detergency

Washing and cleaning have been known as one of the most important applications of surfactants to mankind since the time before Christ. Soap was the primary detergent used for that purpose till the synthetic detergent surfactants came out in the early 20th century. However the detergency of soap in hard water always encounters the unwanted
precipitate with calcium or magnesium ions that wastes the soap and decreases its detergency. After synthetic detergent surfactants were produced, laundry detergents became primary agents in washing and cleaning. In order to have better detergency in the old days, the wash temperature was kept around 95°C, although temperatures between 40°C and 60°C are now common and the trend is toward washing at even lower temperature [Houston, 1995].

Detergency can be defined as the removal of unwanted substances (soil) from a solid surface brought into contact with a liquid [Azemar, 1997]. Several important factors influence the effectiveness of surfactants in laundry detergents and must be taken into consideration in determining the mechanism of soil removal. These factors include the nature and concentration of the washing solution, additives (for examples, lipase enzymes and builders), nature of solid surface (for example, weave of fabrics), hydrodynamic conditions, mechanical action during washing, temperature, water hardness, electrolyte levels, and the composition of soil [Kissa, 1987]. With environmental concern, energy conservation (such as low temperature washing -- approximately between 15°C and 35°C), and increasing use of temperature-sensitive fabrics, better understanding of the mechanism of soil removal and development of improved surfactants and detergent formulations has become focus of interest [Miller, 1993].

The soil may be either liquid or solid, and is usually a combination of these two. Liquid soil is non-volatile and non-aqueous and usually has oily nature. Oily soils include such common soils as skin sebum, dirty motor oil and vegetable oil. Table 1-1 shows the typical composition of human sebum. Protease and lipase enzymes are now used as
additives in detergents to chemically break down polymeric protein soil stains or to hydrolyze triglyceride soils, and thereby aid the surfactant in soil removal. Water hardness also influences profoundly the detergent effectiveness. In hard water, calcium and magnesium ions may precipitate certain surfactants before they are able to act on the soil. Builders such as zeolite, sodium tripolyphosphate (STPP), sodium silicate and sodium carbonate are added in laundry detergents to minimize the negative effects of water hardness on detergency. However with environmental concern phosphates such as STPP are banned from use in some countries. For the same reason builders are absent and surfactants with better resistance to water hardness are used instead in some liquid laundry detergents. The washing temperature not only changes the performance characteristics of the dissolved surfactants, but also changes the physical properties of oily soils left on fabric. Surfactants with high Krafft points may precipitate in cold water and exist as surfactant monomeric solution. With relatively small change in temperature, especially near melting-solidification temperature, oily soils can change to particulate solid soils or solid-liquid mixtures, making them more difficult to remove.

The surface conditions and morphology of fabrics have major effects on detergency of oily soils, and so does the weave of fabrics. Loosely woven fabric is typically easier to clean. An overview considering the detergency processes from the standpoints of surface and colloid chemistry was presented by Carroll [1993] recently. Discussions on the theoretical aspects of the deposition and removal of oily and particulate soils were presented, and consideration was given to the different oily soil removal mechanisms of roll-up and emulsification, which are discussed later in this section. Cotton
fabric contains rough and irregularly shaped hydrophilic fibers. In contrast, synthetic polyester fabric contains uniformly cylindrical and more hydrophobic fibers. The differences in surface properties of these two major materials also affect the mechanism of soil removal from substrates. The so-called roll-up mechanism tends to occur at a solid substrate preferentially wet by the liquid, while the solubilization-emulsification mechanism is most important for hydrophobic substrates. Both mechanisms will be introduced in the following (see Figure 1-1) [Kissa, 1987; Miller, 1993].

Table 1-1: Composition of Human Sebum

<table>
<thead>
<tr>
<th></th>
<th>Lauric</th>
<th>0.4 wt%</th>
<th>20.0 wt%</th>
<th>40.0 wt%</th>
<th>2.4 wt%</th>
<th>24.6 wt%</th>
<th>9.0 wt%</th>
<th>4.0 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Fatty Acids</td>
<td>Myristic</td>
<td>2.4 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Palmitic</td>
<td>5.6 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Stearic</td>
<td>1.4 wt%</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Oleic</td>
<td>9.2 wt%</td>
<td></td>
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<tr>
<td></td>
<td>Linoleic</td>
<td>1.0 wt%</td>
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<tr>
<td>Triglycerides</td>
<td>Tripalmitin</td>
<td>20.0 wt%</td>
<td></td>
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<tr>
<td></td>
<td>Triolein</td>
<td>20.0 wt%</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>n-eicosane</td>
<td>1.2 wt%</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>n-tetracosane</td>
<td>1.2 wt%</td>
<td></td>
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<tr>
<td>Wax Esters</td>
<td>Stearyl oleate</td>
<td>12.3 wt%</td>
<td></td>
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<tr>
<td></td>
<td>Oleyl oleate</td>
<td>12.3 wt%</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Squalene</td>
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<td></td>
</tr>
<tr>
<td>Cholesterol</td>
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</tr>
</tbody>
</table>

1.1.1 Roll-up Mechanism

Roll-up mechanism was first described by Adam and mainly occurs for the removal of oily soils from hydrophilic fabrics such as cotton fibers [Adam, 1937]. It consists of the displacement of soil from a solid substrate through a mechanism of preferential wetting by
the liquid. The conditions for oily soil removal by roll-up mechanism are favorable when the contact angle of oil on fiber is increasing - the interfacial tension between fiber and water is small; the interfacial tension between soil and fiber is large. Lowering the interfacial tension between oil and water increases the contact angle of oil on fiber when the contact angle is greater than 90° (see Figure 1-2). It will also facilitate the roll-up of oily soils.

Figure 1-1: Mechanisms of liquid soil removal [Miller, 1993]

(a) Emulsification resulting from soil-water interfacial tension reduction

(b) Roll-up resulting from fabric wetting

For quite hydrophilic substrates like cotton fibers, the contact angle of oil on fiber is normally greater than 90°. Adsorption of surfactants on fibers decreases the water-solid
(fabric) tension, causing an increase of the contact angle and wettability of the fabric by water and oil stains to be entirely lifted off the fibers. Swelling of the cotton fibers with water increases the hydrophilicity of cotton fabrics and this phenomenon enhances the roll-up mechanism. The lifted oil drops break off fibers into washing solution partially or completely as a result of hydrodynamic forces accompanying agitation in the washing bath. If the contact angle is less than 180° but more than 90°, the oily soils will not be displaced spontaneously but can be removed by hydraulic currents in the washing bath.

Figure 1-2: Schematic drawing of an interfacial force balance for an oil drop attached on a hydrophilic solid substrate in aqueous surfactant solution

\[ \gamma_{ow} \cos(\theta) = \gamma_{sw} - \gamma_{so} \]

When the contact angle is less than 90° on less hydrophilic surfaces, only small portions of oily soils may be displaced at the water-soil interface when subjected to the hydraulic currents in the washing solution and parts of the oily soils still remain attached on the substrates. Mechanical work or some other mechanism, such as solubilization-emulsification mechanism, is required to remove the residual oil on the substrates. Low interfacial tension at the oil-water interface will play an important role in oily soil removal. The thin oil films can be easily deformed to form small emulsion droplets while the contact
angle still remains low. Such an emulsion mechanism is very important in soil removal on hydrophobic surfaces.

1.1.2 Solubilization-Emulsification Mechanism

Synthetic fabrics are more hydrophobic and therefore soil removal through roll-up mechanism can not work very effectively because of the difficulties to increase the contact angle and wettability of fabrics by water. However the removal of oily soils from such hydrophobic substrates can be greatly enhanced through the process of solubilization-emulsification with the formation of intermediate phases at the detergent solution-oil interface. In some situations emulsification of non-polar-polar mixtures without agitation, i.e. spontaneous emulsification, has been observed [Miller, 1993; Fujii, 1980; Stevenson, 1961]. The rates of emulsification may be largely affected by the factors such as the ratio of polar to non-polar oils, the temperature, and the electrolyte concentration.

The maximum detergency of oils may be associated with the presence of an insoluble, surfactant-rich intermediate phase - a middle phase microemulsion [Raney, 1987a; Rosen, 1989] that was found to contain substantial amounts of both oils and surfactants. That is the maximum removal of hydrcarbon soil from cotton/polyester fabrics is achieved at the condition of phase inversion -- where both interfacial tensions along interfaces of oil-middle phase and of middle phase-aqueous phase are minimal [Raney, 1987a, Benson, 1986]. Recent studies showed the maximum removal of mineral oil by linear ethoxylated alcohols, nonionic surfactants, occurs at 15-30°C above the cloud point [Benson, 1986; Raney, 1987a, 1990, 1991]. Conditions are optimum at/near the
temperature called phase inversion temperature (PIT). More detailed description of PIT is
given at Section 2.2.6.

Lim *et al.* [1991] and Raney *et al.* [1990] also showed that very good detergency
for polar soils and mixtures of polar and nonpolar soils occurs whenever the system is
initially above the PIT, where the formation of a liquid crystal intermediate phase was
observed at the detergent solution-oil interface [Kielman, 1979; Fujii, 1980; Stevenson,
1961; Lawrence, 1959]. In the systems Raney *et al.* [1990] studied, cetane/oleyl alcohol
and cetane/oleic acid blends, the PIT is below the cloud points of surfactants, and the
highest level of soil removal is found between PIT and cloud point rather than only at the
PIT.

Laurie Thompson [1992, 1994] of Unilever Research found that in some cases
wettability effects must also be considered in removal of oily hydrocarbon soils from
synthetic fabrics. He summarized that two types of detergency maxima were observed,
one corresponding to the phase inversion condition and one appearing when the surfactant
is more hydrophilic and roll-up is important. At the phase inversion condition the
interfacial tension is low. If the contact angle is such that the oil spreads in the capillaries
between the individual fabric fibers, then oil removal remains poor unless the interfacial
tension between oil and aqueous phase is ultralow indeed (~10^{-3} \text{ mN m}^{-1}). He also
concluded that the failure of the roll-up mechanism to operate under the low interfacial
tension conditions of the phase inversion condition is due to a sudden drop in contact
angle.
Solubilization of oily soils was first proposed by McBain as an important mechanism in soil removal [McBain, 1955]. Substantial amount of oily soil can be solubilized into surfactant micelles directly if surfactant concentrations are high enough -- few times larger than the critical micelle concentration (CMC). Normally CMC of nonionic surfactants is very low, about 2 orders lower than CMC of ionic surfactants [Rosen, 1989], and hence the potential use of nonionic surfactants in laundry detergents for low-temperature washing to solubilize oily soils becomes attractive. Also greater amounts of oil solubilized per unit molecule of surfactant were observed for many nonionic surfactants. In this study, rates of solubilization of triolein, a slightly polar triglyceride oil, into nonionic surfactant micellar solutions were investigated. Soil solubilization rates are often enhanced when surfactant-rich phases are present in washing solution. These middle phase microemulsions can solubilize oily soils directly. For nonionic surfactants such phases exist at temperatures above cloud point temperatures.

Solubilization and emulsification are the major factors in removal of oily soils from hydrophobic, synthetic fabrics [Miller, 1993; Raney, 1987a; Solans, 1992]. Since the solubilization-emulsification mechanism occurs primarily at the oil-detergent solution interface, the detergency is influenced by the phase behavior of corresponding water-oil-surfactant system [Miller, 1993].

1.2 Other Applications of Surfactants

Surfactants have long been used in many products or industries to improve our living. For example, lecithin, most of which comes from soybean oil, is widely used as a
wetting and emulsifying agent, e.g., in animal feeds, baking products and mixes, chocolate, cosmetics and soaps, dyes, insecticides, paints, and plastics. Detergency is one of the most important applications of surfactants. The use of microemulsions in detergency was explored [Dörfler, 1996; Azemar, 1997]. Other applications of surfactants can be seen in pharmaceutical field such as drug delivery and controlled release systems. Surfactants could also be used in tertiary oil recovery, although there is no process established on a commercial scale because of unfavorable economics.

1.2.1 Enhanced Oil Recovery (EOR)

During the first and second energy crises in 1970s and early 1980s, scientists and engineers did not only look for possible substitute fossil fuels. They also investigated ways to increase the oil production from that residual oil trapped in porous rocks of oil reservoirs after primary and secondary oil recovery, which does not usually exceed 30-40% of the original oil in place [Bavier, 1997]. In order to obtain the maximum oil recovery and reduce the capillary forces through the “pore neck“, an ultralow interfacial tension at oil-water interface is necessary. Formation of middle phase microemulsions gives this advantage with its ultralow interfacial tension at interfaces coexisting with an aqueous and an oil phase.

With injection of surfactants to form middle phase microemulsions in reservoir, the oil recovery efficiency is increased. However the efficiency is slowed down sometimes by “fingering“ in the reservoir. Mobility control is required to prevent the redispersion of mobilized oil. Usually the viscosity required for mobility control is obtained by adding
water-soluble polymers. In that situation the mobility of polymer slug must be less than that of surfactant slug. However Lawson et al. proposed another way of mobility control with the use of "foam" with adequate strength by injecting gas after surfactant solution into the reservoir [Lawson, 1980].

Chemical flooding, including surfactant flooding and caustic flooding, was the subject of much research during the energy crisis. However with the slump of oil price after the oil embargo in 70s and Iran-Iraq War during 1980s, oil production by such EOR processes is not economically attractive and hence the research activities of EOR have been largely discontinued.

1.2.2 Extraction of Contaminated Solids

During the past decades, the protection of earth environments, such as air, water and soil, has become more and more important to many people. The need for such protection has been emphasized by scientific discovery, for example, the rising of sea level by unexpectedly fast melting of icebergs due to global warming effects (the Greenhouse effects) and the increasing number of people who suffer from skin cancer resulting from being exposed to higher levels of ultraviolet (UV) radiation due to the depletion of the stratospheric ozone. Most of these harmful UV rays are absorbed by a very thin layer of ozone in atmosphere. However, satellite observation has shown that the depletion holes of ozone over poles, which were never seen before, occur earlier, are bigger, and last longer now. In order to slow down the depletion of the ozone layer over poles, the Montreal Protocol on substances that deplete the ozone layer was signed in 1987. The treaty has
been highly successful and full recovery of stratospheric ozone layer will eventually take place. The potential stratospheric ozone-depleting chemicals such as some types of chlorofluorocarbons (CFCs) are banned from use and even the products made by the processes that used these chemicals are boycotted [Hileman, 1997]. With the threat of Greenhouse effect, potential agreement on a treaty regarding universal global reduction in emissions of greenhouse gases such as total emission of CO₂ is undertaken such as the Earth Summit in Brazil in 1992 and the recent United Nations climate conference at Kyoto, Japan in December of 1997. The Kyoto protocol requires the United States to reduce greenhouse gas emissions by 7% below 1990 levels by 2008-2012. The European Union would reduce them by 8% and Japan by 6%. The accord approved by the Kyoto conference takes effect once it is ratified by 55 nations, representing 55% of 1990 CO₂ emissions.

However there are some important differences in the advances in obtaining clean soil and water in comparison with unpolluted air. Reducing the contents of harmful species in the atmosphere by low-emission techniques and stack gas cleaning can only be done now and in the future. Retrospective reduction is not possible. The conditions on water and soil contamination are much different. Avoiding further input of pollutants is part of the cleaning strategy. Removal of pollutants resulting from the past activities is another. Contaminants in soil could last for long times and even diffuse outward into surrounding clean soil. Therefore contaminant removal from highly polluted soils becomes more important and is a challenging topic.
*In situ* soil washing is an efficient treatment technology for the remediation of contaminated soils. Contaminants can be dissolved in the washing solution and brought up to surface followed by separation of contaminants and clean solution. Similar to enhanced oil recovery, solubilization of contaminants is often involved and release of contaminants from soil surface is made by altering the wettability and lowering the interfacial tension in particular [Bonkhoff, 1997]. As indicated previously, microemulsions are known to have very high solubilization capacity of polar and nonpolar organics, as well as the ultralow interfacial tension along the interfaces with aqueous phase and oil phase, which enhances the uptake of pollutants [West, 1992; Stickdorn, 1994; Baran, 1996]. Surfactant solution is injected into contaminated soil to form a microemulsion that mobilizes contaminants and then is extracted to surface. It is noteworthy that a small amount of microemulsion left over in aquifer is inevitable. The use of biodegradable surfactants is preferred in soil remediation process [Salma, 1997; Szafranski, 1997].

Similarly a surfactant/foam process is being developed for remediation of aquifers contaminated with dense nonaqueous phase liquid (DNAPL) such as chlorinated solvents. Foam is used for mobility control to displace DNAPL from low permeability sands that are often unswept during a conventional remediation process [Szafranski, 1997; Hirasaki, 1997].

1.2.3 The Use of Surfactants in Drugs

It is well known that drug efficiency can be limited and side effects of some drugs can result from their poor aqueous solubilities. Increasing the aqueous solubility of a drug
can improve its efficacy and reduce its dosage. As mentioned above a microemulsion phase has very good solubilization capacity for polar and nonpolar organics. The use of microemulsions in pharmaceutical field has attracted strong interest.

Lipid-soluble vitamins such as vitamin A, D, E and K, are often more stable when solubilized in a microemulsion than when dissolved in vegetable oil. That is, these fat-soluble vitamins can be preserved better in a microemulsion. Chiu et al. [1992] claimed that solubilization within nonionic surfactant micelles protects vitamin E from oxidative degradation. Another example of using microemulsion in drugs is the solubilization of poorly water-soluble steroids in an O/W microemulsion. Several steroids in a nonionic surfactant micellar system and in an oil-in-water microemulsion system were studied [Malcolmson, 1993]. However, there is presently only one microemulsion formulation on the pharmaceutical market. It is an oral microemulsion pre-concentrate formulation of cyclosporin called Neoral® by Sandoz (Basel, Switzerland) [Lawrence, 1996]. It is widely anticipated that there will be more microemulsion, or microemulsion-based, drug delivery systems in the not too distant future.

Vesicles of lipid bilayers have been investigated as drug-delivery vehicles for almost 20 years. The vesicles’ interior space is separated from the surrounding solution because small molecules have only limited permeability through the bilayer [Rosoff, 1996]. Walker et al. [1997] reported that molecular-recognition processes mediated by lipophilic receptors and substrates can be used to produce a multicompartamental aggregate of tethered vesicles encapsulated within a large bilayer vesicle.
1.3 Thesis Objectives and Outline

The first objective of this study was to develop an improved understanding of the solubilization for removal of liquid triglyceride soils. The emphasis was on the rates of solubilization although experiments on equilibrium solubilization capacities and phase behavior were carried out as required to interpret the rate experiments. Since triolein does not exist in nature in pure form but with some fatty acids from hydrolysis, the rates of solubilization of triolein and its mixtures with fatty acids into nonionic surfactant solutions were measured.

The second objective of this study was to study dynamics and to enhance understanding of the rate processes involved in the interaction of water with neat surfactants and surfactant mixtures. Dissolution of surfactants in short times is needed for effectiveness. However, the formation of liposomes is inevitable in some cases. Therefore measuring dissolution rates of nonionic surfactants and methods to enhance complete dissolution of surfactants in water were investigated later in this study.

Necessary background information on nonionic surfactants in aqueous solutions and kinetics of solubilization process is provided in Chapter 2. Experimental procedures and all equipment set-ups are described in Chapter 3. Included are the oil drop contacting experiments and the surfactant droplet dissolution experiments.

Chapter 4 focuses on the rates of solubilization of triolein and triolein/fatty acid mixtures by nonionic surfactant solutions. Our results showed that triolein could be solubilized by double-tailed, secondary alcohol ethoxylate surfactant, Tergitol 15-S-7. The solubilization rates increased very fast as the temperature approached the cloud points
The presence of small amount of oleic acid in oil greatly enhanced the solubilization rates of triolein in the first few minutes after contacting surfactant solutions. The differences of solubilization rates of triolein with/without oleic acid are more obvious in aqueous solutions of linear alcohol ethoxylate surfactants. The triolein drops in C_{12}E_{4}/n-hexadecane microemulsions at ambient temperature (around 23°C) exhibited very high solubilization rates after a certain "induction" period, during which no activity was observed, compared to those lower rates of solubilization for triolein drops in Tergitol 15-S-7 solutions at the same temperature.

The dissolution processes of nonionic surfactants and their mixtures with alcohols are presented in Chapter 5. The diffusivities of intermediate phases of surfactant-water systems can be determined by combining the use of droplet dissolution experiments and vertical cell contacting experiments. The diffusivities obtained from this scheme are in very good agreements with those obtained by the studies of Mullins-Sekerka instabilities of the interface between the liquid crystalline and the isotropic phases. Jetting, budding and deformation of the remaining drops of surfactants in water were also observed in some commercial nonionic surfactants and surfactant-alcohol mixtures in absence of external stirring or change of environments, such as temperature changes.

Chapter 6 discusses the complete dissolution of lipophilic nonionic surfactants with addition of anionic surfactant. Addition of proper anionic surfactants into nonionic surfactants that form insoluble myelinic figures can produce complete dissolution in water. The effects of amounts of anionic surfactants in surfactant mixtures on the dissolution times were also investigated and so was the effect of drop sizes of surfactant mixtures.
Finally, the last chapter summarizes the major findings of this work, and the directions of future work are discussed.
Chapter 2: Background

2.1 Surfactant Classification

The surface-active molecule (surfactant) is partly hydrophilic (water-soluble) and partly lipophilic (soluble in lipids or oils). It consists of two important parts, a hydrophobic tail and a hydrophilic, polar often ionizable, head group. The tail, usually a long hydrocarbon chain and less often fluorocarbon or siloxane chain, acts to reduce solubility in water while the head group has the opposite effect. For surface activity in a particular system the surfactant molecule must have a chemical structure that is amphiphilic in that solvent under the condition of use [Miller, 1985; Rosen, 1989].

Depending on the nature of hydrophilic group, surfactants are classified as anionic surfactants (negative charge), cationic surfactants (positive charge), nonionic surfactants (no charge), and zwitterionic (separate positive and negative charges) or amphoteric surfactants (either positive or negative charge depending on pH or other conditions), because surfactants are primarily applied in aqueous solutions (see Table 2-1).

An anionic surfactant carries negative charge on its surface-active portion, for example, RCOO’Na’ (soap) and RC₆H₄SO₃’Na’ (alkylbenzene sulfonate). Anionic surfactants are used in laundry and hand dishwashing detergents; household cleaners; and personal cleansing products. They made up 64.5% of surfactant production in the United States in 1994, and 63.8% in 2000 (by prediction) [Ainsworth, 1996]. Properties are generally high sudsing. Linear alkylbenzene sulfonates, alcohol ethoxysulfates, alkyl sulfates and soaps are the most common anionic surfactants.
A cationic surfactant has positive charge on its surface-active portion, for example, $\text{R}_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$ (tetraalkylammonium chloride salts). Quaternary ammonium compounds are the principal cationics. Cationic surfactants are widely used in fabric softeners, antistatics, hair conditioners, dispersants, flotation agents, as the disinfecting/sanitizing ingredient in some household cleaners, etc. These were only 9.4% of total surfactant production in the United States in 1994 and about 9.8% in 2000 by prediction [Ainsworth, 1996].

A nonionic surfactant doesn't bear any charge on its surface-active portion, for example, $\text{R}(\text{OC}_2\text{H}_4)_n\text{OH}$ (linear ethoxylated alcohol) and $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_n\text{OH}$ (polyoxy-ethylenated alkylphenol). Nonionic surfactants made up 25.4% of surfactant production in the United States in 1994 and will stay at the same percentage in 2000 by prediction [Ainsworth, 1996]. Nonionic surfactants are low sudsing and are typically used in laundry and automatic dishwasher detergents and rinse aids. Nonionic surfactants most commonly used for detergency process are synthesized by polymerization with ethylene oxide and alcohols over catalysts. For example, $\text{C}_{12}\text{E}_7$ and $\text{C}_{12}\text{E}_3$, of which $\text{C}_m\text{E}_n$ denotes a linear ethoxylated alcohol with m-carbon tail and n-ethylene-oxide as head group, are widely used in formulation of laundry detergents. They are resistant to hard water, polyvalent metallic cations, and electrolyte at high concentration, but may become insoluble in water on heating. Commercial material is a mixture of products with a wide distribution of polyoxy-ethylene chain lengths. In addition to the use in detergents, they are also commonly seen in use as emulsifying agents for paints, cosmetic emulsifiers, food
emulsifiers for bread, ice cream and margarine. Linear ethoxylated alcohols are easily biodegradable.

Due to the concern of “green movement” in Europe advocating the use of environmentally compatible, nontoxic products that are derived from renewable resources, Henkel in Hamburg, Germany first adopted alkylpolyglycoside (APG) in 1988 in their laundry detergent formula. APGs are sugar-based nonionic surfactants derived from glucose and fatty alcohols and are highly foaming. They are used in light duty liquid detergents and a number of other applications such as personal care. They exhibit excellent biodegradability characteristics, have low aquatic toxicity, and are extremely mild [Houston, 1997].

Mixtures of anionic and nonionic surfactants are universally used in liquid detergents for laundry applications since they are more effective than anionic alone for washing synthetic fibers at low temperatures.

A zwitterionic or amphoteric surfactant may carry both positive and negative charges on its surface-active portion, for example, \( \text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{SO}_3^- \) (sulfobetaine). They are compatible with all other types of surfactants and may be adsorbed onto negatively or positively charged surfaces without forming hydrophobic films. Amphoteric surfactants are used in personal cleansing and household cleaning products. They are also used in cosmetics, fabric softeners, and pigment dispersion aids. Imidazolines and betaines are the major amphoteric.
<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>Name</th>
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| Anionic Surfactant | R-C$_6$H$_4$-SO$_3$Na  
  R= C$_{10}$ - C$_{13}$ | Linear Alkylbenzenesulfonates (LAS) |
| Cationic Surfactant | CH$_3$  
  R-N$^+$- CH$_3$Cl$^-$  
  CH$_3$  
  R = C$_{16}$ - C$_{18}$ | Tetraalkylammonium Chloride |
| Nonionic Surfactant | R-O-(CH$_2$CH$_2$O)$_n$-H  
  R= C$_6$ - C$_{16}$ | Linear alcohol ethoxylates |
|                  | CH$_2$OH  
  HO  
  O  
  CH$_2$  
  HO  
  O  
  O---C$_n$H$_{2n+1}$ | Alkylpolyglycoside (APG) |
| Zwitterionic Surfactant | H$_2$C-COO$^-$  
  R-N$^+$-H  
  H$_2$C-COOH  
  R= C$_{12}$ - C$_{18}$ | N-Alkyl-$\beta$-iminodipropionic Acids |
The differences in the nature of hydrophobic groups are not so clear as those of hydrophilic groups. They are mostly long-chain hydrocarbon residues. A few have fluorocarbon chains. They are resistant to biodegradation even when the fluorocarbon chains are straight. Fluorinated surfactants are more surface active in organic solvents than the corresponding hydrocarbon surfactants and can reduce the surface tension of water to much lower values than are obtainable with surfactants containing hydrocarbon groups. They also show better resistance to strong acids and bases, reducing and oxidizing agents, and heat. However, they are much more expensive.

2.2 Surfactant Characteristics

2.2.1 Critical micelle concentration (CMC)

The concentration at which micelles first form in solution is called *critical micelle concentration* (CMC). At any concentration lower than CMC, surfactant molecules arrange themselves in solution as a monolayer along the interface or exist as monomers in bulk solution. Further addition of surfactant to the solution beyond CMC only gives rise to further micelle formation. It is found that at or in the vicinity of CMC many transport or equilibrium properties of bulk solution change very sharply with changing surfactant concentration, e.g., surface tension, solubility, light scattering properties, electric resistance or conductance, osmotic pressure, density, detergency, turbidity, self diffusion, etc. CMC can be experimentally determined by measuring the surfactant concentration at which sudden changes of physical properties occur. At CMC the interface becomes saturated and further addition of surfactant molecules form into micelles and don't change
interfacial properties. For example, surface tension stays almost constant beyond the CMC.

Figure 2-1: Solubility and CMC curves of the sodium dodecyl sulfate (SDS) in water [McBain, 1955]

Nonionic surfactants have very low CMC values of the order of $10^{-5}$ mole/liter.

On the other hand, anionic surfactants have higher CMC values in the order of $10^{-3}$ mole/liter as electrical repulsion of charged head groups acts against aggregation. It is worth pointing out that with comparable chain lengths, CMC's are much lower for nonionic than anionic surfactants, for example, $6.4 \times 10^{-5}$M for $C_{12}E_{5}$ in water at 25°C and
8.2×10³ M for sodium dodecyl sulfate in water at the same temperature [Rosen, 1989].

Evidence shows that the micelles formed initially contain only a relatively small number of surfactant molecules, only around 50 to 100, and are spherical. At higher concentrations these spherical micelles may adopt a cylindrical, disk-like, lamellar, or spherical vesicle-like form.

2.2.2 Krafft point or Krafft temperature

The minimum temperature for micelles to exist is called the Krafft point or Krafft temperature [Miller, 1985; Laughlin, 1994] (see Figure 2-1). Many surfactants are highly soluble in liquid water at high temperatures, but at lower temperatures separate from solution as a crystal phase. The crystal solubility boundary of such surfactants is called Krafft boundary. The solubility of surfactant increases with rising temperature. The solubility-temperature plot of surfactant in water exhibits a very sharp jump in solubility due to the micelle formation in solution. The Krafft point is exactly the intersection point between extrapolation of CMC versus temperature curve and solubility boundary.

For ionic surfactants solubility is really low, less than its CMC, below Krafft temperature and solution contains almost no micelles. Above Krafft temperature micelle formation becomes possible. It is noteworthy that surfactants (detergents) are less effective below Krafft point. Sodium oleate has Krafft temperature about 28°C, which is important in some experiments of this study -- the solubilization rate of triolein/oleic acid mixtures in surfactant solution at alkaline condition. The experiments were conducted at 30°C to assure that the surfactant remained above its Krafft point.
2.2.3 Cloud point temperature

When a micellar solution of nonionic surfactants is heated above a certain temperature that is called cloud point temperature, it becomes turbid. At the cloud point the surfactant solution undergoes phase separation into a surfactant-rich liquid phase and an almost micelle-free dilute solution whose concentration is equal to CMC at that temperature. The phase separation is reversible; when the mixture is cooled down to the temperature below the cloud point temperature, these two phases merge to form a clear phase again. If a clear aqueous solution of pure surfactant separates into mixtures of two liquid phases when it is raised beyond cloud point temperature, these mixtures are invariant with respect to composition (temperature and pressure specified).

The phase separation at cloud point temperature is believed to be due to the decrease in intermicellar repulsion and/or the sharp increase in aggregation number of the micelles except in some surfactant solutions, e.g., C_{12}E_8. As the cloud point is approached, the solubilization of nonpolar solubilizates increases very rapidly, probably because of an increase in aggregation number of the micelles [Carroll, 1981, 1982; O'Rourke, 1987]. Benson et al. showed a high level of detergent activity could be achieved in cold water washing through adjustments of a surfactant system solubility, i.e., cloud point, by addition of various hydrophobic additives [Benson, 1985a, 1985b].

The temperature at which clouding phenomena occur depends on the structure of polyoxyethylenated nonionic surfactants. For example, for nearly pure surfactants, the cloud point temperatures are 10°C for C_{12}E_4, 30°C for C_{12}E_5, 52°C for C_{12}E_8, and 62°C for C_{12}E_7. (Data supplied by manufacturer, Nikko Chemicals. Tokyo, Japan) Huibers et al.
[1997] recently developed a general empirical relationship for estimating the cloud point of pure nonionic surfactants of the alkyl ethoxylate class from their structures.

2.2.4 Phase rule

Phase behavior in a surfactant solution must be consistent with the Gibbs phase rule: [Smith, 1987; Laughlin, 1994]

\[ F = C - P + 2 \quad (2.2-1) \]

This equation implies that, in a system having \( C \) components, the number of phases \( P \) plus the number of degrees of freedom \( F \) is a constant for any mixture of these components. The number of components in surfactant mixtures is the number of chemical compounds present in the system. If the surfactants are involved in chemical reactions in the solution, the number of degrees of freedom is that of equation (2.2-1) minus the number of independent chemical reactions. In applying the Phase Rule, only the number of components and phases are important. It is not necessary to consider the structure of the phases. For example, when SDS (sodium dodecyl sulfate) is dissolved in water, it dissociates into two discrete ions. The number of one ion is equal to the number of the other and the ratio of sodium cations to dodecylsulfate anions can not vary independently. (i.e. electroneutrality or stoichiometry provides another constraint to balance the increase in actual species in solutions.) Thus, it only counts as one component when calculating degrees of freedom of a system. The concept of “phase” was described as: a phase may be regarded as a volume element of a mixture within which smooth variations in space of the density variables exist [Laughlin 1994]. However, from Gibbs’ time to present phases
have been defined primarily in terms of uniformity of composition, but often they are
defined in terms of uniformity of “properties”. The latter concept of “phase” will be used
in counting the number of phases in a system to calculate the degrees of freedom of a
specific system, although no phase is uniform in composition at molecular scales
[Smoluchowski, 1908; Buff, 1965, 1989].

2.2.5 Other Phases Involving Surfactant Aggregates

2.2.5-1 Micellar Phase

At surfactant compositions below the critical micelle concentration (CMC),
surfactant molecules in the bulk liquid are “unstructured” and only surfactant molecular
solution exists. It is called submicellar solution. Surfactant molecules arrange themselves
as monolayer along the interface or exist as monomers in bulk solution. Once it reaches
CMC, further addition of surfactant into solution only forms an isotropic phase, L₁ -- a
micellar solution (Figure 2-2). The shape of micelles can be spherical, rod-like, long
cylindrical, or flexible, thread-like. The size of micellar aggregates varies enormously,
from few tens of molecules to enormous flexible thread-like micellar network that are
cross-linked so as to create a gel-like structure [Clausen, 1992]. In a spherical micelle the
surface is covered with hydrophilic groups. The hydrophobic parts of surfactant molecules
contact preferentially with each other or oily molecules inside the micelle. The rod-like
micelles of anionic surfactants are favored by high concentrations and low temperature,
and the “spherical-to-rod” structural transition in micellar aggregates often occurs within a
Figure 2-2 Phase Diagram of $C_{12}EO_6$/water system [Mitchell, 1983]
very narrow composition range of surfactant as surfactant concentration increases. These changes in micellar structures also change the rheological properties of micellar solutions. For example, dilute phases containing spherical micelles are Newtonian liquids whose viscosities are not much greater than that of liquid water. Liquid phases containing cylindrical (rod) micelles are considerably more viscous, and also display pronounced shear-birefringence [Laughlin, 1994].

At higher temperature or concentration a reversed micellar phase exists as L₂ in many systems - in contrast to the normal micellar phase L₁. Both L₁ and L₂ can exist as a homogeneous phase or in equilibrium with water phase W depending on the concentration and temperature. L₁+W exists at temperatures above cloud point temperature.

2.2.5-2 Liquid Crystal Phases

With further substantial amount of surfactant added into a micellar solution, it forms a new phase -- quite viscous and showing static bright birefringence under crossed-polarizers. This phase is called “liquid crystal”. Surfactant molecules possess substantial order -- positional and orientational, but are not truly crystalline. X-ray diffraction experiments suggest that one such phase consists of many long, parallel, rod-like micelles arranged in hexagonal array. The micelle interiors are fluid, resembling liquid hydrocarbons. The liquid crystalline phase in this case is called the normal hexagonal or simply the hexagonal phase - denoted as H₁ (see Figures 2-2 and 2-3). H₂ is for the reverse hexagonal phase consisting of long, cylindrical aligned reverse micelles. At even higher surfactant concentrations the arrangement of surfactant molecules into bilayers is more
Figure 2-3: Schematic drawings of lamellar and hexagonal liquid crystalline phases [Miller, 1985]

(a) Lamellar phase

(b) Hexagonal phase
favorable and this liquid crystalline phase is known as the lamellar phase - denoted as $L_\alpha$ (Figure 2-3). The lamellar phase also shows bright static birefringence under crossed-polarizers, but has lower viscosity than the hexagonal phase. The liquid crystalline phases melt at sufficiently high temperatures into isotropic phases ($L_1$, $L_2$ or $L_3$ phases). For example, the $H_1$ and $L_\alpha$ phases in Figure 2-2 melt and form the $L_1$ phase at their maximum temperatures of existence. In general, at lower temperatures the $L_\alpha$ phase may undergo a phase transition to the lamellar $L_\beta$ phase where surfactant molecules exhibit various degrees of in-plane positional and orientational order [Smith, 1988, 1990; Roux, 1994].

Cubic phase, denoted as $V_1$ (or $V_2$ for its reversed form), is another type of liquid crystalline phase with different structures that are bicontinuous (Figure 2-2). It is isotropic under crossed-polarizers, not like the other liquid crystalline phases showing very strong birefringence under that circumstance. Its surfactant concentration is between that of the hexagonal phase and of the lamellar phase (Figure 2-2). Other types of cubic phases are also known but are not relevant for the situations of interest in this thesis.

Under crossed-polarizers the textures of different liquid crystalline phases appear greatly different. For example, the texture of the lamellar phase appears like “mosaic” and focal conic, in contrast to a “marble” like texture for the hexagonal phase (Figure 2-4) [Patrick, 1997; Laughlin, 1994]. More photomicrographs of textures of liquid crystalline phases were reported by Rosevear [1954].

Liquid crystals with local orientational order are not as often seen as those with positional orders -- like lamellar, cubic, and hexagonal phases. They are called nematic phases or micellar liquid crystal phases. The nematic phase is the least highly ordered of
Figure 2-4: Drop of C_{12}E_6 in water at 35°C shows H_{1}, V_{1} and L_{\alpha} phases.
the liquid crystal states since only local orientation prevails. There are three distinct structural varieties of micelles. The nematic phase, “canonic” denoted as $N_c$ corresponds to the rod shaped micelles, and the $N_D$, “discotic”, for the disk shaped micelles. The third one is that the micelles may be asymmetric ellipsoids or biaxial platelets that can form a biaxial nematic phase denoted $N_B$. The nematic phases are to be found intermediate to an isotropic micellar solution at high temperatures/low concentrations and lamellar for disks/hexagonal for rods at low temperature/high concentrations. The dimension of these micelles is in the range of 4-8 nm. Photomicrographs of nematic textures can be found in the references [Holmes, 1983; Boden, 1985].

2.2.5-3 Isotropic bicontinuous phase

Another isotropic phase, called “sponge phase” and denoted as $L_3$, forms at temperatures above those where water and lamellar phase coexist for nonionics. The $L_3$ phase exhibits streaming birefringence phenomena under shear. It has low viscosity and is slightly turbid. It is also referred to as $D'$ phase in some of the literature. Its structure has been studied by many experimental techniques, and most of them suggest a bicontinuous structure of highly connected bilayers produced by deforming the large bilayer sheets of the $L_u$ phase [Hoffmann, 1992; Porte, 1996]. It was previously considered that this phase consisted of discrete disc-like aggregates [Miller, 1986, 1990. Ghosh, 1987]. These two proposed models are only different with respect to the question of connectivity but are the same in that both assume a local bilayer structure [Ott, 1992].
The main difference between $L_\alpha$ and $L_3$ is that the initially flat bilayers in $L_\alpha$ are deformed into saddle-like surfaces in $L_3$. Freeze fracture electron micrographs of the $L_3$ phase clearly show that the bilayers are indeed multiconnected and have saddle-shaped microstructures with a negative Gaussian curvature [Strey, 1990, 1992; Hoffmann, 1992]. The connection of the bilayers was also inferred from self-diffusion coefficient measurement of the surfactant molecules by performing fluorescence recovery after fringe pattern photobleaching experiments [Ott, 1992]. That is, the results rule out the isolated disk structure and are consistent with interconnected bilayers.

An interesting phenomenon of epitaxy at the interface between a lamellar $L_\alpha$ phase and an $L_3$ phase in the quasiternary lyotropic system cetylpyridinium chloride/brine/n-hexanol mixture was recently reported by Quilliet et al. [Quilliet, 1996] The phase diagram is shown as Figure 2-5 and the coexistence of $L_\alpha$ and $L_3$ phases ranges from 37-39 to 51-53°C. The interface between $L_\alpha$ and $L_3$ adopts geometry characteristic of a tilted anchoring of the lamellar layers on the sponge phase. From the image of $L_\alpha$ droplet in $L_3$ phase, it indicates that the layers are spherical and concentric. The image analysis of the droplet profile shows that it is a part of a logarithmic spiral centered on the pole. The topology and swelling behavior of a $L_3$ phase is also reported by Maldonado et al. who studied the behavior with the small angle x-ray scattering technique [Maldonado, 1996]

2.2.5.4 Microemulsion phase

Microemulsions were first introduced and discovered by Hoar and Schulman, who used this term to describe the transparent system obtained by titration of turbid emulsions
Figure 2-5: Brine rich part of the phase diagram of cetylpyridinium chloride (CPCI) \(n\)-hexanol/brine (0.2 M NaCl) system [Porte, 1989]

\[
\frac{\psi_A}{\psi_S} \quad (L_3/L_1) \quad L_3
\]

\[
(L_\alpha/L_3) \quad (L_\alpha/L_1) \quad L_1
\]

\(\Phi_S\): the volume fraction of surfactant
\(\Phi_A\): the volume fraction of alcohol
\(\Phi_W\): the volume fraction of brine
with medium chain alcohols [Hoar, 1943]. Since that time many experiments have been performed to determine their structures.

Microemulsions are transparent dispersions containing two immiscible liquids with aggregates on the order of 10 nm, small enough to yield a transparent solution though sometimes with a bluish appearance. Microemulsions may be oil-in-water (O/W), in which water is the continuous phase, or water-in-oil (W/O) where oil is the continuous phase, or a bi-continuous phase (D). Oil-in-water (O/W) microemulsions and water-in-oil (W/O) microemulsions are also denoted as W_m and O_m respectively. O/W microemulsions are produced by emulsifying agents that are more soluble in the water than in the oil, whereas W/O microemulsions are produced by emulsifying agents that are more soluble in the oil than in the water. In a three-phase system, the middle phase between the aqueous phase (W) and the oleic phase (O) is a bicontinuous microemulsion (D). The ultralow tensions at the interfaces between microemulsions and excess oil or excess water phases are one of the important properties of microemulsions. The middle phase normally is clear and has low viscosity.

Microemulsions are considered as thermodynamically stable, in contrast to emulsions that are thermodynamically unstable. Schukin and Rehbinder [1957, 1958] suggested that a colloidal dispersion could be thermodynamically stable provided that interfacial tension was low enough that the increase in interfacial energy accompanying dispersion of one phase in the other could be outweighed by the free energy decrease associated with the entropy of dispersion [Miller, 1985]. Ruckenstein et al. recognized the importance of this effect for microemulsions and developed a suitable analysis to describe
it quantitatively [1975]. Ruckenstein also pointed out that the free energy decrease accompanying adsorption of surfactant molecules from a bulk phase favors the existence of a large interfacial area and hence plays a major role in stabilizing microemulsions [1978]. Microemulsions are generally prepared with surfactant mixtures or with mixtures of cosurfactants and surfactants in conditions with proper balances between hydrophilic and lipophilic properties for the required oil and water phases under the conditions of use.

At low salinities an oil-in-water microemulsion of an anionic surfactant coexists with excess oil. In a test tube with this condition, the microemulsion below oil phase in the test tube is called "lower phase" microemulsion \( W_m \), which is normally water continuous. At high salinities the situation is reversed and an oil-continuous "upper phase" microemulsion \( O_m \) coexists with excess brine. In suitable conditions, for instance at intermediate salinities, a three-phase system exists (\( W+D+O \)) and the middle surfactant phase (D) plays very important roles with its ultra low interfacial tension in some applications, for example, in the solubilization-emulsification soil removal process and in enhanced oil recovery from reservoir rock. The ultralow interfacial tension between microemulsions and the residual petroleum mobilizes the entrapped residual oil in the capillaries of the rock by greatly reducing its capillary pressure. The salinity where the two tensions are equal is called "optimum salinity" which is very important in application. At the optimum salinity the amounts of oil and brine solubilized in the surfactant phase are approximately equal.

Nonionic surfactants are less sensitive to salt than anionics, but sensitivity to temperature changes is quite a distinctive feature of the behavior of nonionic surfactants.
The direction of shift in phase behavior of nonionic surfactants with temperature is the same as that described above for anionics with varying salinity [Shinoda, 1973, 1986; Miller, 1985]. In suitable conditions and systems, multiple phases may coexist in equilibrium. Zourab et al. reported five coexisting phases in a nonionic surfactants/triolein /n-hexadecane/brine system at 18.6°C [Zourab, 1995].

In systems of dilute aqueous surfactant solutions (e.g. less than 5 wt% C_{12}E_{4}, C_{12}E_{5}, C_{12}E_{6}) and long-chain hydrocarbon with comparable amounts of oil and water, the sequence of multiple phase regions observed as the temperature increased were as follows; [Shinoda, 1973,1986; Tungsuputra, 1994]

\[(a) \ W_m + O \rightarrow (b) \ W + D + O \rightarrow (c) \ W + O_m\]

where the temperature of (a) < (b) < (c) (also see Figure 2-6).

Figure 2-6 Phase behavior of the hydrocarbon-water-nonionic surfactant system. [Shinoda, 1973,1986]

(a) \ Oil + Lower phase Microemulsion

(b) \ Middle phase microemulsion + excess oil + excess water

(C) \ Water + Upper phase Microemulsion

Phase Inversion Temperature
The structure of microemulsion phase has attracted many researchers in the past. Bicontinuous structure of microemulsion is now well accepted. With experiments showing that electric conductivity in microemulsion phases varied continuously with salinity, Scriven [1976] proposed that the surfactant phase is bicontinuous, perhaps resembling consolidated porous media where both solid and pore space are continuous or certain mathematical models of bicontinuous structures. Hwan et al. [1979] proposed that it was water-continuous near the transition to the water-continuous lower phase and oil-continuous near the transition to the oil continuous upper phase. In addition to evidence from measurements of electric conductivity, self diffusion (tracer and NMR studies) gave the direct evidence for a bicontinuous structure [Lindman, 1980]. Freeze fracture electron microscopy (FFEM) images of bicontinuous microemulsions also display saddle-shaped structures that are in agreement with NMR-self-diffusion measurements on the same system [Strey, 1994]. For studies of microemulsion structure, NMR together with small angle scattering probably provides the two most important and powerful experimental techniques [Lindman, 1996]. The structure of microemulsions studied by NMR was recently published by Lindman et al. [1996], while a detailed discussion on small angle scattering from microemulsion was given by Glatter et al. [1996].

Recently Kahlweit et al. [1995, 1997] presented recipes for preparing nontoxic microemulsions with unsaturated or saturated fatty acid alkyl esters, or essential oil, biological amphiphiles and alkane-1,2-diols as cosolvents. The features of nonionic microemulsion phase behavior are reviewed and summarized by Schubert and Kaler.
[1996], while the phase behavior of ionic microemulsions is reviewed by Lekkerkerker, et al. [1996]. An overview of microemulsions was recently published by Paul and Moulik [1997]. In addition, another recent overview on theoretical modeling of microemulsions was presented by Widom [1996].

2.2.6 Hydrophilic-Lipophilic-Balance (HLB) and Phase Inversion Temperature (PIT)

In 1949 Griffin made an attempt to classify surface active agents by their hydrophilic-lipophilic balance (HLB), which was made quantitative in terms of HLB numbers [Griffin, 1949]. The smaller the HLB value, the more oil soluble the surfactant. Surfactants with HLB number of 7 have equal oil and water solubilities. The HLB value for some types of nonionic surface-active agents can be calculated from their structural groupings [Griffin, 1954]. Davies [1959] subsequently suggested a simple group method of calculating HLB values from surfactant structures. There have been numerous attempts to determine HLB numbers from other fundamental properties of surfactants (e.g. from cloud points and CMCs) [Rosen, 1989]. The HLB number of the mixture is the weighted average of the individual HLB numbers. An HLB value of 3-6 is the recommended range for W/O emulsification and 8-18 is recommended for O/W emulsification.

The phase inversion temperature (PIT) is that where the surfactant phase (D) has equal interfacial tensions with oil and water. That is the temperature at which an O/W type emulsion inverts to a W/O type emulsion. At PIT surfactant phase is the middle phase (D) in W+D+O system and has equal volumetric solubilization of oil and water. D phase solubilizes substantial amount of oily soil and has very low interfacial tension with water.
According the phase rule, PIT is invariant at constant pressure in a three-component system. This phase transition at PIT was first observed by Shinoda [1964, 1967]. PIT is also referred to as HLB temperature in some of the literature.

Kunieda and Shinoda proposed correlation of HLB (hydrophilic-lipophilic-balance) numbers and oil properties to estimate PIT values [Kunieda, 1985]. The results were in good agreement with experimental values [Solans, 1992]. The PIT is affected by the HLB and the concentration of the surfactant, the polarity of the oil phase, the phase ratio of the bulk phases and the presence of additives in them, and the distribution of polyoxyethylene (POE) chain length in polyoxyethylene nonionics [Shinoda, 1968; Mitsui, 1970]. PIT information is more useful than the HLB number because it takes into account both the nature of the oil and the temperature-dependent phase behavior of the C,E, surfactant [Schubert, 1996]. The recent studies showed that optimum mineral oil removal is achieved at the phase inversion temperature (PIT) where the interfacial tension between soil and water is lowest and the solubilization rate and capacity are highest. Also removal of hydrocarbon oil from cotton/polyester fabric was found maximum within the temperature range that surfactant forms the D phase.(see Section 1.1.2) Addition of hydrophobic long-chain alcohol into the oil phase of a surfactant-water-hydrocarbon system decreases substantially the PIT values of ethoxylated nonionic surfactant systems.

2.3 Kinetics of Solubilization Process

Kinetic measurements of interfacial mass transfer require the simultaneous monitoring of interfacial area and volume as a function of time. The drop-on-fiber,
rotating disk method, and the oil-drop-contacting method are among the few experimental methods suitable to study the oil solubilization kinetics. Oil-drop-contacting method was developed as part of this work and is described later. The drop-on-fiber and droplet contacting methods provide the information in systems with total surfactant concentrations up to few percent, and the rotating liquid disk method does that in even more concentrated systems. In addition, some attempts to obtain kinetics information have been made using observations of turbidity.

2.3.1 The rotating disk method

The use of rotating disk method with well-defined liquid/liquid or solid/liquid geometrical interface allows us to study the interfacial mass transfer process as a function of flow. This method, theoretically systematized by Levich [1962], gives the mass transfer coefficients for a diffusion-controlled solubilization as a function of experimental parameters and physical properties. At first this method was used in studies of solubilization rates of solid lipids in different surfactant solutions by Tao et al. [1974], Chan et al. [1976], Huang et al. [1981] and Shaeiwitz et al. [1981]. They studied the variation of these rates with fluid flow, detergent concentration, acid solubility, temperature and added salts. Later it was modified and extended to study solubilization of liquid lipids in surfactant solutions.

The initial experiments used mixtures of tagged and untagged solid fatty acid solubilizates that were compressed into circular disks. The radioactive disks of solubilizates were rotated with a motor and were immersed in surfactant solutions of
interest. Samples were taken from the surfactant solution at certain intervals and their acid concentrations measured with a scintillation counter.

Some modifications of spinning disks were made to extend this technique to include liquid state solubilizates by using wettable polymer membranes. Huang et al. made spinning disks of liquid with Celegard polymer and epoxy resin [Huang, 1981]. The pores of Celegard film are wet by linoleic acid but not by water. The liquid acid flowed into the disk from a reservoir. However it was not possible to unambiguously determine if the observed data were affected by effects associated with the membrane itself, for example, if diffusion gradients produced within the membrane or interfacial resistances at liquid-membrane were dominating the observed kinetics [Ward, 1995].

Recently with novel invention of polymer foams with very high internal phase volume, these materials replaced the membranes in holding liquids in spinning disks [Ward, 1995] They are open-cell structures which can absorb liquids even up to 95-98% of their geometrical volume, allowing the creation of a body that is greater than 95% liquid but has a well defined geometric shape [Williams, 1988a, 1988b, 1990].

With a mass balance on the total volume of surfactant solution \( V \), the dissolution rate can be expressed as

\[
\frac{V}{A} \frac{dC}{dt} = k(C^{sat} - C) \quad (2.3-1)
\]

where \( A \) is the disk's area; \( k \) is the rate constant; \( C \) and \( C^{sat} \) are the acid concentrations in surfactant solution at time \( t \) and at saturation respectively.
If the dissolution is diffusion controlled, one finds that the following relation is true in both solid and liquid disk systems [Huang, 1981; Shaeiwitz, 1981].

$$\frac{kR}{D} = 0.62 \cdot \left( \frac{R^2 \omega}{u} \right)^{1/2} \left( \frac{u}{D} \right)^{1.3}$$ (2.3-2)

where $D$ is the solute’s diffusion coefficient; $u$ is the solution’s kinematic viscosity; $R$ and $\omega$ are the disk’s radius and rotational speed; the constant 0.62 is given as 0.61 [Levich, 1962] and 0.65 [Chan, 1976] instead.

2.3.2 The drop-on-fiber method

The drop-on-fiber method allows monitoring simultaneously both volume $V$ and the interfacial area $A$ of the oil drop in surfactant solutions of interest as a function of time, and thus calculating the rates of oil solubilization [Carroll, 1976, 1981]. This technique is simple to operate. It defines the system by fixing in space one droplet of emulsion dimensions anchored in surfactant solution by an inert fine cylindrical fiber. Provided that the distortions of drop from gravity are negligible, the shape of the axisymmetric drop is purely determined by capillary forces.

A droplet adhering to a cylindrical fiber will assume an axisymmetrical conformation (see Figure 2-7), if (a) the contact angle is not too high, (b) the droplet dimensions relative to the fiber radius are not too small, and (c) gravitational forces are small in comparison with capillary forces. The contact angle $\theta$, surface area $A$, and volume $V$ of the droplet can be calculated from three linear dimensions, $x_1$, $x_2$ and $L$ shown on Figure 2-4. The formal
expression for the rate of solubilization is \(-(1/A)(dV/dt)\). With the above assumptions the rate is given as

\[
Rate = -\frac{1}{A} \frac{dV}{dt} = -\frac{dx_2}{dt} = -x_1 \frac{dn}{dt} \quad \text{where } n = x_2/x_1. \tag{2.3-3}
\]

Figure 2-7 Profile of the drop-on-fiber system with characteristic parameters

2.3.3 Turbidity Measurement

The method used for the determination of the rate of oil solubilization, which was developed by Herbert L. Benson (Shell Westhollow Research Center, Houston, Texas), consists of determining the decrease in turbidity of a macroemulsion upon addition of a model oil to a surfactant solution [Benson, 1985a; Bolsman, 1988]. Injection of known volume of oil into dilute surfactant solution produces a turbid macroemulsion upon agitation. At \(t_o\), an oil is injected and the turbidity data are sampled and the time elapsed to reach, e.g., 75% and 50% of the initial turbidity value recorded. This yields \(t_{75}\) and \(t_{50}\) with the corresponding turbidities \(T_{75}\) and \(T_{50}\). The solubilization rate is then arbitrarily defined as:
\[
\text{Rate} = \frac{T_{75} - T_{50}}{t_{75} - t_{50}} \quad (2.3-4)
\]

with a rate constant \(K_{50/75}\):

\[
K_{50/75} = \left(\frac{2}{T_{75} + T_{50}}\right) \cdot \left(\frac{T_{75} - T_{50}}{t_{75} - t_{50}}\right) \quad (2.3-5)
\]

In the turbidity decay curves the starting turbidity \(T_{100}\) is normalized to a value of one. \(K\) is pseudo rate constant because the turbidity is not linearly proportional to the amount of unsolubilized oil. \(K_{90/100}\) is often used instead.

However this method is limited in obtaining the quantitative data on the solubilization process because phenomena related to particle size and coalescence also affect the value of turbidity.

2.3.4 Ostwald-Ripening Method

Ostwald ripening is often encountered in emulsions. It is known as the phenomenon that larger crystals or aggregates can grow at the expense of smaller ones because of differences in chemical potential between particles of different sizes [Kabalnov, 1994; Hunter, 1992]. However, in some circumstances coalescence of smaller particles will also form some larger ones, Ostwald ripening can happen even in the conditions that are unfavorable to such coalescence mechanism. The theory of the Ostwald ripening process has been well developed [Lifshitz, 1958; Wagner, 1961].

Ostwald ripening is a phenomenon that involves the solubilization or stability of emulsion droplets. Kabalnov investigated the effect of sodium dodecylsulfate (SDS)
concentration on the rate of Ostwald ripening in undecane-in-water emulsions [Kabalnov, 1994]. His results showed that varying the surfactant concentration did not affect the rate of Ostwald ripening, despite a considerable increase in equilibrium solubilization. McClements et al. studied solubilization kinetics by measuring the time dependence of average size distributions of hydrocarbon emulsion droplets dispersed in nonionic surfactant solutions and time-dependence of the droplet concentration. Their results showed that the droplets did not shrink with time, despite the variation of droplet concentration with time, although one might expect the emulsion droplets to shrink as solubilization proceeded, because of oil molecules moving from the droplets to the surfactant micelles. An explanation of theirs for this phenomenon is that once emulsion droplets shrink below a critical size their water solubility increases dramatically and Ostwald ripening becomes appreciable. Additionally their results suggest that the increase in droplet size owing to Ostwald ripening is more than sufficient to counterbalance the decrease in size caused by solubilization [McClements, 1995; Weiss, 1996, 1997]. That is, solubilization tends to decrease the mean droplet size and Ostwald ripening tends to increase the mean droplet size. The increasing water solubility of oil in droplets of increasing curvature due to Ostwald ripening is given as: [Kabalnov, 1992; Israelachvili, 1992]

$$\ln \frac{S}{S_n} = \frac{2\sigma \cdot V_m}{r} \quad (2.3.6)$$

At the steady-state of the process, the Ostwald ripening kinetics becomes independent of the initial particle size distribution and is characterized by (i) linear growth
of the third power of the mean radius with time and (ii) the scaled particle size distribution that becomes time invariant. The growth rate can be rewritten as follows: [Kibalnov, 1994]

\[
\frac{d\langle r \rangle^3}{dt} = \frac{8\sigma \cdot S_w \cdot V_m \cdot D \lambda(\phi)}{9K_G T}
\] (2.3.7)

where \(\sigma\) is the interfacial tension; \(V_m\) is the molar volume of the substance of the dispersed phase; \(\langle r \rangle\) is the number-average radius; \(S_w\) is the dimensionless solubility of the bulk dispersed phase in the medium (mL/mL, reduced to the density of the solute); \(D\) is the diffusivity of the dispersed phase substance in the medium; \(K_G\) is the universal gas constant; \(T\) is the absolute temperature; and \(\alpha\) is the rate of Ostwald ripening. The coefficient \(\lambda(\phi)\) reflects the dependence of the Ostwald ripening rate on the volume fraction of particles \(\phi\). This parameter takes on the values from 1 (\(\phi\to0\)) to near 2.5 (\(\phi=0.3\)). Local equilibrium is assumed at the interface and interfacial processes are assumed to be fast. Accordingly solubilization rate can be obtained by measuring Ostwald ripening rate.

Grätz recently published the new relations between particle growth and particle size distribution. One can calculate the growth paths of particles with the information contained in scaled particle size distributions measured during steady-state Ostwald ripening processes [Grätz, 1997].

2.4 Nonequilibrium Dynamic Contacting Method

2.4.1 Vertical Cell Contacting Method
Behavior which occurs when two fluids not at equilibrium are brought into contact is interesting in that intermediate phases not present initially can form at the surfaces of contact. Determining how many and which intermediate phases form can provide useful information. For example, the information can be applied to enhanced oil recovery and better formulations of laundry detergents such as to determine conditions for forming microemulsion. Direct observation of the dynamic phenomena is made possible through some microscopic techniques which are described in this section. These techniques employ a videomicroscopy system [Raney, 1985a,b; Benton, 1986; Mori, 1989].

On a cell placed in a vertical configuration of microscope, the aqueous surfactant solution initially fills half of the cell. The oil is then injected very carefully at the top of the cell (see Figure 2-8). The phase changes at the interface are monitored with elapsed time. Intermediate phases can be formed just in a very short time period after contact. The water-oil interface is stabilized by gravity. The interface won’t be distorted by its density difference if the heavier phase is initially placed in the bottom. However, distortion of interface accompanying the formation of intermediate phases or interfacial convections such as Marangoni flow is sometimes observed. The velocities of interfaces and rates of formation of intermediate phases also can be obtained from this technique. With diffusion path theory it is possible to calculate and predict the formation of intermediate phases and spontaneous emulsification. Diffusion path theory was used in the early studies of spontaneous emulsification in oil-water-alcohol systems [Ruschak, 1972].

The vertical contacting technique was used to study the dynamic contacting in water-anionic surfactant-oil systems representative of those used in enhanced oil recovery
processes [Raney, 1985a]. The formation of intermediate phases and spontaneous emulsification in a brine-petroleum sulfonate-hydrocarbon system were found to be predictable from calculated diffusion paths with relevant phase diagrams [Raney, 1987b]. It was also used with nonionics for detergency studies [Benton, 1986; Raney, 1987a]. Experiments were designed to investigate the effects of changes in temperature on the dynamic phenomena which occur when aqueous solutions of pure non-ionic surfactants contact hydrocarbons such as n-tetradecane and n-hexadecane.

Figure 2-8: Rectangular glass capillary cell used in vertical-stage contacting experiments

2.4.2 Oil-Drop-Contacting Method

The oil-drop-contacting method has been successfully used to observe intermediate phase formation when use of a large quantity of experimental materials is not desirable [Raney 1985b; Mori, 1990; Lim, 1991a,b,c, 1992; Tungsbutra, 1992, 1994; Rang, 1995].
The oil drops are injected into a pool of surfactant solution and therefore water-to-oil ratio in this technique is really large, as in practical washing (also see Figure 2-9). It also gives the advantage that the surfactant concentration of aqueous solution is nearly constant while surfactant concentration can change at sufficiently long times in some contacting experiments of vertically mounted cell.

Figure 2-9: Schematic drawing of oil drop contacting experiment

Sealed End (Norland 63)

Oil drop

Glass Cell

Needle

3” x 1” Microscope Slide

Specification:

Syringe: Hamilton Model 1705
Gas Tight, 50μl

Needle: Hamilton Model 91033
OD=210 μm, ID=110 μm

Capillary Cell: Vitro Dynamics
Cat. # 2540
50 mm x 4 mm x 400μm

Unlike the contacting experiments on vertically oriented cells, the concentration of the entire oil phase in this technique varies with time. It can yield some useful information on when the intermediate phases form [Lim, 1991b; Rang, 1995]. It also enables the
observation of intermediate phases which do not form right after initial contact and disappear later. This technique also defines very simple geometry of oily drops which is very easy to be applied to the studies of solubilization kinetics without too much effort in solving very complicated mathematics. In Section 4.1, there is a description of how this technique was modified to be used in studying solubilization kinetics.

Both techniques of contacting methods were also used to obtain the experimental data on dissolution of surfactants. Combining the data from both techniques it is possible to determine the intrinsic diffusion coefficients of water in those intermediate phases occurring after the contact of corresponding surfactant and water. (see Section 5.1)

2.5 Diffusion Path Analysis

The use of diffusion paths is one way in which the isothermal diffusion processes between two nonequilibrium phases can be described. It allows intermediate phases and compositions to be plotted on an equilibrium phase diagram as an time-invariant path between two initial compositions by solving species transport equations with certain assumptions and boundary conditions. Although diffusion path analysis was widely used in metallurgy and ceramics [Kirkaldy, 1958a,1958b,1963; Chang, 1993; Naka,1997]. it has been applied in liquid systems to explain spontaneous emulsification very successfully by Ruschak et al. [1972], and Raney et al. [Raney, 1987b].

Consider mass transport in a ternary system with a planar moving interface. At time zero, two semi-infinite uniform phases are brought to contact at the interface, x=0, in absence of any convection. Ternary diffusion effects and cross-diffusion coefficients are neglected. In addition diffusion coefficients are taken as independent of composition
within any phase. The further assumption is made that the moving planar interface is at its local equilibrium, i.e. diffusion through bulk phases is much slower than adsorption and desorption at the interface.

With this assumptions the diffusion equations can be expressed as

$$\frac{\partial w_j^i}{\partial t} = D_j^i \frac{\partial^2 w_j^i}{\partial x^2} \quad i,j=1,2 \quad (2.5-1)$$

with boundary conditions that $w_j^i$ at infinity is equal to its composition before contact. In equation (2.5-1), $x$ is the distance from the initial surface of contact, $t$ is the time; $w_j^i$ is the local mass composition of species $i$ in phase $j$; $D_j^i$ is the diffusion coefficient of species $i$ in phase $j$. It is noteworthy that only two composition variables of three species are needed to be solved since the sum of $w_j^i$ must be equal to unity. With boundary conditions at infinity given above equations (2.5-1) have similarity solutions [Carslaw, 1959]:

$$w_j^i = a_j^i - b_j^i \text{erf}(\eta_j^i) \quad \text{where} \quad \eta_j^i = x(4D_j^i t)^{1/2} \quad (2.5-2)$$

where $a_j^i$ and $b_j^i$ are constants to be determined from species mass balance equations at the interface; $\text{erf}(\eta_j^i)$ is the error function and has the definition:

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

These solutions must satisfy the following species mass balance equations at the interface.

$$D_j^i \frac{\partial w_j^i}{\partial x} \bigg|_{x=\epsilon} - D_j^2 \frac{\partial w_j^2}{\partial x} \bigg|_{x=\epsilon} = \left[ w_j^i(\epsilon) - w_j^2(\epsilon) \right] \frac{d\epsilon}{dt} \quad (2.5-3)$$

where $\epsilon$ is the location of interface. These equations are consistent with solutions to equation (2.5-2) if the interfacial position $\epsilon = \kappa t$. One may also calculate the relative
velocities of all interfaces, and therefore the growth rates of intermediate phases. This theory predicts that the interfacial position is proportional to the square root of contact time, which was verified in one of contacting experiments on vertically mounted cell described earlier [Miller, 1988; Raney, 1985b].

Diffusion path analysis was also applied to oil-water-surfactant systems [Raney, 1985a, 1987b; Benton, 1982]. In these cases, the use of pseudoternary phase diagrams was required. For example, one can combine all surfactant components into a pseudocomponent. Usually mixtures of hydrocarbons can also be considered as pseudocomponents.

2.6 Analysis of diffusion equations with moving boundary conditions

When the characteristic time \((R^2/D)\) for diffusion within the system for all species is much less than the characteristic time of the experiment, the quasi-steady-state assumption may be used in solving diffusion equation(see Section 5.1.1). In some cases quasi-steady state assumptions fail in systems with very rapid but still diffusion controlled solubilization or dissolution processes, for example, the dissolution of linear ethoxylated nonionic surfactants into water at temperatures below their respective cloud point temperatures (see Chapter 5). Then it is necessary to solve the diffusion equations with moving phase boundary conditions, which describe the systems regarding dissolution of surfactants into water. For a moving-boundary problem the equation is of parabolic type [Crank, 1992]. These problems are often called Stefan problems, named after J. Stefan [1890], who was first interested in the melting of polar ice cap.
The diffusion equation encountered in this work always involves the formation of multiple phases. Therefore different diffusion coefficients in each phase will be used in solving the problem. The numerical approach used in this work is discussed later in Section 5.1.3.

Danckwerts [1950] treated the more general problem in which a moving boundary is involved, for example, the melting of ice in contact with water. In this case the rates of the volume of ice melted is proportional to the volume of water formed.

Analytical solutions are easy to find in the special case that a spherical or cylindrical new phase is growing from negligible radius in an initially uniform medium and the equilibrium conditions are maintained at the growing surface. Frank presents mathematical solutions earlier developed by Rieck [Frank, 1950].

\[
\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D \cdot r^2 \frac{\partial C}{\partial r} \right) \quad \text{(2.6-1)}, \quad \text{where } r \text{ is the radial coordinate.}
\]

If \( s \) is defined by \( s=r/(D \cdot t)^{1/2} \). Then equation (2.6-1) becomes as

\[
\frac{\partial^2 C}{\partial \tilde{x}^2} = \left( \frac{s}{2} + \frac{2}{s^2} \right) \frac{\partial C}{\partial \tilde{x}} \quad \text{(2.6-2)}
\]

Integrating equation (2.6-2), we have \( \frac{\partial C}{\partial \tilde{x}} = -As^{1/2} \cdot \exp(-s^{1/2}) \) and hence

\[
C = A \int_s^{\infty} z^{-2} e^{-\frac{1}{4}s^2} \, dz + C_i \quad \text{(2.6-3)}
\]

where \( A \) is a constant and \( C_i \) is the value of \( C \) at infinity. Integration by parts of equation (2.6-3) gives the solution:

\[
C = C_i + A \left[ \frac{1}{s} e^{-\frac{1}{4}s^2} - \frac{1}{2} \sqrt{\pi} \cdot \text{erfe}(\frac{1}{2}s) \right] \quad \text{(2.6-4)}
\]
Chapter 3: Experimental Procedures

3.1 Materials and Sample Preparations

Tergitol 15-S-7 is a secondary alcohol ethoxylate which is a mixture of species with the alcohol group located at various positions along a chain of 11 to 15 carbon atoms and with an average ethylene oxide number of 7. The CMC of Tergitol 15-S-7 is reported at 0.0039 wt%. It was supplied by Union Carbide Co. (Charleston, West Virginia) and used as received. The pure linear alcohol ethoxylates $C_8E_5$, $C_{12}E_3$, $C_{12}E_4$, $C_{12}E_5$, $C_{12}E_6$, $C_{12}E_8$, and $C_{14}E_6$, were obtained from Nikko Chemical Co. (Tokyo, Japan) and used as received. Their purity was reported to be no less than 99%, determined by gas chromatography. The nonionic surfactants, Neodol 25-7 and Neodol 25-9, are blends of primary alcohol ethoxylates which have carbon chain lengths from 12 to 15 and average number of ethylene oxide groups at 7.3 and 8.9 moles respectively per mole of surfactant. The typical molecular weights of Neodol 25-7 and Neodol 25-9 are 524 and 597. They were supplied Shell Chemical Company (Houston, Texas). The anionic surfactant, sodium dodecyl sulfate (SDS), used in preliminary experiments was reagent grade purchased from Fisher USA and used as received without any recrystallization. Later SDS used in this study was purchased from Sigma Chemical Company (St. Louis, Missouri) and used after being recrystallized twice with 190 proof and absolute alcohol following the procedures described in the following paragraph and suggested by Robert Curtis of Unilever Research Port Sunlight Laboratory (Wirral, UK). The anionic surfactant, 1-octanesulfonic sodium salt, with a purity greater than 99% was purchased from Sigma and used as received.
Solid SDS was dissolved in a minimum amount of boiling solvent of 95/5 ethanol/water in a spoutless beaker with an approximate ratio of 1 gram of SDS to 12 ml of alcohol. The solution was then covered and left to stand until cool, during which time the SDS crystallized as large platelet-like crystals. When cool, the SDS was filtered off and washed with cooled 95/5 ethanol/water and finally ethanol. The crystals were transferred to a large flat dish and dried under vacuum (also see [Hines, 1997]).

After the crystals obtained were ground with a mortar and pestle, sieving was used to obtain particles in the desired range. The fraction of particles caught between a sieve of mesh #140, with mesh size of 106 μm, and a sieve of mesh #170, with mesh size of 90 μm, was used, and so was that caught between a sieve of mesh #170 and a sieve of mesh #325, with mesh size of 45 μm.

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 from J.T. Baker, n-butanol and n-octanol from Fluka, n-decanol from BDH Chemicals (UK), and n-hexadecane from Humphrey Chemical. The ethylhydroxyethyl cellulose polymer Bermacoll E270 FQ, which had a relative molecular mass of 100 000, was supplied by Berol Nobel Industries, Sweden.

Water used for all experiments was doubly distilled with Barnstead Glass Still and deionized with NANOpure II system (Sybron-Barnstead). The resistivity of deionized water was at least 16.7 MΩ/cm measured at the ambient temperature near 23°C. In the early stage of this work, all glassware was cleaned by chromic acid soaking followed by rinsing with double-distilled water. Due to the regulation prohibiting such use of chromic
acid in the United States, inorganic oxidizer Nochromix Reagent in sulfuric acid was used in later work. It was purchased from Fisher Scientific (USA).

Samples for phase behavior and solubility experiments were prepared in 16 × 125 mm (OD × Length), flat bottom, and screw cap type PYREX test tubes (Corning, NY). The samples were mixed for 20 seconds by vortex test tube mixer until they became homogeneous, then rotated overnight prior to being placed on the rack in the temperature controlled environmental room.

3.2 Videomicroscopy Configuration

The videomicroscopy system in our laboratory consists of microscopes, cameras, temperature controllers, video micrometer, time code generators, video recording and editing systems and NeXT workstation.

The microscope used for oil contacting and surfactant dissolution experiments was the Nikon Optiphot-Pol model with usual horizontal stage. A CCTV video camera Javelin JE-7362 (Javelin, CA) was connected on the top of the microscope and that allowed simultaneous observation through microscope eyepiece (10×) and on a video monitor. Four objectives of 4×, 10×, 20× and 40× magnification (Nikon) were used to study dynamic behavior at different perspectives. A polarizer was placed on top of the field lens and adjusted for a cross-polarized view with a built-in analyzer in the top section of microscope. This configuration enabled direct detection of liquid crystalline phase formation.
Temperature controller Mettler FP5 was used to maintain Mettler FP-5 microscope hot stage at the desired temperature. The hot stage was specially modified and placed on top of a Nikon X-Y positioner so that drops could be observed during and right after injection while the sample was maintained at constant temperature.

Another microscope was built with vertical stage configuration. No eyepieces were present with the vertical microscope and the image was sent directly to video monitor with a Javelin JE-3462RGB video camera. Three objectives of 1x, 4x and 10x magnification (Nikon) were used. Polarizing optics were included to identify formation of birefringent liquid crystalline phases.

The signal from both cameras first goes into the video micrometer (JV-6000, Javelin), which was used to measure the sizes of images in X, Y, and diagonal directions. The scale, which appeared on the monitor screen with images, can be calibrated in four different magnifications. The output signal then goes to time code generators (Bio-Electronics TC-3 or Cypher Btx), and finally to video recorders (see Figure 3-1).

Experiments were recorded by a Panasonic AG-7750P S-VHS recorder with NTSC format which has a built in Time Base Corrector (TBC). With NTSC format video signals were recorded into either normal or super VHS format with 30 frames per second. Recording images could be seen on a color monitor with information of real time (from time code generators) and size measurements (from video micrometer).

For editing purposes, a video editor Panasonic AG-A750 and an S-VHS player Panasonic AG-7650P were added to the system. Further image processing, photographs
Figure 3-1: Schematic Drawing of Video Microscopy System

- Panasonic BT-S901Y Video Monitors
- Panasonic AG-7650P S-VHS Video Player
- Panasonic BT-S901Y Video Monitors
- Panasonic AG-A750 Video Editor
- Bio-Electronics TC-3 Time Code Generator
- Panasonic AG-7750P S-VHS Video Recorder/Player
- To NeXT (Figure 3-2)
- Javelin JV-6000 Video Micrometer
- Javelin JE7362 Video Camera
- JVC TMR9U Video Monitor
- Mettler FP5 or Mettler FP 80HT Temperature Controller
- Nikon Optiphot-POL Microscope
Figure 3-2: Schematic Drawing of the NeXT Image Processing System
and picture slides could be done with NeXT workstation and photomodule camera (Dunn
Instruments, Inc.) (Figure 3-2).

3.3 Spinning Drop Interfacial Tension (IFT) Measurement

Interfacial tension measurements were performed using a spinning-drop
tensiometer model 300, developed at University of Texas at Austin. All measurements
were made with a 1.9 mm ID, cylindrical glass tube cleaned by thoroughly rinsing with
deonized water and acetone. After being dried, the tube was rinsed then filled with the
denser fluid, followed by injection of a drop of less dense fluid. Then the tube was very
quickly mounted in the housing of the tensiometer and spinning was initiated. The elapsed
time was recorded from injection of the drop. The temperature was maintained constant in
the temperature controlled environmental room, or by the built-in heater of the
tensiometer.

For an elongated drop with a length-to-diameter ratio greater than four, the
interfacial tension was calculated by the following equation: [Cayias, 1975]

\[
\gamma = \left( \frac{\pi^2}{8} \right) \left( \frac{d}{\eta} \right)^3 \cdot \Delta \rho \cdot \left( \frac{10^6}{\rho^2} \right)
\]  

(3.3-1)

Where \( \gamma \) is the interfacial tension in mN/m, \( \eta \) is the refractive index of the denser
fluid, \( \Delta \rho \) is the density difference between the two liquids in g/cm³, \( \rho \) is the period per
revolution in msec, and \( d \) is the diameter of the drop in cm. The refractive indices were
measured with a Bausch and Lomb Abbe-3L refractometer. The densities of pure
substances were looked up from a Sigma catalog or other literature. Densities of other fluids were determined by weighing a known volume of liquid.

For drops with length-to-diameter ratio smaller than four, the interfacial tension may be calculated following the schemes derived by Cayias et al. or the tables by Princen et al. [Cayias, 1975; Princen, 1967].

In recent years, the performance of a spinning-drop tensiometer was improved with the addition of video equipment and an interface to a personal computer [Borchardt, 1993]. It takes much less time in measuring the drop diameter and calculating the interfacial tension (IFT). Rapidly changing IFT values can be accurately determined at intervals of as little as one second. Solutions to some commonly encountered problems when using spinning-drop tensiometer were also investigated. Clear criteria were developed for the optimum design and successful operation of the instrument [Princen, 1995].

3.4 Equilibrium Solubilization Capacity Experiments

The samples were prepared with the procedure described in Section 3.1. 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 (Brinkmann Instruments Ltd., Westbury, New York) that was connected to a fiber optic probe inserted into the solution. The measurements were
compared to that of a solution with the same surfactant concentration but without any oil added.

3.5 Dynamic Light Scattering Measurements

Dynamic light scattering measurements to determine micelle size were made at Unilever Port Sunlight Laboratory (UK) using a Malvern Instruments device, System 4700, which included a Liconix 0.5 watt Argon ion laser 488 nm. (Malvern Worcs, UK). The software that was used to analyze light scattering data was written by Malvern and was “PCS Software version 1.26”. The light scattering data can be collected from 10 to 150 degrees. For small particles there is no additional information in the angle dependence to measurements that are typically recorded at 90 degrees. When the particles are small and scattering is low, dust (or small air bubbles) contamination can be a problem. Improved discrimination against dust can be achieved by measuring at higher angles.

Some measurements of micelle sizes were also conducted at Rice University using a COULTER® N4 Plus Submicron Particle Sizer (Miami, Florida) which included a 10 mW Helium-Neon laser 632.8 nm and a built-in Peltier regulated controller ranging from 0 to 90°C±0.1 @ 20°C. The light scattering data were collected at 90 degrees and analyzed by Size Distribution Processor (SDP) Analysis that is provided with the instrument. The SDP analysis provides a histogram of the sample particle-size distribution and yields peak data and overall mean data of particle size/molecular weight analysis, which can be calculated in terms of an intensity or weight distribution. The conversion of the intensity distribution to a weight distribution uses the exact Mie equation.
3.6 Oil Drop Contacting Experiments

Rectangular optical glass capillaries (Vitro Dynamics Inc., Cat. No. 2540) were used to contain the liquid of interest. These capillaries are 50 mm long, 4 mm wide and have optical path length of 400 μm. They were cleaned by chromic acid soaking at least 24 hours followed by rinsing with double-distilled water several times, and then dried in the oven.

The surfactant solution of interest was imbibed into such a glass cell by capillary action, then the glass cell was sealed in one end and attached to a standard microslide (3 in by 1 in) with photopolymer adhesive (Norland Products Inc. Adhesive No. 63, New Brunswick, NJ) which was cured with ultraviolet light of 250-380 nm by a fiber optical gun (Norland Products Inc. New Brunswick, NJ). The cell was then transferred to a the thermal stage, Mettler FP-5, mounted on Nikon Optiphot-Pol microscope. The temperature controller of the thermal stage was Mettler FP-52. The thermal stage was modified for the purpose of these experiments and maintained at constant temperature with variation less than 0.1°C. After it was sufficiently equilibrated at the desired experimental temperature, oil drops were injected into the surfactant solution with a very thin hypothermic needle (Model 91033, 210μm OD, 110μm ID, Hamilton Co., Reno Nevada) and 50 μl syringes (Model No. 1705, Hamilton Co.). The diameters of injected drops were mainly between 40 and 80 μm. It should be noted that the water-to-oil ratio in these experiments was very large (see Figure 2-8).
However, due to the differences of densities of oil and surfactant solution, the lighter oil drop tends to float on the top of heavier surfactant solutions, which can lead in some cases to coalescence of the drop with the top wall of the glass capillary. Solubilization rates could not be measured when this behavior occurred.

In one set of experiments, the oil drop was injected using a microinjection system to be described later in Section 3.8 which had advantage of allowing the injected oil drop size to be followed from the very beginning of its injection.

3.7 Vertical Cell Contacting Experiments

Direct observation of the dynamic interfacial phenomena was made possible with use of a vertically mounted microscope where comparable volumes of oil and surfactant solution were employed in contrast to the large water-to-oil ratio on a horizontally mounted microscope where oil drop contacting experiments were conducted (Figure 2-7).

Similar to the preparation of sample cells described above, sample cells with the denser phase in the bottom half were placed on a specially designed microscope that allowed the cells to be placed in a vertical configuration in a controlled temperature environment. The lighter phase was then very carefully injected from the top of the cell by use of a 50 μl syringe (Model No. 1705, Hamilton Co.) to minimize initial mixing effects. The density difference between these two phases tended to stabilize the interface. The use of these small vertically mounted glass capillaries on microscope allowed the clear observation of interfacial motion, intermediate phase formations, and the small-scale instabilities.
The vertically mounted microscope was designed and built to allow the sample to remain in a vertical configuration for viewing. The microscope can be viewed as a conventional transmission microscope that has been taken apart and reassembled on its side. However no eyepieces are present. Instead, the image is sent directly through an extension tube to the camera and VCR system.

3.8 Surfactant Droplet Dissolution Experiments

Because neat nonionic surfactants are quite viscous, it was not possible with the same technique to inject small drops having diameters of 50-100 μm as in the oil solubilization experiments. Instead the initial diameters of injected surfactant drops were 300-350 μm, which is very close to the thickness of cell. To address this problem, we purchased a microinjection system, Picospritzer II, from General Valve Division of Parker Hannifin Company (NJ, USA). With this microinjection system, the initial diameters of injected surfactant drops could be as small as 100 μm. Although initial diameters could be made even smaller, it was unrealistic to conduct experiments with such small drops since they dissolved in water very quickly.

Picospritzer II is a system with a high speed solenoid valve that supplies repeatable pressure pulses. Volumes dispensed are linear with pulse duration time and pressure of the driving gas. They also depend on inside diameters of the micropipettes and on the viscosities of both injected liquid and bulk liquid. The manufacturer suggests using compressed air or nitrogen, but never oxygen, as driving gas. Pressure cannot exceed 100 psi. (Figure 3-3)
Micropipettes used here were pulled from capillaries with outside diameters of 1 mm, purchased from Drummond Scientific Co. of Broomal, PA (Catalog number: 1-000-0300), and had inside diameters from 30 µm to 100 µm, mostly around 50 µm. The hypodermic needle used previously had an outside diameter of about 210 µm. As glass flows at temperatures above its glass transition temperature, capillaries attached with small weights were heated up very carefully with minimum flame from a gas burner (Fisher Scientific Co.). That is, micropipettes were pulled by gravity. Once the temperature on some segments of the capillaries was high enough, the capillaries started elongating and immediately moved away from the flame. Otherwise, capillaries would be broken into two parts with continuing heating. Here the small weight attached to capillaries was a 3/4" in length of binder clip. Micropipettes with longer shanks would be more convenient when injecting surfactant or oil drops into bulk liquid of interest. The inside diameter and the length of shanks can be controlled by adjusting the free falling distance and speed of that small weight and the length of heating zone on capillaries.

The alternative way to make micropipettes is to use Micropipette Puller PB-7/PB-10 of Narishige (Tokyo, Japan), which was originally designed to pull micropipettes by gravity with very short shanks for embryo injection and thus needs some modifications for our purposes [Menger, 1997; Hou, 1997; Kuo, 1996; Deshikan, 1995]. One end of a capillary is attached on a fixed unit of the Micropipette Puller and the other on a sliding unit, whose falling velocity controls the length of the shank of micropipette. The capillary passes through a heating coil about 5 mm in length. When using Micropipette Puller PB-7/PB-10, hold the sliding unit and let it fall down as slowly as possible when it starts
motion. That is, the heated segment of the capillary can be stretched out continuously without breaking. It is necessary to make sure that the sliding unit touches the safety switch in the bottom that turns off heating power to prevent breaking the micropipette from continued heating. The other pullers from Narishige, like PN-30, are not adequate to make micropipettes because they are designed to make micropipettes for embryo injection by using magnetic force. With this method it is not feasible to slow down the sliding unit and thus to make micropipettes with longer shanks for use in our experiments.

The sample preparation of the glass cells was the same as that described above in 3.6 and 3.7.
Figure 3-3: Schematic Diagram of Microinjection System

Valve Control Cable

110 V AC

1/4" Pressure Tubing

PICOSPRITZER II

Manual Time Power

Remote

阀

300

Valve

Duration Time

Gauge

Regulator

Mount Remote Valve

Pressure

Pressure

Foot Pedal

out

in

1/8" OD Teflon Tubing (6')

1/16" OD Teflon Tubing (3')
DO NOT stretch the tubing out in a line

Micropipette and Holder (1 or 1.6 mm)

Air or Nitrogen
Source < 100 PSI
DO NOT USE OXYGEN

Source:
Compressed Air or Nitrogen under 100 PSI

Useful Pressure Range:
10 - 100 psi, self-bleeding pressure valve

Duration Time:
2-999 msec. 1 msec intervals
0.1-99.9 seconds 3 decade thumbwheel
0.1-99.9 minutes

Pulse Initiation:
Stimulator, panel or remote-pushbutton (foot pedal)

Power Requirement:
Standard 100-120 V AC, 50-60 Hz, 3/4 amp
Switchable to 220-240 V AC
4.1 Rates of Solubilization Measured with Oil-drop-contacting Method

The oil-drop-contacting method is a new but very good and simple way to study kinetics of oil solubilization in a system with very large water-to-oil ratios. Since oil drops have very simple geometry, it is convenient to estimate the rates of solubilization without using complicated mathematics. As described in Section 3.6 in the technique of oil-drop-contacting method the change of drop radius is carefully recorded and monitored with elapsed time from the moment of injection, and thus the rate of solubilization of oil drop into surfactant solution is calculated.

The volume of oil drop is equal to \((4/3)\pi R^3\) and the surface area of oil drop is \(4\pi R^2\), where \(R\) is radius of oil drop. Therefore the rate of solubilization, \(-\frac{1}{A}(dV/dt)\), could be easily simplified as \(-dR/dt\):

\[
Rate = -\frac{1}{A} \frac{dV}{dt} = -\frac{dR}{dt} \quad (4.1-1)
\]

Although an oil drop, due to the density difference, tends to rise to the top of the glass cell, oil-drop-contacting method has the benefit of simple geometry that gives a simple way to get data on the solubilization rates. Oil drops in the contacting experiments of this work were not greatly deformed by gravity since Bond number, \((\Delta \rho g R^2 / \gamma)\), in these systems is much less than 1. For example, an oil drop having 75/25 triolein/oleic acid (by weight) has initial radius of 30 \(\mu\)m and is injected into 2 wt\% Tergitol 15-S-7 solution at 30\(^{\circ}\)C. The density difference is 0.095 g/ml; the minimum interfacial tension is near 0.005 mN/m. In this worst case, its maximum Bond number is about 0.18. In contrast, the
minimum interfacial tension for a oil drop having 85/15 triolein/oleic acid (by weight) is an
order of magnitude higher and its maximum Bond number is an order of magnitude less. If
a pure triolein drop having initial radius of 30 μm is injected into 2 wt% Tergitol 15-S-7
solution at 30°C, the density difference is 0.09 g/ml; the minimum interfacial tension is 0.4
mN/m. Its maximum Bond number is only 0.002 and again much less than 1. With the
improvement of the videomicroscopy system, it is more convenient and simpler to use this
oil-drop-contacting method to study kinetics of oil solubilization than the use of drop-on-
fiber method (described in Section 2.3.2). This method as well as drop-on-fiber method
work best in surfactant solutions below their respective cloud point temperatures, since
the oil drops must be viewed through surfactant solutions where they are immersed.

4.2 Solubilization of Triolein into Nonionic Surfactant Solutions

4.2.1 Oil Drop Contacting Experiments

Solubilization rates were measured using the basic oil drop contacting procedure
described previously.

Figure 4-1 shows how the radius R of a triolein drop varied with time after its
injection into a 2 wt% solution of the commercial secondary alcohol ethoxylate Tergitol
15-S-7 at 35°C, about 2°C below its cloud point temperature. It shows that (-dR/dt),
which is equal to the solubilization rate per unit area [-(1/A)(dV/dt)], eventually reached a
constant value of about 0.21 μm/min after an initial "lag" or "induction" period of about
15 minutes during which drop radius remained nearly constant at 51 μm. The initial lag
period was shorter for smaller drops and probably was associated with diffusion of
surfactant into the drop. The constant value of \((-dR/dt)\) was independent of initial drop size.

In contrast, Figure 4-2 shows that minimal solubilization occurred at the same temperature when the surfactant was the pure linear alcohol ethoxylate \(C_{14}E_6\), which has a cloud point temperature of 40°C. Solubilization was negligible over a period of 4 hours. Indeed, drop diameter increased slightly owing to dissolution of surfactant in the triolein.

During the latter part of the experiment with Tergitol 15-S-7 (Figure 4-1) where the rate, \((-dR/dt)\), was constant, tiny droplets were observed inside the triolein drop (see Figure 4-3). These small droplets are believed to be water (see Section 4.2.4). Direct observation and review of the videotape revealed that the droplets were in motion, i.e. significant convection existed. This behavior was different from that during the initial lag period when few droplets and little convection were observed. Nor was convection observed during the experiment of Figure 4-2 with \(C_{14}E_6\). Interfacial tension as measured by spinning drop technique showed that the tension fell and then remained nearly constant at a value of about 0.4 mN m\(^{-1}\) for triolein in 2 wt% Tergitol 15-S-7 at 30°C. This value is comparable to 0.22 mN m\(^{-1}\) found previously for 1 wt% \(C_{12}E_4\) and triolein at the same temperature [Mori, 1989] and 0.17 mN/m for 2 wt% \(C_{12}E_4\) and triolein at the same temperature (see appendix).

Table 4-1 summarizes results for triolein and hydrocarbon drops in Tergitol 15-S-7 solutions and shows that asymptotic solubilization rates of triolein are proportional to surfactant concentrations (items 1-4, see Figure 4-4) and increase with increasing temperature, the rate becoming larger as the cloud point is approached (see Figure 4-5).
Addition of 2500 ppm of a water-soluble polymer to the surfactant solution, which more than doubled the viscosity from 1.2 cp to 2.8 cp at 35°C, had no effect on the rate of solubilization of triolein. (Table 4-1, items 8-12) If the mass transfer rates in the bulk aqueous phase were limiting the solubilization rate, an increase in viscosity would decrease the solubilization rate. In fact, the solubilization rate increased when polymer concentration was increased to 4000 ppm, a result for which we have no explanation at present, although it was reproducible.

Finally Table 4-1 indicates that the solubilization rates in 2 wt% Tergitol 15-S-7 increased slightly when the solution was buffered at pH 9. Perhaps there was some oleic acid in the triolein which promoted solubilization. It will be discussed in Section 4.3.2, when oleic acid was deliberately added into triolein in alkaline condition.

For comparison (-dR/dt) was found to be about 1.1 μm/min for n-hexadecane in 2 wt% Tergitol 15-S-7 at 35°C, about 5 times higher than for triolein and of the same order of magnitude as seen by Carroll for pure linear alcohol ethoxylates and n-hexadecane. We found, as Carroll did, that there was no observable initial lag period during solubilization of hydrocarbon drops [Carroll, 1981, 1982; O'Rourke 1987]. The lag is apparently associated with surfactant partitioning into the oil drop. Nonionic surfactants are considerably less soluble in n-hexadecane than in triolein. Interfacial tension decreased at first and then leveled off at a steady state value of about 0.17 mN/m for the n-hexadecane and 2 wt% Tergitol 15-S-7 system at 35°C and about 0.21 mN/m at 30°C (see appendix).
Experiments were conducted to confirm that improved solubilization of triolein by Tergitol 15-S-7 solutions was not simply due to this commercial surfactant being a mixture of various species or having twin-tailed molecules. Table 4-2 (items 4-6) shows minimal solubilization of triolein by linear alcohol ethoxylate solutions --C_{14}E_{6}, and mixtures of C_{12}E_{6} with C_{12}OH, and with C_{12}E_{3} --at temperatures slightly below their respective cloud point temperatures. In contrast, a mixture of 2 wt% C_{12}E_{6} and 0.3 wt% n-hexanol having cloud point of 41°C solubilized triolein at a rate not much below that of Tergitol 15-S-7. Interfacial tension measurements of triolein in 2 wt% C_{12}E_{6} with addition of 0.3 wt% n-hexanol or 0.1 wt% n-dodecanol show the same steady state value of 0.8 mN/m at 30°C, which is twice of that of triolein with 2 wt% Tergitol 15-S-7. The difference is that interfacial tension with addition of 0.3 wt% n-hexanol reaches the steady state value much faster than that with the other system (see appendix).

Addition of short-chain alcohols to 2 wt% solutions of Tergitol 15-S-7 in amounts small enough to keep the cloud point temperature above 35°C also affected the solubilization rates. Table 4-3 summarizes the results. The highest solubilization rates, obtained from the drops with 0.30 wt% n-pentanol and 0.15 wt% n-hexanol, were 0.51 and 0.53 μm/min respectively, a factor of about 2.5 times greater than in the absence of alcohol. It is noteworthy that interfacial tension of triolein with 2 wt% Tergitol 15-S-7 does not decrease with addition of 0.15 wt% n-hexanol at 30°C (see appendix), but the solubilization rate increases from 0.21 μm/min in the absence of alcohol to 0.53 μm/min with addition of 0.15 wt% n-hexanol at 35°C (Table 4-3).
The results so far deal with solubilization into micellar solutions. Solubilization into oil-in-water microemulsions was also investigated. Table 4-4 shows solubilization rates of triolein can be greatly enhanced (to about 0.6 μm/min) by microemulsion phases that have *n*-hexadecane-to-C_{12}E_{4} ratio from 1 to 1½ in 5 wt% C_{12}E_{4} microemulsions. However, they all showed very long initial lag periods before they swelled and then shrank (see Figure 4-6). The induction periods decreased with increasing surfactant concentrations in solutions. In some experiments, drop volume could increase to three times the initial volume, which will be discussed in Section 4.2.5. Interfacial tension as measured by spinning drop technique showed that the tension fell to a value of 0.0074 mN m^{-1} and then increased and remained nearly constant at a value of about 0.02 mN m^{-1} for triolein and a microemulsion of 5 wt% C_{12}E_{4} and 6.25 wt% *n*-hexadecane at ambient temperature of about 22°C (see Figure 4-7).

In contrast to solubilization rate of triolein in microemulsion of 5 wt% C_{12}E_{4} and 6.25 wt% *n*-hexadecane at ambient temperature of about 22°C, *n*-hexadecane was solubilized at much slower rate in the same system at the same condition (0.17 μm/min for *n*-hexadecane compared to 0.52 μm/min for triolein). It is noteworthy that it did not swell at all in contrast to triolein (Figure 4-8). All experiments done in microemulsion phases at 22°C (Table 4-4 items 1-6) were conducted without using thermostat, and therefore the data shown in Table 4-4 might not have reflected the temperature effects. However, the temperature of experiments done at 25°C in the corresponding systems were controlled well. Table 4-4 (items 1-3) shows that microemulsions containing the least *n*-hexadecane would have the highest rates of solubilization and also the longest induction periods.
Table 4-1: Solubilization Rates, $-dR/dt$, of Oil Drops in Tergitol 15-S-7 Solutions with Cloud Point Temperature at 37°C

Unit of Rate = $\mu$m/min = $10^{-6}$ m/min

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35°C</th>
<th>33°C</th>
<th>30°C</th>
<th>29°C</th>
<th>22°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Triolein</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.21</td>
<td>0.12</td>
<td>0.09</td>
<td>0.084</td>
<td>0.023</td>
</tr>
<tr>
<td>(2) Triolein</td>
<td>3% 15-S-7</td>
<td></td>
<td>0.30</td>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>(3) Triolein</td>
<td>4% 15-S-7</td>
<td></td>
<td>0.40</td>
<td></td>
<td></td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>(4) Triolein</td>
<td>5% 15-S-7</td>
<td></td>
<td>0.47</td>
<td></td>
<td></td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>(5) Triolein</td>
<td>2% 15-S-7</td>
<td>pH 9</td>
<td>0.28</td>
<td></td>
<td>0.10</td>
<td></td>
<td>(A)</td>
</tr>
<tr>
<td>(6) Triolein</td>
<td>3% 15-S-7</td>
<td>pH 9</td>
<td>0.43</td>
<td></td>
<td>0.16</td>
<td></td>
<td>(A)</td>
</tr>
<tr>
<td>(7) Triolein</td>
<td>4% 15-S-7</td>
<td>pH 9</td>
<td>0.51</td>
<td></td>
<td>0.39</td>
<td></td>
<td>(A)</td>
</tr>
<tr>
<td>(8) Triolein</td>
<td>2% 15-S-7</td>
<td>0.1% E270</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) Triolein</td>
<td>2% 15-S-7</td>
<td>0.25% E270</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10) Triolein</td>
<td>2% 15-S-7</td>
<td>0.4% E270</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11) Triolein</td>
<td>2% 15-S-7</td>
<td>0.2% C16</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td>(#)</td>
</tr>
<tr>
<td>(12) Triolein</td>
<td>2% 15-S-7</td>
<td>0.3% C16</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
<td>(#)</td>
</tr>
<tr>
<td>(13) TO/C16</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.80(I), 0.27(L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(14) C16</td>
<td>2% 15-S-7</td>
<td></td>
<td>1.10</td>
<td></td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(15) C16/SQ</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.73</td>
<td></td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(16) SQ</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.20</td>
<td></td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TO=Triolein  
C16=n-Hexadecane  
SQ=Squalane

E270 = Bermocoll E270 FQ, nonionic water-soluble-polymer surfactant

(I)= Rate for first stage  
(L)=Rate for long times  
(#) = Rate for long times, initially had slight swelling  

(A): Buffer solution with pH=9 by using 0.05M NH4Cl and 0.05M NH4OH
Table 4-2: Solubilization Rates, -dR/dt, of Oil Drops in Surfactant Solutions of Linear Ethoxylated Alcohol with Short-Chain Alcohols Added

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35°C</th>
<th>30°C</th>
<th>22°C</th>
<th>Cloud Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Triolein</td>
<td>2% C12E6</td>
<td>0.5% C5OH</td>
<td>0.13</td>
<td></td>
<td></td>
<td>42°C</td>
</tr>
<tr>
<td>(2) Triolein</td>
<td>2% C12E6</td>
<td>0.3% C6OH</td>
<td>0.16</td>
<td>0.030</td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(3) Triolein</td>
<td>2% C12E6</td>
<td>0.15% C7OH</td>
<td>0.10</td>
<td></td>
<td></td>
<td>38°C</td>
</tr>
<tr>
<td>(4) Triolein</td>
<td>2% C12E6</td>
<td>0.1% C12OH</td>
<td>0.035</td>
<td>0.001</td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(5) Triolein</td>
<td>1.4% C12E6</td>
<td>0.6% C12E3</td>
<td>&lt;0.008</td>
<td></td>
<td></td>
<td>25-30</td>
</tr>
<tr>
<td>(6) Triolein</td>
<td>2% C14E6</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>40°C</td>
</tr>
<tr>
<td>(7) TO/C16=50/50</td>
<td>2% C12E6</td>
<td>0.3% C6OH</td>
<td>1.20(I), 0.20(L)</td>
<td></td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(8) C16</td>
<td>2% C12E6</td>
<td>0.3% C6OH</td>
<td>1.82</td>
<td>0.96</td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(9) C16/SQ=50/50</td>
<td>2% C12E6</td>
<td>0.3% C6OH</td>
<td>0.79</td>
<td>0.5(I), 0.25(L)</td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(10) SQ</td>
<td>2% C12E6</td>
<td>0.3% C6OH</td>
<td>0.28</td>
<td>0.095</td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(11) TO/C16=50/50</td>
<td>2% C12E6</td>
<td>0.1% C12OH</td>
<td>0.49(I), 0.06(L)</td>
<td></td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(12) C16</td>
<td>2% C12E6</td>
<td>0.1% C12OH</td>
<td>1.16</td>
<td>0.67</td>
<td></td>
<td>39°C</td>
</tr>
<tr>
<td>(13) C16/SQ=50/50</td>
<td>2% C12E6</td>
<td>0.1% C12OH</td>
<td>0.41</td>
<td>0.29</td>
<td></td>
<td>39°C</td>
</tr>
</tbody>
</table>

C16=n-Hexadecane  SQ=Squalane  TO=Triolein  (I)=Rate for first stage  (L)=Rate for long times  * denotes that experiments were done at ambient temperature (around 22°C) without using thermostat.

Table 4-3: Solubilization Rates, -dR/dt, of Oil Drops in Tergitol 15-S-7 Solutions with Short-Chain Alcohols Added

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Triolein</td>
<td>2% 15-S-7</td>
<td>0.4% IPA</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>(2) Triolein</td>
<td>2% 15-S-7</td>
<td>0.4% IBA</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>(3) Triolein</td>
<td>2% 15-S-7</td>
<td>1% IBA</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>(4) Triolein</td>
<td>2% 15-S-7</td>
<td>0.4% C4OH</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>(5) Triolein</td>
<td>2% 15-S-7</td>
<td>0.3% C5OH</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>(6) Triolein</td>
<td>2% 15-S-7</td>
<td>0.15% C6OH</td>
<td>0.53</td>
<td>0.20</td>
</tr>
<tr>
<td>(7) Triolein</td>
<td>2% 15-S-7</td>
<td>0.1% C6OH</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>(8) C16</td>
<td>2% 15-S-7</td>
<td>0.15% C6OH</td>
<td>1.91</td>
<td>1.19</td>
</tr>
</tbody>
</table>

C16=n-Hexadecane  IPA=Isopropanol  IBA=Isobutanol
Figure 4-1: Variation with time of radius of triolein drop injected into 2 wt% Tergitol 15-S-7 solution at 35°C

\[ R_0 = 50.9 \mu m \]
\[ \frac{dR}{dt} = -0.21 \mu m/min \]
Figure 4-2: Variation with time of radius of triolein drop injected into 2 wt% \( C_{14}E_6 \) solution at 35°C

![Graph showing the variation of radius with time. The initial radius \( R_0 = 28.7 \, \mu m \).]
Figure 4-3: Videoframe showing small droplets inside triolein drop being solubilized by 2 wt% Tergitol 15-S-7 at 35°C
Figure 4-4: Solubilization rates of triolein in Tergitol 15-S-7 solutions

Figure 4-5: Solubilization rates of triolein in 2 wt% Tergitol 15-S-7 solutions
Figure 4-6: Variation with time of radius of triolein drop injected into microemulsion having 5 wt% C\textsubscript{12}E\textsubscript{4} and 6.25 wt% \textit{n}-hexadecane at 25°C

Ro = 36.6 \mu m \\
dR/dt = -0.65 \mu m/min

Ro = 26.5 \mu m \\
dR/dt = -0.61 \mu m/min

Ro = 25.4 \mu m \\
dR/dt = -0.60 \mu m/min
Figure 4-7: Interfacial tension as a function of time for triolein drop injected into microemulsion having 5 wt% $C_{12}E_{4}$ and 6.25 wt% $n$-hexadecane at $22^\circ$C
Figure 4-8: Variation with time of radius of \( n \)-hexadecane drop injected into microemulsion having 5 wt\% C\textsubscript{12}E\textsubscript{4} and 6.25 wt\% \( n \)-hexadecane at 22\(^\circ\)C.

- \( R_0 = 38.7 \mu\text{m} \)
- \( \frac{dR}{dt} = -0.17 \mu\text{m/min} \)

- \( R_0 = 28.9 \mu\text{m} \)
- \( \frac{dR}{dt} = -0.17 \mu\text{m/min} \)
Table 4.4: Solubilization Rates, -dR/dt, of Oil Drops in Microemulsions

| Unit of Rate = \(\text{\mu m/min} = 10^{-6} \text{m/min}\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Oil Drop        | Surfactant      | Additive        | 25°C            | 22°C *          | CP              |
| (1) Triolein    | 5% C12E4        | 5% C16          | 0.83            | 0.83            | 27°C            |
| (2) Triolein    | 5% C12E4        | 6.25% C16       | 0.63            | 0.52            | 27°C            |
| (3) Triolein    | 5% C12E4        | 7.5% C16        | 0.53            | 0.64            | 27°C            |
| (4) Triolein    | 8% C12E4        | 10% C16         | 1.03            | 24°C            |
| (5) Triolein    | 10% C12E4       | 10% C16         | 1.91            | 24°C            |
| (6) Triolein    | 10% C12E4       | 12.5% C16       | 3.10            | 24°C            |
| (7) C16         | 5% C12E4        | 6.25% C16       | 0.17            | 27°C            |

C16=n-Hexadecane   CP=Cloud Point

4.2.2 Dynamic Light Scattering Measurements

Light scattering measurements shown in Table 4-5 (a) were done in September of 1995 at Unilever Research Port Sunlight Laboratory. Light scattering results showed that addition of alcohols acted to narrow the size distribution of the cylindrical micelles of Tergitol 15-S-7. For a solution containing 2 wt% of the surfactant at 30°C the micelle size distribution featured two slightly overlapping peaks at 12.4 and 20.4 nm with most of the surfactant in the shorter micelles. For 2 wt% surfactant with 0.15 wt% n-hexanol only a single peak at 16.0 nm was observed. The increase in the micelle length upon addition of alcohols is expected because n-hexanol makes surfactant films more lipophilic, i.e., reduces spontaneous curvature.

Light scattering measurements presented in Table 4-5 (b) were conducted in December 1997 at Rice University, which were recorded at 90 degrees. Tergitol 15-S-7 used here was exactly the same one used in measurements to generate Table 4-5 (a) and C12E6 was "fresh sample" received from Barnet, the North American agent of Nikko
Chemical. Table 4-5 (b) showed that addition of hydrocarbons acted to decrease the sizes of surfactant aggregates, where rodlike micelles were presumably transformed into more globular aggregates [Hoffmann, 1987]. The micelle size distributions of 2 wt% Tergitol 15-S-7 in Table 4-5 (b) are greater than those in Table 4-5 (a) as Tergitol 15-S-7 had presumably deteriorated with time. The ethoxide chains in surfactants are easily broken under the light and heat [Sallen, 1997], and thus the average ethoxylate number in this Tergitol 15-S-7 should be smaller than before. Therefore, it becomes more lipophilic and the intermicellar attractions are greater.

From the measurements conducted at Rice University, the mean micelle size of 2 wt% Tergitol 15-S-7 with added 0.15 wt% \( n \)-hexanol at 30°C is about 2½ times bigger than that without addition of \( n \)-hexanol at the same temperature. Addition of 0.15 wt% \( n \)-hexanol to the Tergitol 15-S-7 solution effectively decreases the cloud point to 33°C, compared to that of 36°C when it was measured before for solubilization-rate experiments. Table 4-5 (b) also shows that the sizes of surfactant micelles increase with increasing temperature as intermicellar attractions increase. The difference becomes more distinct when 0.15 wt% \( n \)-hexanol was added to 2 wt% Tergitol 15-S-7 solution. The micelle size of 2 wt% \( \text{C}_{12}\text{E}_8 \) was measured for comparison, since it is known to have a spherical shape.

It should be mentioned that most of the solubilization rate experiments were conducted within a few months before/after the measurements shown in Table 4-5(a) that were made at Unilever Research Port Sunlight Laboratory.
Table 4-5: Summary of micelle size distributions of 2 wt% surfactant solutions with addition of alcohols and oils

(a) Measurements done at Unilever Port Sunlight Laboratory

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Additives</th>
<th>size distributions</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt% Tergitol</td>
<td>none</td>
<td>12.4[3.9], 20.4[4.4]</td>
<td>two peaks</td>
</tr>
<tr>
<td></td>
<td>0.4 wt% IPA</td>
<td>11.2[1.3], 16.1[5.4]</td>
<td>two peaks</td>
</tr>
<tr>
<td>15-S-7</td>
<td>0.4 wt% IBA</td>
<td>15.2[3.0]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4 wt% C₄OH</td>
<td>16.1[2.3]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4 wt% C₅OH</td>
<td>17.9[0.3]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15 wt% C₆OH</td>
<td>16.0[0.1]</td>
<td></td>
</tr>
</tbody>
</table>

IPA = Isopropyl Alcohol  
IBA = Isobutyl Alcohol  

(b) Measurements done at Rice University

<table>
<thead>
<tr>
<th>Surf.</th>
<th>Alcohol</th>
<th>Oil</th>
<th>30°C</th>
<th>25°C</th>
<th>20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt% Tergitol</td>
<td>None</td>
<td>None</td>
<td>29.9[6.7]</td>
<td>20.2[9.0]</td>
<td>15.0[5.3]</td>
</tr>
<tr>
<td></td>
<td>0.18wt% TO</td>
<td>12.0[4.8]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-S-7</td>
<td>0.56wt% C₁₆</td>
<td>13.0[4.5]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15 wt% C₆OH</td>
<td>None</td>
<td>75.2[31.5]</td>
<td>33.9[10.7]</td>
<td>22.2[9.2]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.31wt% TO</td>
<td>12.1[3.1]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75wt% C₁₆</td>
<td>14.7[4.8]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt% C₁₂E₆</td>
<td>None</td>
<td>None</td>
<td>21.1[8.8]</td>
<td>11.4[3.9]</td>
<td></td>
</tr>
<tr>
<td>0.3 wt% C₅OH</td>
<td>None</td>
<td>None</td>
<td>34.1[6.0]</td>
<td>34.0[11.6]</td>
<td>23.2[9.7]</td>
</tr>
<tr>
<td>0.2wt% TO</td>
<td>33.6<a href="25%25">6.6</a></td>
<td>9.2[1.6]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.6<a href="75%25">4.2</a></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.65wt% C₁₆</td>
<td>10.6[1.9]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 wt% C₁₂OH</td>
<td>None</td>
<td>None</td>
<td>41.1[13.6]</td>
<td>30.0[10.4]</td>
<td>24.3[10.6]</td>
</tr>
<tr>
<td>0.12wt% TO</td>
<td>50.8<a href="70%25">8.0</a></td>
<td>51.0<a href="53%25">15.1</a></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.9<a href="30%25">3.1</a></td>
<td>12.0<a href="47%25">4.2</a></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.55wt% C₁₆</td>
<td>11.1[2.8]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt% C₁₂E₈</td>
<td>None</td>
<td>None</td>
<td>7.1[3.1]</td>
<td>6.8[1.6]</td>
<td>10.4[2.8]</td>
</tr>
</tbody>
</table>

TO = Triolein  
C₁₆ = n-Hexadecane  
and peak amount of C % if two peaks were observed
4.2.3 Equilibrium Solubilization Experiments

Table 4-6 shows the equilibrium solubilization of triolein and n-hexadecane at 30°C in 2 wt% Tergitol 15-S-7 with and without addition of 0.15 wt% n-hexanol. The corresponding solubilization rates at this temperature are also shown. For both oils, addition of n-hexanol increases equilibrium solubilization by about 50% but more than doubles the solubilization rates. Similar results are obtained when n-hexanol is used instead of n-dodecanol with C_{12}E_6. The results of Table 4-6 demonstrate that solubilization rates are not, in general, proportional to the corresponding values of equilibrium solubilization.

Table 4-6: Solubility of Triolein and Hexadecane in Surfactant Solutions at 30°C

<table>
<thead>
<tr>
<th>Surfactant Solutions</th>
<th>Additive</th>
<th>Triol</th>
<th>n-Hexad</th>
<th>Solubility</th>
<th>Rate</th>
<th>Solubility</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 2 % 15-S-7</td>
<td>None</td>
<td>0.24 - 0.30</td>
<td>0.09</td>
<td>0.69 - 0.75</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) 2 % 15-S-7</td>
<td>0.15% C_{6}OH</td>
<td>0.40 - 0.46</td>
<td>0.20</td>
<td>0.95 - 1.0</td>
<td>1.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3) 2 % C_{12}E_6</td>
<td>0.1% C_{12}OH</td>
<td>0.15 - 0.20</td>
<td>0.01</td>
<td>0.68 - 0.75</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) 2 % C_{12}E_6</td>
<td>0.3% C_{6}OH</td>
<td>0.25 - 0.30</td>
<td>0.03 - 0.049</td>
<td>0.82 - 0.91</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Alcohols were added to surfactant solutions to maintain their cloud points at about 37°C.

4.2.4 Vertical Cell Experiments

When triolein was contacted with 2 wt% Tergitol 15-S-7 at 35°C in the vertical cell, convection was observed with many small, individual droplets in the oil phase. The droplets, which became more numerous with time, were apparently water as they occasionally were seen to coalesce with the aqueous phase. No evidence of an
intermediate phase forming at the interface was seen. Similar behavior was found when 0.4 wt% \textit{n}-butanol was added to the surfactant solution.

4.2.5 Summary

In this section data on solubilization of triolein into nonionic surfactant solutions have been presented. The main results are

(1) Triolein is solubilized very slowly into solutions where the micelles are made up of pure species having straight chains of uniform length, e.g., C_{14}E_6 and C_{12}E_6/C_{12}OH mixtures.

(2) The commercial secondary ethoxylate Tergitol 15-S-7, which is a mixture of twin-tailed surfactants having different chain lengths, is able to solubilize triolein at an appreciable rate. The rate is about the same as that for squalane in the same solution but only one fifth of that for \textit{n}-hexadecane.

(3) The rate of solubilization of triolein into Tergitol 15-S-7 is proportional to surfactant concentration and increases with increasing temperature, the increase being especially fast just below the surfactant cloud point.

(4) Addition of various short-chain alcohols in amounts which have minimal effect on the cloud point produces significant increases in solubilization rates, especially for pure linear alcohol ethoxylates.

(5) Solubilization rates are not, in general, proportional to equilibrium solubilization even in a given surfactant solution. In particular, the rate of triolein solubilization is less than would be expected based on multiplying the rate of solubilization of \textit{n}-hexadecane by the ratio of the equilibrium solubilization capacities.
(6) The asymptotic rate of solubilization of a triolein drop into oil-in-water microemulsions containing C_{12}E_4 and n-hexadecane is higher than for micellar solutions. However, substantial swelling of the drop occurs initially as it takes up surfactant and hydrocarbons before shrinkage begins.

4.2.6 Discussion

The rate of decrease (-dR/dt) of the drop radius was found to be nearly constant in most of our experiments, although frequently not until after an initial lag period. That is, the solubilization rate per unit area was constant, the same result as obtained by Carroll [1981] for solubilization of hydrocarbons with his drop-on-fiber technique. The result indicates that the rate of solubilization is controlled by the rates of processes occurring at the interface. For if, in a stagnant system the rate of solubilization was limited by diffusion of micelles to the interface or diffusion of oil-containing micelles away from the interface, it can be shown that the solubilization rate per unit area would increase with decreasing drop size, and (-dR^2/dt) would have a constant value independent of drop size. However our data are not consistent with such behavior. The failure of an increase in surfactant solution viscosity caused by the addition of water-soluble polymer to decrease the solubilization rate of triolein in Tergitol 15-S-7 solutions also suggests that mass transfer in the bulk solutions was not limiting. Finally, the convection observed during the triolein experiments would, if anything, have increased mass transfer rates. Yet triolein was solubilized more slowly by a given surfactant solution than n-hexadecane, for which no
convection was seen and interfacial processes are known to be rate-limiting [Carroll, 1981]. Hence, interfacial processes likewise dominate for triolein.

The result that triolein solubilization by Tergitol 15-S-7 is proportional to the surfactant concentration indicates that the rate-limiting step for a given system is "adsorption" of micelles by the oil drop, as pointed out by Huang et al. [1981] and Carroll [1981]. The rapid increase in solubilization rate near the cloud point temperature is also consistent with adsorption control because attraction of micelles to an interface having an adsorbed film should increase along with intermicellar attraction.

Carroll [1981] has suggested that "adsorption" of surfactant molecules may result from dissociation of micelles located very near the interface. If so, the solubilization rate would increase with decreasing micelle dissociation time $\tau_2$, a property that can be measured by temperature jump or other kinetic techniques [Lang, 1987]. The basic idea is that adsorbed molecules would subsequently be reemitted as micelles containing solubilized oil. Although some known trends in variation of $\tau_2$, for instance the decrease in $\tau_2$ caused by addition of short-chain alcohols [Lang 1987], are generally consistent with the trends in our experimental results if the above idea is accepted, no quantitative comparison exists between measured values of $\tau_2$ and solubilization rates in particular systems.

The alternate mechanism is adsorption or partial fusion of entire micelles to the surfaces of larger oil drops. This is supported by the fact that if we have $n$-hexadecane in micelles or microemulsions, it seems to have no trouble getting into the larger drop. With micelle dissociation one might think surfactant adsorbs preferentially to $n$-hexadecane. It
should be noted that temporary partial fusion as a mechanism of transport between phases has been suggested previously by Plucinski, Nitsch and coworkers to explain their results of solubilization of metal ions and amino acids by water-in-oil microemulsions [Plucinski, 1995; Nitsch, 1997]. The fusion occurs between a droplet in the microemulsion and the aqueous phase and allows solute transfer to the droplet to occur before it breaks off from the interface and returns to the bulk microemulsion phase (Figure 4-9a).

A variant of the above mechanism is complete coalescence of micelles with the drop and subsequent emission of micelles containing solubilized oil from the surface of the drop (Figure 4-9b). Of course, partial fusion and coalescence/emission are not mutually exclusive. Indeed, computer simulations of the solubilization process indicated that both would occur in one particular case [Karaborni, 1993]. It may well be that one or the other dominates in different systems.

Let us consider behavior after the initial transient period during which surfactant dissolves in the drop. When partial fusion of a micelle occurs, the curvature of at least some of the surfactant originally in the micelle decreases or possibly even reverses. Since the surfactant film has a spontaneously curvature of the order of micelle curvature, energy must be supplied to bend the film to the configuration which exists during partial fusion. The source of this energy is thermal fluctuations which can, for example, impart kinetic energy to a micelle approaching the drop. If complete coalescence occurs, partial fusion is presumably an intermediate step, so that an energy input to overcome resistance to bending is again required. Moreover, if some surfactant dissolves in the drop during coalescence, its concentration is increased to a value above/near that in equilibrium with
Figure 4-9: Schematic diagram of micelle collision with interface resulting in mass transfer

(a) Partial fusion of micelle on drop surface [Plucinski, 1993]

1. Approach

2. Sticky Collision Leading to Partial Fusion

3. Mass Transfer

4. Incipient Separation

5. Emission
Figure 4-9: Schematic diagram of micelle collision with interface resulting in mass transfer
(b) Complete coalescence of micelle with drop surface

A: Drop of Triolein/Oleic Acid
(1) Approach

W: Surfactant Solution

B: Micelle

(2) Sticky Collision Leading to Complete Coalescence

W

(3) Thermal Fluctuation of Surfactant Film

The amplitude of capillary wave on surfactant film is enhanced by low interfacial tension [Buff, 1989]. Vigorous fluctuation would reemit the micelle with solubilized oil back to the bulk solution.

(4) Incipient Separation Due to Vigorous Fluctuation of Surfactant Film

B

(5) Emission of micelle
the micellar solution, a process which also involves an increase is associated with bending effects.

This view of the adsorption process provides some insight regarding the increase in triolein solubilization rates observed when the hydrocarbon chain portion of the surfactant films is made thinner or less ordered by changing from systems where all surfactant chains are straight and of the same length, e.g., C₁₄E₆ and C₁₂E₆/C₁₂OH, to systems where chains are branched and/or of variable length, e.g., Tergitol 15-S-7 and mixtures of surfactants with short-chain alcohols. Because it is known that thinner and/or less ordered films are more flexible, i.e., they have lower bending modulus \( \kappa \) [Safran, 1994]. The results strongly suggest that increasing surfactant film flexibility favors faster solubilization. With flexible films the energy required for partial fusion or coalescence is lower, and the rate of adsorption should increase.

While adsorption of micelles requires input of energy from thermal fluctuations, emission of micelles releases energy because the surfactant film of the micelles has a large curvature and is closer to its spontaneous curvature. Moreover, an overview of the situation reveals that the state of the system after adsorption of an oil from micelles and emission of a micelle containing solubilized oil is closer to the equilibrium state and thus of lower free energy than the state which existed previously. That micelle emission (or break-off of micelles transiently joined to the drop) is a spontaneous process reducing system free energy is consistent with the conclusion reached above that the solubilization rate in a given system is limited by micelles adsorption, not emission. Of course, an energy barrier
may have to be surmounted during emission before the net decrease in free energy can be realized.

Flexibility could also be a factor in the more rapid solubilization of \( n \)-hexadecane than triolein by a given surfactant solution - more than can be explained by differences in equilibrium solubilization (Table 4-6). In this case it is flexibility of the surfactant film after it has been in contact with oil that is of interest. The smaller hydrocarbon molecules are able to penetrate the monolayer at the interface more readily than the large triolein molecules, increasing film flexibility. While the adsorption rate may be about the same for drops of both oils in a particular surfactant solution, more hydrocarbon than triolein leaves during emission. Not only is there more hydrocarbon than triolein in the micelle surface, but greater film flexibility allows larger fluctuations of the interface, as discussed below, so that hydrocarbon can be more readily incorporated into the micelles interior. In addition to the film flexibility, the size difference of both oil molecules also needs to be considered, which will be discussed later in this section.

The discussion thus far has emphasized the importance of energy changes caused by bending the surfactant film. One may ask whether energy changes caused by changes in area are also significant. To answer this question, let us consider deformation of an initially plane interface, a good approximation for deformation of the interface of an oil drop provided that the wavelength is much smaller than the drop radius. After deformation the interface can be described by a sinusoidal function, \( Bf(x,y) \), where \( B \) is the amplitude, and the wavelength \( \lambda \) is described as \( 2\pi/\alpha \) and taken as a typical micelle size of 60\( \text{Å} \), i.e. wave number \( \alpha = 10^7 \text{ cm}^{-1} \). The work required to increase interfacial area is \cite{Miller, 1985}
\[ W_{BF} = \frac{1}{2} \gamma \alpha^2 B^2 \| \ell^2 \]  \hspace{1cm} (4.2.1), where \( \gamma \) is the interfacial tension.

The bending work is expressed as

\[ W_B = \frac{1}{2} \kappa \alpha^4 B^2 \| \ell^2 \]  \hspace{1cm} (4.2.2), where \( \kappa \) is the bending modulus.

The bending modulus has a dimensionality of energy and covers the range from \( \sim 1 \text{ k}_B \text{T} \) ("flexible" monolayer) to \( \sim 10 - 100 \text{ k}_B \text{T} \) ("rigid" monolayer) [Kabalnov, 1996]. It should be mentioned that the general form of bending energy is given by [Helfrich, 1973]:

\[ E \Omega = \frac{1}{2} \kappa \int_\Omega dA \left( C_1 + C_2 - C_0 \right)^2 + \kappa_0 \int_\Omega dA C_1 C_2 \]  \hspace{1cm} (4.2.3)

The variables \( C_1 \) and \( C_2 \) denote two principal curvatures and \( C_0 \) is the spontaneous curvature which is phenomenologically introduced in order to account for a possible asymmetry of the bilayer. The constant \( \kappa_0 \) is known as the Gaussian curvature modulus or the saddle-splay modulus. The second term gives the integrated Gaussian curvature which is constant for topologically equivalent shapes, such as \( V_1 \) cubic phase and \( L_3 \) sponge phase.

Suppose that \( \gamma \) is taken as 0.4 mN/m, i.e. 0.4 erg/cm\(^2\), (see Figure A-2, also a representative of triolein drop) and \( \kappa \) is taken as 1 k\(_B\)T for flexible monolayers, i.e. \( 4.18 \times 10^{-14} \) erg at 30°C. Accordingly, the values of \( W_{BF} \) and \( W_B \) are

\[ W_{BF} = 2 \times 10^{13} \text{ (erg/cm}^2\text{)} \times B^2 \| \ell^2 \]

\[ W_B = 2.1 \times 10^{14} \text{ (erg/cm}^2\text{)} \times B^2 \| \ell^2 \]

Clearly the bending energy effect does dominate for small wavelengths comparable to micelle size.

When the micelles initially contain solubilized hydrocarbon, the case for the micelle adsorption mechanism seems particularly strong. Consider the solubilization of triolein by
2 wt% Tergitol 15-S-7 and 0.3 wt% \( n \)-hexadecane (see Figure 4-10) or by 5 wt% \( \text{C}_{12}\text{E}_4 \) and 6.25 wt% \( n \)-hexadecane (see Figure 4-6). In the initial 20 minutes or so of these experiments, drop volume increased by more than about 30% in the experiment with solubilized hydrocarbon, or even more than 300% in the microemulsion experiment as surfactant and especially hydrocarbon were taken up. This relative rapid growth seems inconsistent with a mechanism based on micelle dissociation time \( \tau_2 \) because adding hydrocarbon to micelles is known to increase \( \tau_2 \) [Zana, 1987]. Instead one might imagine that, following initial fusion of a micelle with the drop, flow from micelle to drop occurs owing to the local interfacial tension gradient, the tension of the hydrocarbon-containing micelle presumably being lower than that of the triolein drop based on previous measurements in similar systems (Figures 4-7 and A-1) [Mori, 1989]. That is, the interfacial tension gradient promotes coalescence. As the hydrocarbon content of the drop increases, this interfacial tension gradient diminishes until its effect is offset by the chemical potential gradient favoring triolein transport into the micelle. Apparently a situation is eventually reached where drop composition reaches a steady state and the radius decreases at a constant rate.

It is noteworthy that a drop of \( n \)-hexadecane in the same microemulsion system as that of Figure 4-6 did not swell at all (see Figure 4-8), even though there was some induction period, since there was no interfacial tension gradient between microemulsion drops and large \( n \)-hexadecane drops.

The occurrence of extensive convection during the steady shrinkage of triolein drops (Figure 4-3) may also be caused by interfacial tension gradients, though on a larger
Figure 4-10: Variation with time of radius of triolein drop injected into 2 wt% Tergitol 15-S-7 and 0.3 wt% n-hexadecane at 35°C.

Radius [μm]

0 10 20 30 40 50 60 70 80

Time [min]

Ro = 23.12 μm
\frac{dR}{dt} = -0.17 μm/min
scale. The more lipophilic species of Tergitol 15-S-7 will partition preferentially into the drop during the initial lag period, probably reaching a concentration of about 10% based on the work with other nonionic surfactants [Mori, 1987]. Then, if a fluctuation causes interfacial tension to decrease locally at a point on the drop surface, the resulting outward flow along the interface generates flow within the drop bringing more of the lipophilic surfactant species from the interior to the surface. As a result, interfacial tension decreases further there, which amplifies the flow. This hydrodynamic instability could produce the convection seen in Figure 4-3. Some emulsification of water droplets inside the triolein drops could be caused by this convection, and some could be produced by local supersaturation during the initial diffusion of surfactant into the drop according to the mechanism described by Ruschak and Miller [1972].

Donegan and Ward [1987] found that the solubilization rates of several pure straight-chain hydrocarbons, \( C_nH_{2n-2} \) (n=8-16), in solutions of a pure nonionic surfactant were proportional to the respective equilibrium solubilization capacities. In addition, Weiss et al. [1997] studied the solubilization of hydrocarbon emulsion droplets, \( C_nH_{2n} \) and \( C_nH_{2n-2} \) (n= 14, 16, 18), in Tween 20 micelles and found that the solubilization rate can be written as:

\[
Rate = K (C_o - C) (C_{sat} - C) \tag{4.2.4}
\]

where \( C \) is the mass fraction of oil solubilized in the aqueous micellar solution at time \( t \), \( C_o \) is the initial mass fraction of oil present as the emulsion droplets; \( C_{sat} \) is the equilibrium solubilization capacity of oil in surfactant solution, and \( K \) is a constant. The second term of equation 4.2.4, \( (C_o - C) \), stands for the mass fraction of oil present as
emulsion drops at time $t$. If $C$ is much smaller than $C_o$ and $C_{sat}$, which is true in the system studied in this work, equation 4.2.4 is equivalent to what Donegan and Ward [1987] found.

However, a similar relationship did not hold for triolein and $n$-hexadecane in our experiments. Neither did B.G.C. O’Rourke et al. [1987] and Carroll et al. [1982] find it to hold for $n$-hexadecane and squalane solubilized by $C_{12}E_5$ and $C_{12}E_6$ systems. A possible interpretation of this phenomena was advanced by Carroll et al. [1982] where it was postulated that the number of surfactant monomers in the nascent aggregate leaving the interface differed from the number in the final equilibrium state and that the constants of proportionality linking the kinetic and equilibrium values were different for the two oils [O’Rourke, 1987]. As mentioned in Section 4.2.2, Hoffmann et al. [1989] observed that long rod-like micelles become shorter and are transformed to those with globular structures with increasing amounts of solubilized aliphatic hydrocarbons. The globular micelles increase in size until saturation is reached. The attractive forces between the micelles become smaller. In addition, the results of dynamic light scattering measurements in Table 4-5 also confirmed that the sizes of micelles with solubilized triolein and $n$-hexadecane changed. That is, the number of surfactant monomers in the aggregates changes with solubilized hydrocarbons present in micelles.

This suggestion by Carroll [1982] to account for the discrepancy, two factors which may contribute to it are bending and steric effects. The bending effect that is discussed earlier in this section to account for the difference in the rapid solubilization rate of $n$-hexadecane and the slower one of triolein in surfactant solutions. Unlike liquid
hydrocarbons such as n-hexadecane, triolein does not readily form water-continuous and bicontinuous microemulsions, which have more flexible surfactant films, in systems containing water and pure linear alcohol ethoxylates except at rather high temperatures [Mori, 1989]. In contrast, Tungsubutra [1994] found that triolein can form microemulsions with Tergitol 15-S-3 and 15-S-5 at 30°C. That is, the surfactant films of Tergitol micelles fused to the larger triolein drop are more flexible.

The other possible explanation may stem from the steric effects of oil molecules entering the micelles through the neck temporarily fused on the oil drop. Each triolein molecule consists of a glycerol backbone and 3 oleic chains that have 18 carbon molecules each. One can imagine that each triolein molecule is almost equivalent to a molecule built from 3 different n-hexadecane molecules on a short 3-carbon backbone and thus each triolein molecule will have much larger cross sectional area than n-hexadecane. Therefore, if the neck temporarily connecting the micelle is not large enough, triolein molecule would encounter more difficulty to get into inside the micelle than the n-hexadecane molecule. If instead the complete coalescence of micelles occurs on the oil drop surface, surfactant monomers need to cover more surface area to encapsulate triolein molecules before they are emitted to the bulk phase. It means triolein molecules still have more difficulty to get inside the micelles, even complete coalescence happens. That is, the number of effective collisions required for solubilization of a given amount of triolein will be much less than for n-hexadecane and, therefore, the solubilization rate of triolein is slower. However, in the “limit” of long times and many effective collisions, solubilization equilibrium can be reached.
To address the steric effects of triolein and $n$-hexadecane, both molecular volumes were calculated and compared to the micellar size shown on Table 4-5. With the density and the molecular weight, one can find the volume of each molecule. Each $n$-hexadecane molecule occupies 0.488 nm$^3$ and triolein has 1.615 nm$^3$. If every triolein or $n$-hexadecane molecule is a cube, the side length of $n$-hexadecane cube is 0.787 nm and that of triolein is 1.173 nm, which is about 49% larger or 122% larger in cross sectional area. In another extreme case, $n$-hexadecane molecule does not coil together and extends as a linear and rectangular shape. One could estimate the dimension of $n$-hexadecane molecule as about 0.384 nm $\times$ 0.384 nm $\times$ 3.284 nm using the approximate cross section of a hydrocarbon chain. Triolein molecule would have even much larger dimension, since it consists of 3 oleic chains.

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

4.3.1 Triolein-Oleic Acid Drops at Neutral pH

Figure 4-11 shows the variation of radius 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. Particularly striking is the rapid initial decrease in drop size, during which $(-dR/dt)$ has a value of about 2.1 μm/min. The volume of the drop in Figure 4-11 decreased by about 46% in five minutes, a process accompanied by vigorous convection. Later in the experiment the solubilization rate decreased by an order of magnitude, eventually reaching a constant value of 0.20
\( \mu \text{m/min} \), about the same as found previously for pure triolein and the same surfactant solution at the same temperature (see Table 4-1 and Figure 4-1).

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 and was approximately proportional to surfactant concentration (see Figure 4-12) but relatively insensitive to temperature (see Figure 4-13) and to the addition of short-chain alcohols (see Figure 4-14). The results are shown in Table 4-7. The asymptotic solubilization rates at long times were comparable to those found previously for pure triolein (see Tables 4-1 and 4-3) and thus increased sharply with increasing temperature and with addition of \( n \)-butanol, \( n \)-pentanol, and \( n \)-hexanol.

In addition, these experiments showed that the reduction in drop volume during the initial period of rapid solubilization decreased slightly as surfactant concentration increased from 1 wt% to 4 wt% (see Figure 4-12), but it was little influenced by temperature or by addition of alcohol (see Table 4-8, Figures 4-13 and 4-14). 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. Although strong convection was seen, no intermediate phase formed at the interface.
Figure 4-11: 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\(^\circ\)C

\[ R_0 = 43.7\mu m \]
\[ \frac{dR}{dt} = -2.08\mu m/min \text{ (initial)} \]
\[ \frac{dR}{dt} = -0.20\mu m/min \text{ (long times)} \]
Figure 4-12: Initial and final solubilization rates and amount of initial solubilization as a function of surfactant concentration for oil containing 85/15 triolein/oleic acid (by weight) in Tergitol 15-S-7 solutions at 35°C

![Graph showing solubilization rates and amount of initial solubilization as a function of surfactant concentration.]

Figure 4-13: Initial and final solubilization rates and amount of initial solubilization as a function of temperature for oil containing 85/15 triolein/oleic acid (by weight) in Tergitol 15-S-7 solutions at 35°C

![Graph showing solubilization rates and amount of initial solubilization as a function of temperature.]

Figure 4-14: Effects of addition of short-chain alcohols to 2 wt% Tergitol 15-S-7 on initial and final solubilization rates and amount of initial solubilization of oil having 85/15 triolein/oleic acid (by weight) at 35°C
Table 4-7: Solubilization Rates, -dR/dt, of Mixtures of Triolein and Oleic Acid in Surfactant Solutions

Unit of Rate = μm/min = 10^{-6} m/min

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35 °C</th>
<th>33 °C</th>
<th>30 °C</th>
<th>29 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) TO/OAc=75/25</td>
<td>2% 15-S-7</td>
<td></td>
<td>2.12(I), 0.24(L)</td>
<td>1.39(I), 0.18(L)</td>
<td>1.72(I), 0.084(L)</td>
<td></td>
</tr>
<tr>
<td>(2) TO/OAc=80/20</td>
<td>2% 15-S-7</td>
<td></td>
<td>1.73(I), 0.26(L)</td>
<td>1.77(I), 0.17(L)</td>
<td>1.82(I), 0.10(L)</td>
<td></td>
</tr>
<tr>
<td>(3) TO/OAc=85/15</td>
<td>1% 15-S-7</td>
<td></td>
<td>0.96(I), 0.058(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td></td>
<td>2.08(I), 0.20(L)</td>
<td>1.80(I), 0.14(L)</td>
<td>1.85(I), 0.087(L)</td>
<td>1.98(I), 0.083(L)</td>
</tr>
<tr>
<td>(5) TO/OAc=85/15</td>
<td>3% 15-S-7</td>
<td></td>
<td>2.65(I), 0.24(L)</td>
<td></td>
<td>2.24(I), 0.097(L)</td>
<td></td>
</tr>
<tr>
<td>(6) TO/OAc=85/15</td>
<td>4% 15-S-7</td>
<td></td>
<td>3.54(I), 0.31(L)</td>
<td></td>
<td>2.58(I), 0.11(L)</td>
<td></td>
</tr>
<tr>
<td>(7) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% IPA</td>
<td>1.63(I), 0.195(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% IBA</td>
<td>1.84(I), 0.30(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>1% IBA</td>
<td>2.40(I), 0.44(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% C₂OH</td>
<td>1.68(I), 0.26(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.3% C₃OH</td>
<td>1.68(I), 0.47(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.15% C₄OH</td>
<td>1.49(I), 0.90(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(13) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 9</td>
<td>0.19</td>
<td>~0</td>
<td>(A)</td>
<td></td>
</tr>
<tr>
<td>(14) TO/OAc=85/15</td>
<td>3% 15-S-7</td>
<td>pH 9</td>
<td>0.22</td>
<td>0.069</td>
<td>(A)</td>
<td></td>
</tr>
<tr>
<td>(15) TO/OAc=85/15</td>
<td>4% 15-S-7</td>
<td>pH 9</td>
<td>0.36</td>
<td>0.12</td>
<td>(A)</td>
<td></td>
</tr>
<tr>
<td>(16) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 10</td>
<td>0.11</td>
<td></td>
<td>(B)</td>
<td></td>
</tr>
<tr>
<td>(17) TO/OAc=85/15</td>
<td>3% 15-S-7</td>
<td>pH 10</td>
<td>0.21</td>
<td></td>
<td>(B)</td>
<td></td>
</tr>
<tr>
<td>(18) TO/OAc=85/15</td>
<td>4% 15-S-7</td>
<td>pH 10</td>
<td>0.36</td>
<td></td>
<td>(B)</td>
<td></td>
</tr>
<tr>
<td>(19) TO/OAc=85/15</td>
<td>2% C₁₂E₆</td>
<td></td>
<td>2.81(I), 0(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(20) TO/OAc=85/15</td>
<td>2% C₁₂E₆</td>
<td>0.3% C₃OH</td>
<td>1.73(I), 0.15(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(21) TO/OAc=85/15</td>
<td>2% C₁₂E₆</td>
<td>0.2% OAc</td>
<td>1.17(I), 0(L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(22) TO/OAc=85/15</td>
<td></td>
<td>pH9 - pH13</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TO = Triolein  OAc = Oleic acid  IPA = Isopropanol  IBA = Isobutanol  (I) = Rate for initial shrinking  (L) = Rate for long times  (A): Buffer solution with pH=9 by using 0.05 M NH₄Cl and 0.05M NH₃OH  (B): Buffer solution with pH=10 by using 0.1M NaHCO₃ and 0.1M Na₂CO₃
Table 4-8: Ratio of drop volume after initial rapid shrinkage to initial drop volume for mixtures of triolein and oleic acid in surfactant solutions

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35°C</th>
<th>33°C</th>
<th>30°C</th>
<th>29°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) TO/OAc=75/25 2% 15-S-7</td>
<td></td>
<td></td>
<td>0.31</td>
<td>0.30</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>(2) TO/OAc=80/20 2% 15-S-7</td>
<td></td>
<td></td>
<td>0.44</td>
<td>0.39</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>(3) TO/OAc=85/15 1% 15-S-7</td>
<td></td>
<td></td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td></td>
<td>0.54</td>
<td>0.55</td>
<td>0.56</td>
<td>0.53</td>
</tr>
<tr>
<td>(5) TO/OAc=85/15 3% 15-S-7</td>
<td></td>
<td></td>
<td>0.56</td>
<td></td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>(6) TO/OAc=85/15 4% 15-S-7</td>
<td></td>
<td></td>
<td>0.64</td>
<td></td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>(7) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td>0.4% IPA</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td>0.4% IBA</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td>1% IBA</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td>0.4% C4OH</td>
<td>0.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td>0.3% C5OH</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12) TO/OAc=85/15 2% 15-S-7</td>
<td></td>
<td>0.15% C6OH</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(13) TO/OAc=85/15 2% C_{12}E_6</td>
<td></td>
<td></td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(14) TO/OAc=85/15 2% C_{12}E_6</td>
<td></td>
<td>0.3% C6OH</td>
<td>0.59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(15) TO/OAc=85/15 2% C_{12}E_6</td>
<td></td>
<td>0.2% OAc</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TO=Triolein  OAc=Oleic acid  IPA=Isopropanol  IBA=Isobutanol  C16=n-Hexadecane

Interfacial tension was also measured at 30°C for the same surfactant solution and oil compositions. Tension fell during the first few minutes of the experiments to about 0.045 mN/m, remained constant for some time, then rose slowly, reaching a value greater than 0.2 mN/m at the end of experiment (see Figure 4-15). This value is of same magnitude as that reported previously at the same temperature for 2 wt% Tergitol 15-S-7 and pure triolein. Variation of interfacial tension with time for a drop having 25 wt% oleic acid in 2 wt% Tergitol 15-S-7 solution was similar to that described above except the minimum interfacial tension was lower -- about 0.005 mN/m
The initial rate of solubilization (-dR/dt) by 2 wt% Tergitol 15-S-7 solutions was about the same at 35°C for drops having oleic acid contents of 15, 20, 25 wt% (see Figure 4-16). However the amounts solubilized during the rapid solubilization period were 46, 56, 69% by volume respectively.

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 for drops containing 25 wt% oleic acid. For drops having 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.

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\textsubscript{12}E\textsubscript{6} for the experiment (see appendix), behavior during the first five minutes of the experiment was similar although the solubilization rate was a little higher, 2.8 vs. 2.1 \(\mu\)m/min (Table 4-7 item 19). The fractions of the initial drop volume solubilized during this time, 44% for C\textsubscript{12}E\textsubscript{6} and 46% for Tergitol 15-S-7, agreed within experimental error. However, no further solubilization occurred for the C\textsubscript{12}E\textsubscript{6} solution after this time, which is consistent with the negligible solubilization rate found with this surfactant solution for pure triolein at 35°C. Addition of 0.3 wt% \(n\)-hexanol had little effect on the initial solubilization rate or the amount solubilized by C\textsubscript{12}E\textsubscript{6} but yielded an asymptotic solubilization rate of 0.15 \(\mu\)m/min, again about the same as found previously for pure triolein.
Figure 4-15: Interfacial tension as a function of time for the system of Figure 4-11 at 30°C
Figure 4-16: Initial and final solubilization rates and amount of initial solubilization as a function of oleic acid in triolein drops for 2 wt% Tergitol 15-S-7 solutions at 35°C
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. 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 4-11 for a triolein/oleic acid mixture. Subsequently, neither significant convection nor further drop shrinkage was observed. The PIT for this system is about 43°C [Raney, 1990]. 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 [Lim, 1991].

The rates of solubilization of triolein are shown to be greatly enhanced with the presence of oleic acid that is one of the products from the hydrolysis of triolein. It implies that the detergency can be also greatly improved with the use of lipase which helps the hydrolysis of triolein. Therefore triolein is solubilized not only in its pure form but also accompanied with the oleic acid from its hydrolysis.

4.3.2 Triolein-Oleic Acid Drops at Alkaline Conditions

The experiment of Figure 4-11 was repeated with the surfactant solution buffered to pH 10 by a mixture of NaHCO₃ and Na₂CO₃. The temperature was maintained at 30°C because addition of salts had reduced the cloud point temperature from its initial value of 37°C to a value below 35°C. The drop size remained nearly constant for some time, then decreased at a rate of about 0.11 μm/min (Table 4-7), which is close to the value of 0.09 μm/min for pure triolein in 2 wt% Tergitol 15-S-7 at neutral pH at this temperature (Table
4-1). Interfacial tension fell very rapidly to about 0.003 mN/m, then rose almost immediately to about 1 mN/m (Figure 4-17).

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. Similarly, no rapid initial solubilization was seen when another buffer solution at pH 9 was used (see Table 4-7).

From vertical cell experiments, very distinct roll cells produced by vigorous Marangoni flow were observed initially as well as extensive spontaneous emulsification in the aqueous phase. After 45 seconds, the convection stopped and the emulsion was pushed away from the oil phase by a distance that increased with time (Figure 4-18). The existence of vigorous Marangoni convection for situations where a mixture of nonpolar oil and a fatty acid contacts an alkaline surfactant solution is not surprising though previous studies have used hydrocarbons instead of triglycerides as the nonpolar oil.[Raney, 1985b; Rudin, 1993] The spontaneous emulsification in the aqueous phase 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 pH is lower than in the bulk aqueous phase. When the micelles reach the bulk surfactant solution, the higher pH converts some of the acid to soap, making the micelles too hydrophilic to solubilize all the triolein present. As a result, spontaneous emulsification of triolein occurs.

No measurable solubilization occurred when drops containing 75 and 85 wt% triolein and 25 and 15 wt% oleic acid respectively were injected into surfactant-free solutions with pH value between 9 and 13.
Figure 4-17: Interfacial tension as a function of time for the system of Figure 4-11 at pH 10 and 30°C
Figure 4-18: Videoframes from vertical cell contacting experiment for the system of Figure 4-11 at pH10 and 30°C

(a) Vigorous Marangoni flow and spontaneous emulsification at 32 sec after injection

(b) Flow is minimal at 72 seconds after injection
4.3.3 Drops of Triolein Mixed with Other Long-Chain Polar Compounds

Drops of triolein-oleyl alcohol mixtures containing 15 and 25 wt% alcohol were injected into 2 wt% Tergitol 15-S-7 at neutral pH and at temperatures between 29°C and 35°C. The rates and amounts of solubilization in the first rapid shrinkage were similar to the corresponding results for mixtures of triolein and oleic acid.

In contrast, much less initial rapid solubilization occurred when oleic acid was replaced by lauric (dodecanoic) acid for a drop containing 15 wt% acid (see Table 4-9 and 4-10). The initial rate was about half that seen for the corresponding oleic acid system, and only 18% by volume of the drop was solubilized.

The vertical cell experiments showed no significant convection at any time. An intermediate phase apparently formed immediately at the surface of contact, and it became visible at one minute after contact. Its thickness was linearly proportional to the square root of time, which implied that it was diffusion controlled (see Figure 4-19).

Addition of small amounts of short chain alcohols to the surfactant solutions did not improve significantly the rates or amounts of initial solubilization. The volume fractions initially solubilized decreased slightly. However the solubilization rates at long times increased as found in previous experiments for pure triolein. (see Figure 4-20).

At pH 9 or pH 10 no initial rapid solubilization was observed, the same as for triolein-oleic acid systems. Addition of 0.8 wt% n-butanol to the surfactant solution failed to restore the initial rapid solubilization.
Figure 4-19: Thickness of intermediate phase for the vertical cell experiment of oil containing 85/15 triolein/oleic acid (by weight) and 2 wt% Tergitol 15-S-7 at 35°C.
Figure 4-20: Effects of addition of short-chain alcohols to 2 wt% Tergitol 15-S-7 on initial and final solubilization rates and amount of initial solubilization of oil having 85/15 triolein/lauric acid (by weight) at 35°C.

Figure 4-21: Initial and final solubilization rates and amount of initial solubilization for drops containing triolein and mixtures of oleic and lauric acid at 35°C.
Table 4-9: Solubilization Rates, -dr/dt, of Mixtures of Triolein and Lauric Acid in Surfactant Solutions

Unit of Rate = \( \mu \text{m/min} = 10^{-6} \text{m/min} \)

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35 °C</th>
<th>30 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) TO/OAc=75/25</td>
<td>2% 15-S-7</td>
<td>1% IPA</td>
<td>1.11(I), 0.22(L)</td>
<td></td>
</tr>
<tr>
<td>(2) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% IPA</td>
<td>1.29(I), 0.21(L)</td>
<td></td>
</tr>
<tr>
<td>(3) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% IBA</td>
<td>0.30(L)</td>
<td></td>
</tr>
<tr>
<td>(4) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>1% IBA</td>
<td>0.47(I), 0.51(L)</td>
<td></td>
</tr>
<tr>
<td>(5) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% C4OH</td>
<td>0.82(I), 0.27(L)</td>
<td></td>
</tr>
<tr>
<td>(6) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.3% C5OH</td>
<td>0.91(I), 0.54(L)</td>
<td></td>
</tr>
<tr>
<td>(7) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.15% C6OH</td>
<td>0.85(I), 0.27(L)</td>
<td></td>
</tr>
<tr>
<td>(8) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 9</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>(9) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 9</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>(10) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 9</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>(11) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 10</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>(12) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 10</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>(13) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>pH 10</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>(14) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>1.56(I), 0.23(L)</td>
<td>1.75(I), 0.092(L)</td>
<td></td>
</tr>
<tr>
<td>(15) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>1.58(I), 0.24(L)</td>
<td>1.32(I), 0.105(L)</td>
<td></td>
</tr>
<tr>
<td>(16) TO/OAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.2% OA</td>
<td>0.29(I), 0.0(L)</td>
<td></td>
</tr>
</tbody>
</table>

TO=Triolein, OAc=Oleic acid, LAc=Lauric (dodecanoic) Acid, IPA=Isopropanol, IBA=Isobutanol

(I)=Rate for initial shrinking, (L)=Rate for long times

(A): Viscous phase formed around the oil drop initially
(B): No initial shrinkage, and very viscous phase formed initially
(C): Buffer solution with pH=9 by using 0.05 M NH₄Cl and 0.05M NH₃OH
(D): Buffer solution with pH=10 by using 0.1M NaH CO₃ and 0.1M Na₂CO₃

Experiments were also conducted with drops having 85 wt% triolein and mixtures of oleic acid and lauric acid. About 37% by volume was solubilized during the initial few minutes of experiments for a drop having 10 wt% oleic acid and 5 wt% lauric acid. When the amounts of oleic acid and lauric acid were reversed, the corresponding value was 34%
by volume. Both values lie between 46% for oleic acid and 18% for lauric acid (see Figure 4-21).

Drops containing mixtures of triolein and capric (decanoic) acid showed similar behavior to that for triolein-lauric acid mixtures. A small amount of initial solubilization was seen at pH 9, but none at pH 10.

Table 4-10: Ratio of drop volume after initial rapid shrinkage to initial drop volume for mixtures of triolein and lauric acid in surfactant solutions

<table>
<thead>
<tr>
<th>Oil Drop</th>
<th>Surfactant Solution</th>
<th>Additive</th>
<th>35°C</th>
<th>33°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) TO/LAc=75/25</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) TO/LAc=85/15</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3) TO/LAc=85/15</td>
<td>3% 15-S-7</td>
<td></td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) TO/LAc=85/15</td>
<td>4% 15-S-7</td>
<td></td>
<td>0.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) TO/LAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% IPA</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6) TO/LAc=85/15</td>
<td>2% 15-S-7</td>
<td>1% IBA</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) TO/LAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.4% C4OH</td>
<td>0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) TO/LAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.3% C5OH</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) TO/LAc=85/15</td>
<td>2% 15-S-7</td>
<td>0.15% C6OH</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10) TO/OAc/LAc=85/10/5</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.63</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>(11) TO/OAc/LAc=85/5/10</td>
<td>2% 15-S-7</td>
<td></td>
<td>0.66</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>(12) TO/LAc=85/15</td>
<td>2% C12E6</td>
<td>0.2% OAc</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TO=Triolein LAc=Lauric acid OAc=Oleic acid
IPA=Isopropanol IBA=Isobutanol
(A): Viscous phase formed around the oil drop initially

4.3.4 Equilibrium solubilization of triolein/fatty acids or triolein/fatty alcohol mixtures in surfactant solutions at 30°C

Table 4-11 shows the equilibrium solubilization of triolein/fatty acids or triolein/oleyl alcohol mixtures at 30°C in 2 wt% Tergitol 15-S-7 and 2 wt% C_{12}E_{6} with and
without addition of alcohols. The amounts of oleic acid, lauric acid and oleyl alcohol present in oils greatly affect the capacities of equilibrium solubilization in 2 wt% Tergitol 15-S-7 solutions with or without addition of 0.15 wt% \( n \)-hexanol and 0.30 wt% \( n \)-pentanol. The presence of large amounts of fatty acids and oleyl alcohol decreases the cloud point of surfactant solutions. Thus they may reach cloud limit first and exhibit bluish solutions, before reaching the solubilization limit where milky emulsion particles could be seen. The solutions which reach the cloud points are designated by asterisks in Table 4-11.

Table 4-11: Equilibrium Solubilization Capacities of Triolein/Fatty Acid and Triolein/Fatty Alcohol Mixtures in Surfactant Solutions at 30°C

<table>
<thead>
<tr>
<th>Surfactant Additive</th>
<th>2% Tergitol 15-S-7</th>
<th>2% ( C_{12}E_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15% C(_6)OH</td>
<td>0.30% C(_5)OH</td>
</tr>
<tr>
<td>Triolein</td>
<td>0.24 - 0.30</td>
<td>0.40 - 0.46</td>
</tr>
<tr>
<td>TO/OAc=85/15</td>
<td>0.50 - 0.55</td>
<td>0.60 - 0.65</td>
</tr>
<tr>
<td>TO/OAc=80/20</td>
<td>0.65 - 0.70</td>
<td>&lt; 0.06*</td>
</tr>
<tr>
<td>TO/OAc=75/25</td>
<td>0.17 - 0.20</td>
<td>&lt; 0.06*</td>
</tr>
<tr>
<td>TO/OAc/LA=85/10/5</td>
<td>0.47 - 0.51</td>
<td>&lt; 0.06*</td>
</tr>
<tr>
<td>TO/LA=85/15</td>
<td>0.55 - 0.60</td>
<td>&lt; 0.04*</td>
</tr>
<tr>
<td>TO/LA=75/25</td>
<td>0.12 - 0.14*</td>
<td>&lt; 0.04*</td>
</tr>
<tr>
<td>TO/OA=85/15</td>
<td>0.41 - 0.49</td>
<td>0.55 - 0.60</td>
</tr>
<tr>
<td>TO/OA=75/25</td>
<td>0.21 - 0.25*</td>
<td>&lt; 0.04*</td>
</tr>
</tbody>
</table>

TO=Triolein          OAc=Oleic Acid LA=Lauric Acid OA=Oleyl Alcohol
* denotes that sample reached cloud point first.

However, for those solutions that reached solubilization limit first, the amount of triolein solubilized increased with increasing content of fatty acids. Among oleic acid, lauric acid, and oleyl alcohol, the addition of oleic acid showed the greatest increase in amount of triolein solubilized in 2 wt% Tergitol 15-S-7.
Strikingly the amount of oil having a composition of 85/15 triolein/oleic acid (by weight) solubilized in 2 wt% C₁₂E₆ was greatly enhanced by about an order of magnitude with addition of 0.30 wt% n-hexanol to surfactant solution, which decreased the cloud point temperature to 39°C from 52°C without alcohol added. The solubility of triolein in 2 wt% Tergitol 15-S-7 with addition of 0.15 wt% n-hexanol was found to be the greatest compared to that without alcohol added and that with addition of 0.30 wt% n-pentanol. However with 15 wt% oleic acid present initially in triolein/oleic acid mixtures, the equilibrium solubilization capacity of oil in 2 wt% C₁₂E₆ with 0.30 wt% n-hexanol was higher than those in 2 wt% Tergitol 15-S-7 without or with addition of 0.15 wt% n-hexanol or 0.30 wt% n-pentanol. All the cloud point temperatures of Tergitol 15-S-7 solutions mentioned in this section are between 36° and 37°C.

4.3.5 Discussion

Since the solubilization rates of triolein and fatty acid mixtures at long times in nonionic surfactant solutions appeared to be very close to or the same as those of pure triolein in the same solution under the same conditions, one could assume that (nearly) all acids are solubilized in the initial rapid solubilization processes, i.e., only triolein was left in the drops after initial rapid solubilization. With this assumption and from the volume fraction initially solubilized, 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. (see Table 4-8). 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 (Table 4-1). For 2 wt\% \( C_{12}E_6 \) at 35°C the initial ratio of triolein to acid solubilized is again about two. 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 4-12 shows that the initial solubilization rate is proportional to 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 (also see Section 4.2.5) [Carroll 1981; Huang, 1981]. 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 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 bulk surfactant concentration in these experiments if adsorption were very fast.
Figure 4-12 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 4-16 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 [Carroll, 1981]. If controlled by this mechanism of adsorption, the solubilization rate should increase with decreasing micelle dissociation time $\tau_2$. Experiments for other surfactants have shown that $\tau_2$ decreases when short-chain alcohols are added [Lang, 1987]. 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 rates of Figure 4-16 when the drops are nearly pure triolein do increase upon addition of alcohols. As indicated previously, this increase may be influenced by micelle dissociation, but is most likely due to increased film flexibility.

On the other hand, the presence of oleic acid facilitates the initial step of partial fusion between micelle and drop because it increases the spontaneous curvature in the transition or neck region. As a result the bending energy required to produce partial fusion for triolein drop, which was discussed in Section 4.2.6, is greatly decreased. Thus, the partial fusion or coalescence model can explain why oleic acid produces a large increase in the rate of micelle adsorption.
As discussed in Section 4.2.5, the proportionality between the solubilization rates and the equilibrium solubilization capacities for several pure straight-chain hydrocarbons in solutions of a pure nonionic surfactant did not hold for triolein and \( n \)-hexadecane in contrast to what Donegan et al. [1987] found. 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 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 4-11. Moreover, limited equilibrium solubilization data presented in Table 4-11 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 two (see Tables 4-7 and 4-9). Because the initial solubilization rate is relatively insensitive to temperature, alcohol content, and nonionic surfactant structure, it seems unlikely to be proportional to equilibrium solubilization, which is affected by these variables.

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. Adsorption of micelles is much faster than for pure triolein, but micelle dissociation seems not to be the explanation for this effect. Instead, adsorption involves temporary partial fusion of micelles and drop and/or complete
coalescence of micelles with the drop, as illustrated schematically in Figures 4-9a and 4-9b. 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.

Since the initial rate of triolein solubilization from its mixtures with oleic acid is relatively insensitive to temperature (Figure 4-13), alcohol content (Figure 4-16), and nonionic surfactant structure (Table 4-7), in contrast to the situation for pure triolein discussed in Section 4.2, the solubilization mechanism is apparently different and not so dependent on surfactant film properties. It seems likely that formation of a neck between a micelle and the drop surface as shown in Figure 4-9a is much easier to achieve when oleic acid is present, at least from the perspective of the drop surface. Not only is the interfacial tension low (Figure 4-15), but also the initial surfactant film is rich in oleic acid and hence lipophilic with a tendency to curve toward a water-in-oil configuration. As a result, energy is not required and, on the contrary, is released when local mean curvature of the drop surface changes sign and becomes of the water-in-oil type at the neck. 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 and facilitates solubilization. Implications for emulsion stability of formation of such a neck between macroscopic drops have been discussed by Kabalnov and Wennerstrom [1996].
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.

In Section 4.2.5 a partial fusion model is adopted to explain the initial swelling of oil drops being solubilized in surfactant solutions with solubilized hydrocarbon or in microemulsions (Figure 4-9). However, additional insight can also be gained from this model as to why initial solubilization is so rapid and the ratio of moles of triolein to oleic acid solubilized is about six even though oleic acid dominates in the interfacial film. Immediately upon fusion a substantial local interfacial tension gradient exists between the drop surface (A of Figure 4-9) where tension is low and the acid-free micelle (B of Figure 4-9) where tension is higher. Such a gradient produces flow from the drop into the micelle, i.e., from A to B, opposing coalescence and increasing triolein content of the micelle and promoting its break-off into the aqueous solution. Recall that the interfacial tension was oppositely directed and promoted coalescence when microemulsion droplets containing \( n \)-hexadecane came into contact with triolein drop (see Section 4.2.6).

If instead complete coalescence of the micelle occurs, the low tension and high flexibility of the drop interface make conditions favorable for development of large-amplitude local fluctuations in interfacial shape. If any such fluctuations become unstable,
e.g., if they are nearly cylindrical and experience the well-known capillary instability of a cylinder, triolein-rich micelles would be formed and ejected into the surfactant solution.

Both these mechanisms depend on the drop interface being more lipophilic than the somewhat hydrophilic micelle surface. That this is indeed the case is confirmed by the interfacial tension results. Interfacial tension first decreases as surfactant adsorbs and makes the interface more hydrophilic.

The initial decrease and subsequent increase in interfacial tension depicted in Figure 4-15 are evidence of an increasing proportion of surfactant and decreasing proportion of oleic acid in the interfacial film during the solubilization process. As indicated above, the initial film is rich in oleic acid and thus lipophilic. Tension initially falls as the film becomes more hydrophilic with increasing surfactant content. It reaches a minimum when hydrophilic and lipophilic properties are balanced, then rises as oleic acid content of the drop and film continue to decrease and the film becomes hydrophilic.

Initial rapid solubilization does not occur when the surfactant solution is buffered at pH 10. As Figure 4-17 shows, an interfacial tension minimum occurs at pH 10 but much more quickly at than at neutral pH (Figure 4-15). 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 4-17) largely or completely eliminates the local tension gradient
promoting solubilization. Moreover, the rate of adsorption of micelles is presumably decreased substantially.

The vigorous Marangoni convection observed during the first 45 seconds for the vertical cell experiment at pH 10 (Figure 4-18) and the low interfacial tensions seen at short times in Figure 4-17 raise the question of whether substantial initial shrinkage occurred for the drop experiment of Figure 4-11 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 seconds 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 4-11 when the drop was injected with a micropipette, drop diameter was measured within one second after detachment from the micropipette. No shrinkage was observed after this time. This observation confirms the conclusion that the amount of initial solubilization is small at pH 10.

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 4-19 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 lauric acid.

The intermediate phase in the system of Figure 4-19 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 L₁ 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 85/15 triolein/oleic acid, which did exhibit rapid initial solubilization.

4.4 Summary

In this chapter data on solubilization of triolein and its mixtures with fatty acids and fatty alcohols by nonionic surfactant solutions have been presented. The main conclusions are summarized as follow:

(1) Rate of triolein solubilization is controlled by phenomena at interface, not mass transfer in bulk liquid. For any given system solubilization rate is proportional to rate of "adsorption" of micelles.

(2) Rate of triolein solubilization is less (sometimes much less) than would be expected from the product of rate of solubilization of n-hexadecane and ratio of equilibrium solubilization capacities of triolein and n-hexadecane. Apparently low diffusion coefficients and/or steric effects hinders triolein transfer from oil phase into micelles
temporarily joined to interface or breaking off interface. These effects are due to large size of triolein molecules (perhaps made larger if there is association H-bonding between two triolein molecules or between a triolein and a surfactant molecule, a matter that could be investigated experimentally).

(3) Rate of triolein solubilization can be increased by changing surfactant and/or adding short-chain alcohols to decrease interfacial tension and especially to increase film flexibility. The latter not only makes it easier to have local deformation so that triolein can overcome steric effects and enter micelles joined to the interface but also decreases the work required for a micelle in solution to became attached or coalesce.

(4) The ease with which solubilized hydrocarbon is transferred from micelles to bulk oil phase seems to favor adsorption of micelles as a mechanism rather than micelle dissociation near the interface followed by adsorption mainly of surfactant. For ionic surfactants hydrocarbon reduces the rate of micelle dissociation.

(5) Triolein solubilization is much higher when modest amounts of oleic acid are present (but not enough to form $L_\alpha$ intermediate phase). Although the experiments here cannot identify conclusively the detailed mechanism at the interface, a likely mechanism is local Marangoni flow from drop to micelle. At high pH, considerable acid at the interface is ionized, and there is little rapid initial solubilization because large interface tension gradient no longer exists.
Chapter 5: Dissolution of Nonionic Surfactants and Their Mixtures with Alcohols into Water

5.1 Theoretical approach

This section reviews theoretical results that will be used in interpreting experimental results from drop dissolution experiments and contacting experiments on vertical cells presented later. It discusses the case of slow drop dissolution of binary mixtures in water and the case of rapid dissolution of pure nonionic surfactants in water with formation of intermediate phases. It also provides a numerical scheme to determine diffusivities of intermediate phases of nonionic surfactants by combining experimental data from drop dissolution and contacting experiments on vertically oriented cells.

5.1.1 Diffusion equation of ternary system in spherical coordinates with pseudo-steady-state assumptions

For a system having the characteristic time of diffusion for all species much less than the characteristic time of experiment, diffusion equations can be easily treated with quasi-steady state approximations [Lim, 1991b; Rang, 1995]. It is of interest to predict the dissolution process of droplets of binary mixtures into water, for example, mixtures of surfactant and alcohol. Consider a spherical drop injected into a large quantity of aqueous surfactant solution. With the assumptions of constant diffusion coefficients, no convection, and negligible cross-diffusion effects, the mass balance for each species can be simplified with the quasi-steady-state approximation to

$$\frac{d}{dr}\left(r^2 \frac{dw_i}{dr}\right) = 0 \quad (5.1-1)$$
where \( w_i \) is the mass fraction of species \( i \). The general solution to above equation inside drop is

\[
w_i = w_i(t), \text{ since } dw_i/dr = 0 \text{ at } r=0 \quad (5.1-2)
\]

and outside drop:

\[
w_i' = w_i'_{\infty} + \frac{a_i(t)}{r} \quad (5.1-3)
\]

where \( w_i' \) and \( w_i'_{\infty} \) are the local and bulk concentrations of species \( i \) in the aqueous phase; \( a_i(t) \) is to be determined from boundary conditions. Equations (5.1-2) and (5.1-3) can be solved with appropriate boundary conditions at drop surface \( r=R(t) \). If no adsorption of any species occurs at interface, the species mass balance equations are given by [Slattery, 1990]

\[
\frac{d}{dt} \left( \frac{4}{3} \pi R^3 w_i \rho \right) = D_i' \rho \left( \frac{4}{3} \pi r^2 \frac{dw_i'}{dr} \right) \bigg|_{r=R(t)} + 4 \pi R^2 w_i' \rho' \left( \frac{dR}{dt} \right) \quad (5.1-4)
\]

where \( D_i' \) is the diffusivity of species \( i \) in the aqueous solution; \( \rho \) and \( \rho' \) are the densities inside drop and of the aqueous solution, both of which are assumed constant; \( i=1 \) denotes alcohol, \( i=2 \) surfactant and \( i=3 \) water. The assumption of local equilibrium at interface is valid only when diffusion through bulk phase is slow in comparison to adsorption and desorption at the interfaces.

Take dimensionless variables:

Dimensionless radius: \( R_D = R/R_o \)

Dimensionless time: \( t_D = t D_{\infty}^2 R_o^2 \)
Dimensionless concentration:

\[
    x = 1 - \frac{w_{1o} - \frac{\rho'}{\rho} w'_{1R}}{w'_{1o} - \frac{\rho'}{\rho} w'_{1R}} \quad \text{and} \quad
    y = 1 - \frac{w_{2o} - \frac{\rho'}{\rho} w'_{2R}}{w'_{2o} - \frac{\rho'}{\rho} w'_{2R}}
\]

where \( w_{1o} \) and \( w_{2o} \) are the initial concentrations of alcohol and surfactant inside drop; \( w'_{1R} \) and \( w'_{2R} \) are the concentrations of alcohol and surfactant in the aqueous solution at interface. For alcohols with carbon chain lengths greater than 9, \( w'_{1R} \) is negligible since they are virtually insoluble in water [Perry’s Handbook, 1984]. It is noteworthy that \( w'_{2R} \) should be below CMC and may have the same order of magnitude as CMC near and above PIT. CMCs of nonionic surfactants are usually very small and thus \( w'_{2R} \) is often taken as a constant or negligible compared to \( w_{2o} \). Furthermore, \( w'_{1x} \) and \( w'_{2x} \) are assumed to be zero for the system studied in this work, since the drops were injected into pure water. Rewriting individual species mass balance equation with dimensionless variables, one gets:

\[
    \frac{d}{dt} \left[ R_{\alpha}^3 \right] = -3 \left( \frac{D_1'}{D_2'} \right) \left( \frac{\rho'}{\rho} \right) \left( \frac{w'_{1R}}{w'_{1o} - \frac{\rho'}{\rho} w'_{1R}} \right) \cdot R_{\alpha} \quad (5.1-5)
\]

and

\[
    \frac{d}{dt} \left[ R_{\beta}^3 \right] = -3 \left( \frac{\rho'}{\rho} \right) \left( \frac{w'_{2R}}{w'_{2o} - \frac{\rho'}{\rho} w'_{2R}} \right) \cdot R_{\beta} \quad (5.1-6)
\]

From equation (5.1-5) and (5.1-6) with initial condition, \( R_{\alpha}, R_{\beta} = 1, x = 0, y = 0 \) at \( t = 0 \), one can get the following relation:

\[
    R_{\alpha}^3 = \frac{1 - \alpha_{\alpha}}{(1 - x) - \alpha_{\alpha}(1 - y)} \quad \text{where} \quad \alpha_{\alpha} = \left( \frac{D_1'}{D_2'} \right) \left( \frac{w'_{1R}}{w'_{1o} - \frac{\rho'}{\rho} w'_{1R}} \right) \left( \frac{w'_{2R}}{w'_{2o} - \frac{\rho'}{\rho} w'_{2R}} \right) \quad (5.1-7)
\]
It is of interest to consider some special cases. If a drop of a mixture of surfactant and long-chain alcohol is dissolved in pure water, for example, mixtures of $C_{12}E_8$ and $C_{16}OH$, $\alpha_o$ is zero since $C_{16}OH$ is practically insoluble in water [Perry's Handbook, 1984].

$R_D$ can be simplified as

$$R_D = (1-x)^{\frac{1}{2}} \quad (5.1-8)$$

Substitute $R_D$ into equation (5.1-5) and (5.1-6), and combine both equations. Then one obtains:

$$\frac{d}{dt} \left( \frac{1-y}{1-x} \right) = -3 \cdot b_o \cdot (1-x)^{-1} \quad \text{where} \quad b_o = \left( \frac{\rho_o}{\rho} \right) \left( \frac{w_o}{w_2} \right) \quad (5.1-9)$$

Suppose that the following expression is a good approximation to the coexistence curve on segments of interest.

$$w_2 = A_1 \cdot \left( \frac{x}{A_2} - 1 \right) \quad \text{or} \quad 1-y = (1-x)(A_1 x - A_2) - A_3 \quad (5.1-10)$$

Substitute equation (5.1-10) into equation (5.1-9) and integrate it with the initial condition: $x=0$ at $t=0$. The result comes out as

$$t = \frac{A_1}{4b_o} (R_{z_2}^z - 1) - \frac{A_3}{2b_o} (R_{z_2}^z - 1) \quad (5.1-11)$$

That is, the relation between drop radius of surfactant mixtures and contact time can be predicted with the above equation. For the special case of dissolution of mixtures of surfactant and water insoluble alcohols, the relation among drop radius, contact time, and the alcohol contents is predicted by:

$$R = R_o \left( \frac{w_o}{w_2} \right)^{\frac{1}{2}}$$
\[ t \cdot \frac{D_i'}{R_o^2} = \frac{A_i}{4b_i} \left[ \left( \frac{w_i'}{w_o} \right)^{4/3} - 1 \right] - \frac{A_i}{2b_i} \left[ \left( \frac{w_i'}{w_o} \right)^{-2.3} - 1 \right] \] (5.1-12)

5.1.2 Diffusion equation in one dimensional Cartesian coordinate with moving boundaries

As shown in Section 2.5, the transport equations can be written as equation 2.5-1, when two large quantity of liquids of uniform concentrations are brought into contact without convection at an interface in a one-dimensional configuration. The solutions are given as equation 2.5-2.

Equation 2.5-2 also applies when the systems have intermediate phases. If locations of interfaces in each phase are known from experiments, there are three unknown variables, \( a_i', b_i', \) and \( D_i' \), in composition profile equation of species \( i \) in each phase \( j \). Supposing that compositions at both ends of each phase are known from the published phase diagram, there is only one degree of freedom in each phase. However, with the further assumption that the mass of species \( i \) must be conserved at each interface, the whole system still has one more degree of freedom in order to be completely determined because the number of interfaces is one less than the number of phases. If no adsorption of any species occurs at interface, the mass balance of species \( i \) over interface \( S \) can be expressed as the following equation [Slattery, 1990]

\[ -\rho \cdot D_i' \frac{d(w_i')}{dz} \cdot -\rho \cdot w_i' \frac{d(w_i')}{dz, dt} \cdot -\rho \cdot D_i' \frac{d(w_i')}{dz, dz} \cdot -\rho \cdot w_i' \frac{d(w_i')}{dz, dt} \cdot \cdot \cdot \] (5.1-13)

where \( S^- \) and \( S^+ \) denote both sides of interface.
If the composition is continuous at interfaces, such as in published phase diagrams for this C_{12}E_6-water system at 30°C (phase diagram shown as Figure 2-2), equation (5.1-13) can be further simplified as:

\[ \sqrt{D_i} \cdot b_i \cdot \exp(-\frac{z^2}{4D_i t}) = \sqrt{D_i} \cdot b_i \cdot \exp(-\frac{z^2}{4D_i t'}) \]  \hspace{1cm} (5.1-14)

It is possible to fully determine all variables in the composition profile equations by combining the data for the same system with moving boundaries but in spherical coordinates (described in Section 5.1.3).

5.1.3 Diffusion equation in spherical coordinates with moving boundaries

When dissolution of surfactant into water or solubilization of oil into aqueous surfactant solution takes place, the phases may expand or shrink. If the phase boundary is moving at a speed that can not be considered as "motionless", one often needs numerical methods to integrate the diffusion equation with the moving boundary conditions. Finite difference method is often used in differentiating the spatial coordinate. For simplicity an explicit method of integration with suitable time interval is used. It saves computer storage space and computing time at the price of the strict stability requirement that the Courant number cannot exceed 1/2.

Unsteady diffusion equation in spherical coordinates with only radial concentration variation can be expressed as

\[ \frac{\partial C}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) \] \hspace{1cm} (5.1-15)
With assumptions of constant diffusion coefficients, no convection, and negligible cross-diffusion coefficients one single value of diffusion constant in each phase is used for each component. A forward-time-center-block finite difference scheme was chosen in this study to integrate the above equation (5.1-15) which turned out to be

$$
\frac{C_{i}^{j+1} - C_{i}^{j}}{\Delta t} = \frac{1}{r_i^2} \cdot \frac{A_{i+\frac{1}{2}}^{j+\frac{1}{2}} - A_{i-\frac{1}{2}}^{j+\frac{1}{2}}}{\Delta r} \quad \text{where} \quad A_{i+\frac{1}{2}}^{j+\frac{1}{2}} = r_{i+\frac{1}{2}}^2 \cdot D_{i+\frac{1}{2}} \cdot \frac{C_{i}^{j+1} - C_{i}^{j}}{\Delta r} \quad (5.1-16)
$$

The Courant number, $D_{i}^j \Delta t / (\Delta r)^2$, must be less than 0.5 to get stable solutions. $C_{i}^{j}$ denotes the concentration $C$ at spatial point $i$ and at time step $j$. The concentration $C_{i}^{j+1}$ can be calculated from equation (5.1-16) with all known concentrations $C_{i}^{j}$. It is noteworthy that the Courant stability requirement is needed in applying the explicit forward-time-center-block finite difference scheme to integrate equation (5.1-15). The Courant stability requirement won’t be needed if any implicit method is used. However, algebraic equation solvers for a tridiagonal matrix will definitely be needed for implicit methods.

5.1.4 Special case - diffusion equation in spherical coordinates with moving boundaries for dissolution of surfactant system with equal diffusion coefficients in all phases

Consider the dissolution of neat $C_{12}E_5$ into water at a temperature slightly below its cloud point temperature (phase diagram shown as Figure 5-1 and Figure 5-2). A liquid
Figure 5-1 Phase Diagram of C₁₂E₅/water system [Mitchell, 1983]
Figure 5-2 Phase Diagram of $C_{12}E_5$/water system [Strey 1990, 1996]
crystalline phase, \( L_\alpha \), is the only intermediate phase which appears in the dissolution process. Assume there is no concentration jump at \( L_1/L_\alpha \) and \( L_2/L_\alpha \) interfaces as the phase diagram indicated, and all phases have the same diffusivities. The surfactant concentrations at phase boundaries are known from the published phase diagram [Mitchell, 1983; Strey, 1991, 1994]. Section 2.6 presents Frank’s approach to find analytical solutions for a system where a spherical or cylindrical new phase is growing from negligible radius in an initially uniform medium and the equilibrium conditions are maintained at the growing surface [Frank, 1950]. Similar to this approach, analytical solutions by the present author and Dr. Patrick Warren of Unilever Research Port Sunlight Laboratory (UK) were found for this system.

The diffusion equation to describe the dissolution of a surfactant drop of finite initial radius in water is the same as equation (5.1-15). It also assumes the diffusivity in each phase is the same. It is solved with the following initial condition and boundary conditions:

\[
IC: \quad C(r,0) = C_0 \quad \text{for } r = \{0, R_o\}, \quad \text{otherwise } C(r,t) = 0
\]

\[
BC 1: \quad C(0,t) = \text{Finite}
\]

\[
BC 2: \quad C(r,t) = 0 \quad \text{when } r \text{ is large enough (} r = pR_o \text{ is taken here where } p \text{ is a large number.)}
\]

Using separation of variables to solve equation (5.1-15), one gets the power series solution:
\[ C(r,t) = \sum_{\alpha=1}^{\infty} \alpha_n e^{-\alpha_n^2Dt/r} \frac{\sin(\alpha_n r)}{r} \]

where \( \alpha_n = \frac{n\pi}{pr} \) and \( \alpha_n = \frac{2C_0}{n\pi} \left[ \frac{\sin(\alpha_n R_o)}{\alpha_n} - \frac{R_o \cos(\alpha_n R_o)}{\alpha_n} \right] \) \hspace{1cm} (5.1-18)

where \( R_o \) is the initial radius of drop; \( D \) is the lumped diffusivity coefficient; \( pr \) is the cut-off distance. If 50 is chosen for \( p \), an average error of \( 8 \times 10^{-4}\% \) over entire domain at steady state is expected for its concentration. However with \( p \) equal to 100, the error percentage is minimal -- only \( 10^{-4}\% \).

Dr. Patrick Warren of Unilever Research used the transformed variable \( rC(r,t) \) instead of \( C(r,t) \) itself. The boundary condition, \( BC \) 2 of equation (5.1-16), was then taken as \( rC(r,t) \to 0 \) when \( r \to \infty \). He obtained an analytical solution using Laplace transformation method, which is equivalent to equation (5.1-18):

\[ C(r,t) = \frac{1}{2} \left[ \text{erf} \left( \frac{r+R_o}{\sqrt{4Dt}} \right) - \text{erf} \left( \frac{r-R_o}{\sqrt{4Dt}} \right) \right] + \frac{\sqrt{Dt}}{r \sqrt{\pi}} \left[ e^{-\left(\frac{r+R_o}{\sqrt{4Dt}}\right)^2} - e^{-\left(\frac{r-R_o}{\sqrt{4Dt}}\right)^2} \right] \] \hspace{1cm} (5.1-19)

5.2 Dissolution of nonionic surfactants

5.2.1 Dissolution of liquid nonionic surfactants

Surfactant droplet dissolution experiments were conducted using the basic procedures described in Section 3.6 for some pure surfactants and surfactant/alcohol mixtures below their cloud point temperatures.

Table 5-1 provides information obtained from experiments using the drop technique of Section 3.8 on the time required for complete dissolution of drops of various surfactants at temperatures below their respective cloud points. All of the drops of pure
linear alcohol ethoxylates dissolved rather quickly (10-100 sec) and all exhibited, as expected from known phase diagrams (Figures 2-1, 5-1, and 5-2), an intermediate lamellar liquid crystalline phase (Lα). From experiments for drops of neat C_{12}E_{5} and C_{12}E_{6} with similar initial diameters but at different temperatures, it was found that dissolution time decreased with increasing temperature. Moreover, drops of C_{12}E_{5} at 28°C, 3°C below its cloud point, dissolved in water faster than drops of C_{12}E_{6} with similar initial sizes at 30°C -- about 20°C below its cloud point. The difference may stem from the occurrence of intermediate hexagonal (H₁) and cubic phases (V₁) for C_{12}E_{6} but not C_{12}E_{5} near 30°C. (see Figure 2-4)

More complicated behavior was seen during dissolution processes of the commercial nonionic surfactants Tergitol 15-S-7 and Neodol 25-7, which are mixtures of species ranging from quite hydrophilic to rather hydrophobic. The commercial secondary alcohol ethoxylate, Tergitol 15-S-7, dissolved much more slowly than the pure surfactants. Although initial dissolution was fast, the last small amount took much longer for complete dissolution at both 30°C and 35°C, temperatures just below the cloud point of 37°C (see Table 5-1). Moreover, considerable spontaneous emulsification within the drops was observed. The droplets formed during the emulsification processes are believed to be water, presumably containing some dissolved surfactant, as they were observed frequently to coalesce with the external water phase. (see Figure 5-3)

In contrast to the experiments with pure linear alcohol ethoxylates, where dissolution was always faster at higher temperatures. Table 5-1 shows that the time needed for complete dissolution of a Neodol 25-7 drop at 45°C was about 2.5 times
longer than at 35°C with the same initial drop size. The cloud point of this surfactant is 50°C. Similarly, the total dissolution time of Tergitol 15-S-7 drops was longer at 35°C than at 30°C. The differences of dissolution processes between commercial nonionic surfactants and pure nonionic surfactants will be discussed later in Section 5.4.

For Tergitol 15-S-7 the small drop remaining near the end of the experiment at 30°C always became elongated and frequently exhibited conical protrusion before it finally disappeared (see Figure 5-4). An even more interesting phenomenon occurred in one case at 35°C, where the small drop was deformed into a crescent shape and emitted a small jet of liquid. This behavior was also seen for a drop of Tergitol 15-S-7 at 30°C. Similar phenomena were observed in the experiments with Neodol 25-7 drops at 45°C, which is only 5°C below the cloud point, but were never seen in the same system at 35°C nor in the experiments with Neodol 25-9 at 30°C and 35°C that were some 50°C below the cloud point. The possible mechanism will be discussed later in Section 5.4.

The complete dissolution time for the pure surfactants varies linearly with the square of the initial drop radius at constant temperature (see Figures 5-5 and 5-6), which implies that dissolution of C₁₂E₅ and C₁₂E₆ into water is controlled by diffusion. From the slope of Figure 5-6 for drops of C₁₂E₆ dissolving in water at 30°C, the overall effective diffusivity is calculated as 9.9×10⁻¹¹ m²/sec with equivalent schemes derived by the present author and Dr. Patrick Warren at Unilever Research respectively (described in Section 5.1.4). This calculation assumes equal diffusivities of the surfactant in the various phases present including L∞, V₁ and H₁. As shown in Section 5.1.4, one assumes a diffusivity and calculates the "dissolution time" needed for the surfactant concentration at the center of a
Figure 5-3: Drop of Tergitol 15-S-7 in water at 30°C shows emulsification
Figure 5-4: Drop of Tergitol 15-S-7 in water at 30°C shows elongated shape and jetting phenomenon.
Figure 5-5(a): Plot of squares of initial radii of $C_{12}E_5$ drops w.r.t. the dissolution times in water at 28°C

Diffusion Coefficients Used in Calculation:
$D_L = 0.73 \times 10^{-10} \text{ m}^2/\text{sec}$
$D_L = 2.0 \times 10^{-10} \text{ m}^2/\text{sec}$
$D_L = 1.9 \times 10^{-10} \text{ m}^2/\text{sec}$

(b) Sensitivity tests of $D_{L2}$ values on calculate dissolution times for a drop with a radius of 80 μm in the system of Figure 5-5(a)
Figure 5-6: Plot of squares of initial radii of $C_{12}E_6$ drops w.r.t. the dissolution times in water at $30^\circ C$.

Slope = $3.8 \times 10^{-10} \text{ m}^2/\text{sec}$

$D_{\text{eff}} = 0.99 \times 10^{-10} \text{ m}^2/\text{sec}$
Table 5-1 Average time for complete dissolution of nonionic surfactants in water at temperatures below the cloud point

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>C_{12}E_{5}</td>
<td>31.5°C</td>
<td>28°C</td>
<td>150</td>
<td>12.4</td>
<td>Lα</td>
</tr>
<tr>
<td>(2)</td>
<td>C_{12}E_{5}</td>
<td>31.5°C</td>
<td>28°C</td>
<td>191</td>
<td>17.3</td>
<td>Lα</td>
</tr>
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<td>(3)</td>
<td>C_{12}E_{5}</td>
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<td>28°C</td>
<td>232</td>
<td>22.1</td>
<td>Lα</td>
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<td>(4)</td>
<td>C_{12}E_{5}</td>
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<td>30°C</td>
<td>300 - 350</td>
<td>40.2</td>
<td>Lα</td>
</tr>
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<td>(5)</td>
<td>C_{12}E_{6}</td>
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<td>30°C</td>
<td>119</td>
<td>10.2</td>
<td>V1, H1, Lα</td>
</tr>
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<td>(6)</td>
<td>C_{12}E_{6}</td>
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<td>157</td>
<td>16.1</td>
<td>V1, H1, Lα</td>
</tr>
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<td>(7)</td>
<td>C_{12}E_{6}</td>
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<td>30°C</td>
<td>166</td>
<td>20.8</td>
<td>V1, H1, Lα</td>
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<td>C_{12}E_{6}</td>
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<td>30°C</td>
<td>187</td>
<td>22.3</td>
<td>V1, H1, Lα</td>
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<td>C_{12}E_{6}</td>
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<td>30°C</td>
<td>300 - 350</td>
<td>99.8</td>
<td>V1, H1, Lα</td>
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<td>35°C</td>
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<td>11.3</td>
<td>V1, H1, Lα</td>
</tr>
<tr>
<td>(11)</td>
<td>C_{12}E_{6}</td>
<td>52.5°C</td>
<td>35°C</td>
<td>200</td>
<td>18.5</td>
<td>V1, H1, Lα</td>
</tr>
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<td>C_{12}E_{6}</td>
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<td>35°C</td>
<td>300 - 350</td>
<td>78.8</td>
<td>V1, H1, Lα</td>
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<td>(13)</td>
<td>C_{12}E_{6}</td>
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<td>40°C</td>
<td>300 - 350</td>
<td>28.1</td>
<td>Lα</td>
</tr>
<tr>
<td>(14)</td>
<td>C_{12}E_{6}/C_{12}E_{3}=80/20</td>
<td>35.5°C</td>
<td>30°C</td>
<td>300 - 350</td>
<td>35.5</td>
<td>Lα</td>
</tr>
<tr>
<td>(15)</td>
<td>C_{12}E_{6}/C_{12}E_{4}=80/20</td>
<td>40.5°C</td>
<td>30°C</td>
<td>300 - 350</td>
<td>35.7</td>
<td>Lα</td>
</tr>
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<td>(16)</td>
<td>C_{12}E_{6}/C_{12}E_{4}=80/20</td>
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<td>35°C</td>
<td>300 - 350</td>
<td>30.6</td>
<td>Lα</td>
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<td>C_{12}E_{6}/C_{12}E_{8}=80/20</td>
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<td>30°C</td>
<td>300 - 350</td>
<td>50.2</td>
<td>V1, H1, Lα</td>
</tr>
<tr>
<td>(18)</td>
<td>C_{12}E_{6}/C_{12}OH=95/5</td>
<td>36.0°C</td>
<td>30°C</td>
<td>300 - 350</td>
<td>49.3</td>
<td>Lα</td>
</tr>
<tr>
<td>(19)</td>
<td>C_{12}E_{6}/C_{12}OH=95/5</td>
<td>36.0°C</td>
<td>35°C</td>
<td>300 - 350</td>
<td>42.4</td>
<td>Lα</td>
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<tr>
<td>(20)</td>
<td>Neodol 25-7</td>
<td>50.0°C</td>
<td>30°C</td>
<td>300 - 350</td>
<td>102.0</td>
<td>Lα</td>
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<td>35°C</td>
<td>300 - 350</td>
<td>78.6</td>
<td>Lα</td>
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<td>(22)</td>
<td>Neodol 25-7</td>
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<td>35°C</td>
<td>123</td>
<td>10.2</td>
<td>Lα</td>
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<td>Neodol 25-7</td>
<td>50.0°C</td>
<td>45°C</td>
<td>123</td>
<td>26.9</td>
<td>Lα</td>
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<td>(24)</td>
<td>Neodol 25-9</td>
<td>74.0°C</td>
<td>30°C</td>
<td>300 - 350</td>
<td>94.0</td>
<td>Lα</td>
</tr>
<tr>
<td>(25)</td>
<td>Neodol 25-9</td>
<td>74.0°C</td>
<td>35°C</td>
<td>300 - 350</td>
<td>67.7</td>
<td>Lα</td>
</tr>
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<td>(26)</td>
<td>Tergitol 15-S-7</td>
<td>37.0°C</td>
<td>30°C</td>
<td>300 - 350</td>
<td>375.2</td>
<td>Lα</td>
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<td>30°C</td>
<td>135</td>
<td>18.5</td>
<td>Lα</td>
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<td>(28)</td>
<td>Tergitol 15-S-7</td>
<td>37.0°C</td>
<td>35°C</td>
<td>300 - 350</td>
<td>&gt; 50 min</td>
<td>Lα</td>
</tr>
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<td>(29)</td>
<td>Tergitol 15-S-7</td>
<td>37.0°C</td>
<td>35°C</td>
<td>150</td>
<td>38.4</td>
<td>Lα</td>
</tr>
</tbody>
</table>

Experiments with initial diameters less than 200 μm were all conducted with microinjection system.

(26), (28): Most of surfactant drop dissolved in the first 2 minutes, but the remaining part took a long time for complete dissolution.

Small water drops were seen near the edge of surfactant drops initially but later everywhere inside surfactant drops.

(27): Drops of surfactant were elongated in later stage of every experiment.
Table 5-2: Summary of diffusion coefficients from contacting experiments of small drops

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Temperature [°C]</th>
<th>(R_i^2/\text{time} [\mu\text{m}^2/\text{sec}])</th>
<th>Effective Diffusivity [m(^2)/sec]</th>
<th>Diameter of Droplet [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) C(_{12})E(_5)</td>
<td>28</td>
<td>811</td>
<td>1.57\times10^{-10}</td>
<td>150 - 230</td>
</tr>
<tr>
<td>(2) C(_{12})E(_6)</td>
<td>30</td>
<td>376</td>
<td>0.99\times10^{-10}</td>
<td>120 - 190</td>
</tr>
<tr>
<td>(3) C(_{12})E(_6)</td>
<td>35</td>
<td>639</td>
<td>1.68\times10^{-10}</td>
<td>145 - 200</td>
</tr>
</tbody>
</table>

\(R_i\): Initial radius of injected surfactant drop

time: time required for complete dissolution of injected surfactant drop

surfactant drop with known initial radius to reach the surfactant concentration at the \(L_i/H_i\) interface. Each assumed diffusivity has a corresponding calculated "dissolution time."

When this "dissolution time" is equal to the complete dissolution time observed from surfactant droplet dissolution experiments, the corresponding diffusivity is the overall effective diffusivity. The overall effective diffusivity can be viewed as the average of diffusivities of all phases involved in dissolution processes. Similarly the overall effective diffusivity of C\(_{12}\)E\(_6\) at 35°C is 1.68\times10^{-10} m\(^2\)/sec, and that for C\(_{12}\)E\(_5\) at 28°C is 1.57\times10^{-10} m\(^2\)/sec (see Table 5-2).

For comparison the self-diffusion coefficient of C\(_{12}\)E\(_5\) monomer at infinite dilution and at 25°C is estimated to be 3.5\times10^{-10} m\(^2\)/sec [Johnströmer, 1991]. However, the self-diffusion coefficient of C\(_{12}\)E\(_5\) in 20-50 wt% solutions at 25°C, which contain micelles, is only about 2\times10^{-11} m\(^2\)/sec. The self-diffusion coefficient of 1 wt% C\(_{12}\)E\(_6\) in D\(_2\)O is reported to decrease from 4\times10^{-11} to 2\times10^{-11} m\(^2\)/sec as temperature changes from 25°C to at 45°C [Penders, 1994]. Moreover, the diffusivity of C\(_{12}\)E\(_6\) at the critical micelle concentration of 1.25 g/L\(^{-1}\) and at 30°C was found to be about 4\times10^{-11} m\(^2\)/sec using NMR techniques [Brown, 1983]. With the exception of that for C\(_{12}\)E\(_5\) monomer these values are somewhat
lower than those reported above. However, as discussed below, diffusivities in the liquid crystalline phases also influence dissolution rates.

5.2.2 Vertical cell contacting experiments

Contacting experiments on vertically mounted cells were conducted using the basic procedures described in Section 3.7 for some pure surfactants below their cloud point temperatures. The lower half of the cell was filled with deionized water or aqueous surfactant solution and the bottom of the cell sealed. Then the cell was placed in a thermal stage on the microscope, and surfactant was very carefully injected into the upper half of the cell using a syringe in such a way as to minimize mixing during contact.

Figure 5-7 shows the schematic drawing of intermediate phases of C_{12}E_6/water system on vertical cell at 30°C. The position of each phase boundary in vertical cell experiments was recorded with time. Thus, the growth rate of each phase and the velocity of each interface were known. With this information and the assumption based on available phase diagrams (Figures 2-1 and 5-1) that there was negligible concentration “jump” at each phase boundary, the mass transport equations in one dimension could be solved. (see Section 5.1.2)

Figure 5-8 shows that the interfacial positions of all intermediate phases of C_{12}E_6/water system at 30°C on vertical cell experiments were proportional to the square root of the contact time. Table 5-3 lists the growth rates for all intermediate phases formed for dissolution of C_{12}E_6 in both water and aqueous C_{12}E_6 solutions. Even with this information it is not possible to determine values of the binary diffusivities for all the
phases, since one more degree of freedom is left to completely solve the diffusion
equations. However, if the value of diffusivity in one phase is known or assumed, those in
the other phases can be calculated from the scheme described in Section 5.1.2 (see Figure
5-9). It is noteworthy that the measured rates of growth of the various phases can be
matched both when all diffusivities and the corresponding fluxes are high and when they
are low. The interface between two intermediate phases that have larger diffusivities can
move at the same speed as that between phases with smaller diffusivities. However the
concentration profiles calculated with larger diffusivities are more flat than those
calculated with smaller diffusivities.

It is possible in principle to combine the information from the drop dissolution and
vertical cell experiments to obtain values for diffusivities of all the phases. This approach
requires a numerical solution of the equations governing drop dissolution, taking into
account the moving boundaries between the various intermediate phases (see Section
5.1.3). This scheme can be elucidated using C_{12}E_8 and Figure 5-9 as an example.

Figure 5-7: Schematic drawing of intermediate phases of C_{12}E_8/water system
on vertical cell at 30°C

<table>
<thead>
<tr>
<th></th>
<th>Surfactant Concentration by weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_2</td>
<td>1.0</td>
</tr>
<tr>
<td>L_α</td>
<td>0.837</td>
</tr>
<tr>
<td>V_1</td>
<td>0.644</td>
</tr>
<tr>
<td>H_1</td>
<td>0.5</td>
</tr>
<tr>
<td>L_1</td>
<td>0.407</td>
</tr>
</tbody>
</table>


Figure 5-8: Growth rates of intermediate phases of C_{12}E_{6}/water at 30°C

(a) the change of position of L_1-H_1 interface with contact time

(b) the growth rates of H_1 and V_1 phases
(Continued from the previous page)

(c) the growth rates of $L_\alpha$ of $C_{12}E_6$ in water at $30^\circ C$
Figure 5-9: Calculated diffusivities of intermediate phases from $\text{C}_{12}\text{E}_6$ contacting experiments on vertical cells with water and aqueous $\text{C}_{12}\text{E}_6$ solution at 30°C.
Table 5-3: Summary of diffusion coefficients from contacting experiments in vertical cells

<table>
<thead>
<tr>
<th></th>
<th>Surfactant</th>
<th>Bulk Solution</th>
<th>Temperature [°C]</th>
<th>Intermediate Phase</th>
<th>Growth Rate [mm/min(^{1/2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>C(_{12}E_5)</td>
<td>Deionized Water</td>
<td>28</td>
<td>L(_{α})</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L(<em>{1} - L</em>{α})</td>
<td>~0</td>
</tr>
<tr>
<td>(2)</td>
<td>C(_{12}E_6)</td>
<td>Deionized Water</td>
<td>30</td>
<td>L(_{α})</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V(_{1})</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_{1})</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L(_1 - H_1)</td>
<td>-0.042</td>
</tr>
<tr>
<td>(3)</td>
<td>C(_{12}E_6)</td>
<td>10 wt% C(_{12}E_6)</td>
<td>30</td>
<td>L(_{α})</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V(_{1})</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_{1})</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L(_1 - H_1)</td>
<td>-0.074</td>
</tr>
<tr>
<td>(4)</td>
<td>C(_{12}E_6)</td>
<td>20 wt% C(_{12}E_6)</td>
<td>30</td>
<td>L(_{α})</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V(_{1})</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_{1})</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L(_1 - H_1)</td>
<td>-0.060</td>
</tr>
</tbody>
</table>

Basically one assumes a value for one diffusivity, for example D\(_{H1}\) and uses ratios from Figure 5-9 to get the other diffusivities. Then with these diffusivities, one finds the complete dissolution time where the concentration at center of drop is that at L\(_1\)/H\(_1\) phase boundary. The calculated dissolution time is compared with experimental dissolution time. One repeats this calculation process until agreement between calculated and experimental dissolution times is obtained. It is noteworthy that with the overall effective diffusivity, described in Section 5.2.1, it requires less effort to guess the range of D\(_{H1}\) and pick up possible diffusivity sets since it can be viewed as the average of diffusivities of all intermediate phases.

The resulting best estimates of the various diffusion coefficients for the C\(_{12}E_6\)/water system at 30°C are listed in Figure 5-10 and provide good agreement between...
measured and calculated dissolution times for drops of different initial sizes, as the figure shows. Diffusivities for all three liquid crystalline phases and the $L_1$ phase are of order $10^{-10}$ m$^2$/sec, and their ratios are consistent with Figure 5-9. Moreover, Sallen et al. [1997] recently studied the Mullins-Sekerka instability at the hexagonal-micellar interface in a lyotropic system of $C_{12}E_6/H_2O$ and reported the diffusivities of $L_1$ and $H_1$ phases of $C_{12}E_6/H_2O$ system by measuring the critical and the drift velocities at freezing and melting fronts of micellar-hexagonal interface at azeotropic composition. Their values of diffusivities are $1.2 \times 10^{-10}$ m$^2$/s for micellar phase, $2.3 \times 10^{-10}$ m$^2$/s for hexagonal phase in parallel direction and $0.85 \times 10^{-10}$ m$^2$/s for hexagonal phase in perpendicular direction, which is in good agreement with the values presented in this work.

There are differences between the diffusivities of $L_2$ phase, $D_{L2}$, obtained from Figure 5-9 and the best estimates listed in Table 5-4. Experimental error is greatest for $L_\alpha/L_2$ interface which has a large influence on $D_{L2}$. Its value was assumed instead of using the value from Figure 5-9. The sensitivity tests show that its value won’t change the calculated dissolution time much and the reason is probably because $L_2$ is rapidly converted to $L_\alpha$ early in the dissolution process (see Figure 5-11). This point is important because the equations describing the vertical cell experiment did not yield a value of $D_{L2}$ for the estimated value of $D_{H1}$ given in Figure 5-10. In contrast, the calculated dissolution times are rather sensitive to the change of $D_{H1}$ values (see Figure 5-11).

Similar results for $C_{12}E_6$/water at 28°C were also shown as Figure 5-5, and the diffusivities found are of the same order of magnitude as for $C_{12}E_6$/water at 30°C. Similar
Figure 5-10: Plot of squares of initial radii of C₁₂E₆ drops w.r.t. the dissolution times in water at 30°C

Diffusivities used in calculation 1:
- \( D_{L1} = 0.86 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{V1} = 2.32 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{H1} = 1.06 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{L2} = 2.19 \times 10^{-10} \text{m}^2/\text{sec} \)

Diffusivities used in calculation 2:
- \( D_{L1} = 0.71 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{V1} = 2.16 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{H1} = 2.01 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{L2} = 2.01 \times 10^{-10} \text{m}^2/\text{sec} \)

- ○ ○ ○ Experimental Data
- □ □ □ Theoretical Calculation 1 (Best Fit)
- ▼ ▼ ▼ Theoretical Calculation 2 (NOT Best Fit)

Figure 5-11: Sensitivity tests of \( D_{L2} \) and \( D_{H1} \) values on calculated dissolution times for a drop with a radius of 80μm in the system of Figure 5-10

Diffusivities used in calculation for a drop with a radius of 80μm:
- \( D_{L1} = 0.86 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{V1} = 2.32 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{L2} = 2.19 \times 10^{-10} \text{m}^2/\text{sec} \)
- \( D_{H1} = 1.08 \times 10^{-10} \text{m}^2/\text{sec} \) used for \( D_{L2} \) test
- \( D_{H1} = 1.0 \times 10^{-10} \text{m}^2/\text{sec} \) used for \( D_{H1} \) test

- ○ ○ ○ Sensitivity test of \( D_{L2} \) values
- □ □ □ Sensitivity test of \( D_{H1} \) values
to C\textsubscript{12}E\textsubscript{6}/water system, the value of D\textsubscript{L2} is assumed and the sensitivity tests show that its value will not change the calculated dissolution time significantly (Figure 5-5).

Dissolution experiments of C\textsubscript{12}E\textsubscript{6} were extended to systems with 10 wt\% and 20 wt\% C\textsubscript{12}E\textsubscript{6} micellar solutions. The results are shown as Figures 5-12 and 5-13. Table 5-4 lists all the best estimates of diffusion coefficients combining the drop dissolution experiments and vertical cell experiments. All the coefficients are shown to have the same order of magnitude and are generally in good agreement with those reported by Sallen et al. [1997]. Increasing the concentration of C\textsubscript{12}E\textsubscript{6} present in the bulk solutions decreases the diffusion coefficients. Although D\textsubscript{L2} was often assumed rather than obtained from Figure 5-9, it was found to be 1.18×10\textsuperscript{-10} m\textsuperscript{2}/sec resulting from the experiments of C\textsubscript{12}E\textsubscript{6} in 10 wt\% C\textsubscript{12}E\textsubscript{6} micellar solution using Figure 5-9. It should be mentioned that the dissolution times presented here are the averages of at least 10 different runs at the same conditions. The results were reproducible and within about 10\% from the averages.

<table>
<thead>
<tr>
<th>Surf.</th>
<th>Bulk Solution</th>
<th>Temp. [°C]</th>
<th>Diff. L\textsubscript{1}</th>
<th>H\textsubscript{1}</th>
<th>V\textsubscript{1}</th>
<th>L\textsubscript{\alpha}</th>
<th>L\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) C\textsubscript{12}E\textsubscript{6}</td>
<td>Water</td>
<td>28</td>
<td>0.73</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>1.0*</td>
</tr>
<tr>
<td>(2) C\textsubscript{12}E\textsubscript{6}</td>
<td>Water</td>
<td>30</td>
<td>0.86</td>
<td>1.08</td>
<td>2.32</td>
<td>2.19</td>
<td>1.0*</td>
</tr>
<tr>
<td>(3) C\textsubscript{12}E\textsubscript{6}</td>
<td>10 wt% C\textsubscript{12}E\textsubscript{6}</td>
<td>30</td>
<td>0.37</td>
<td>0.93</td>
<td>1.53</td>
<td>2.03</td>
<td>1.18</td>
</tr>
<tr>
<td>(4) C\textsubscript{12}E\textsubscript{6}</td>
<td>20 wt% C\textsubscript{12}E\textsubscript{6}</td>
<td>30</td>
<td>0.45</td>
<td>0.57</td>
<td>1.31</td>
<td>1.58</td>
<td>1.0*</td>
</tr>
</tbody>
</table>

* denotes the value is assumed in calculation rather than obtained from Figure 5-9.
Figure 5-12: Plot of squares of initial radii of $C_{12}E_6$ drops w.r.t. the dissolution times in 10 wt% $C_{12}E_6$ solution at 30°C

Diffusivities used in calculation [unit=$10^{-10}$ m$^2$/sec]

$D_{L1} = 0.37$  $D_{H1} = 0.93$  $D_{V1} = 1.53$  $D_{L1} = 2.03$  $D_{L2} = 1.18$

Slope = 256.2 μm$^2$/sec

- ○ From Experimental Data
- □ From Theoretical Calculation
Figure 5-13: Plot of squares of initial radii of $C_{12}E_6$ drops w.r.t. the dissolution times in 20 wt% $C_{12}E_6$ solution at 30°C.

Diffusivities used in calculation [unit=$10^{-10}$ m²/sec]

- $D_L=0.45$
- $D_H=0.57$
- $D_V=1.31$
- $D_{LH}=1.58$
- $D_{LV}=1.0$

Slope = 100 μm²/sec
5.3 Dissolution of nonionic surfactant/alcohol mixtures

5.3.1 Dissolution of mixtures of C\textsubscript{12}E\textsubscript{8} and C\textsubscript{10}OH

Experiments were conducted with well defined mixtures in view of intriguing phenomena described above for commercial surfactants, which are mixtures of surfactants ranging from quite lipophilic to rather hydrophilic. For example, typical distribution of weight percent of ethylene oxide (EO) groups in Neodol 25-7 is from 3 wt\% with 0 EO to 4 wt\% having more than 18 EO [Shell]. Therefore the ternary system C\textsubscript{12}E\textsubscript{8}-C\textsubscript{10}OH-H\textsubscript{2}O is chosen here since its phase diagram at 25°C is available (Figure 5-14) [Yoshida, 1991].

When small drops (about 200 \( \mu \)m in diameter) of neat C\textsubscript{12}E\textsubscript{8} were injected into water at temperatures between 25°C and 35°C, only an \( H_1 \) intermediate phase was seen, and the drops dissolved in water quickly. Probably there was also a thin layer of isotropic \( V_1 \) phase adjacent to the isotropic \( L_2 \) phase. Because, during experiments where pure C\textsubscript{12}E\textsubscript{8} contacted water in vertical cells, a very thin layer of \( V_1 \) (compared to the layer of \( H_1 \)) was observed. These observations are consistent with the phase diagram for the binary system. Since phase behavior of the ternary system C\textsubscript{12}E\textsubscript{8}-C\textsubscript{10}OH-H\textsubscript{2}O is available only at 25°C (Figure 5-14), the remaining results presented here are all from dissolution experiments at this temperature.

When 5 wt\% C\textsubscript{10}OH was present in the drop of C\textsubscript{12}E\textsubscript{8}, the \( L_\alpha \) phase was observed and was surrounded by the \( H_1 \) phase during dissolution experiments. The drops dissolved very quickly except for a very small amount that took about 96 seconds to disappear. When C\textsubscript{10}OH content was increased to 15 wt\%, only the \( L_\alpha \) phase was seen, and it dissolved quickly too. Later, some emulsification of small droplets was observed in the \( L_1 \)
drop remaining near the end of the experiment, and these small droplets coalesced with the external water phase. During this time the overall drop became elongated in a manner similar to that observed in the dissolution experiments of Tergitol 15-S-7 reported previously. These phenomena will be discussed later in Section 5.4. When the experiments were conducted at 30° and 35°C just 7° or 2°C below the cloud point (37°C), not only extensive emulsifications and coalescence but also the protrusions from drops were often observed similar to those observed in the dissolution experiments of Tergitol 15-S-7 and C_{12}E_{4}/SDS (unrecrystallized) mixtures reported in Section 6.2.2 (see Figure 5-15).

The result was very different when drops containing 20 wt% C_{10}OH were injected into water. Myelinic figures formed initially but later were converted into some small drops, probably of the L_{1} phase (Figure 5-16). Figure 6-4 and Figure 6-5 show similar myelinic figures growing out from drops of C_{12}E_{3} and C_{12}E_{4} in water. One hour after injection both lamellar and L_{1} phases remained. Similar results were obtained for drops having the ratio C_{12}E_{8}/C_{10}OH equal to 70/30 (by weight). The schematic phase diagram of this system is shown as Figure 5-17. Based on equilibrium phase behavior experiments, the final state of C_{12}E_{8} with less than 15 wt% C_{10}OH added at 25°C is L_{1} in contrast to W+L_{1}+L_{α} for C_{12}E_{8} with more than 20 wt% C_{10}OH added at the same temperature. A sample of 2 wt% surfactant solution having 85/15 C_{12}E_{8}/C_{10}OH (by weight) indicates that the cloud point temperature of this system is about 34°C.

When a drop with a 60/40 weight ratio of C_{12}E_{8}/C_{10}OH was injected into water, myelinic figures grew out from the drop surface and continued to develop with time. At 20 minutes after injection, a few drops of an isotropic liquid, probably the L_{1} phase, were
Figure 5-14: Phase diagram of $C_{12}E_8/C_{10}OH/water$ system at 25°C [Yoshida, 1991]
Figure 5-15: Drop having an initial ratio of $\text{C}_{12}\text{E}_8/\text{C}_{10}\text{OH}$ equal to 85/15 (by weight) in water at 25°C

(a) Showing emulsion droplets

(b) Showing protrusion
Figure 5-16: Drop having a ratio of $C_{12}E_8/C_{10}OH$ equal to 80/20 (by weight) in water at 25°C shows myelin dispersions at 0.23 seconds after injection.
Figure 5-17: Schematic phase diagram of a $C_{12}E_8/C_{10}OH$/water system at 25°C
observed forming in a very compact mass of myelins. More and bigger L₃ drops were seen among the myelinal figures later in the experiments. The myelin dispersion persisted for 150 minutes and never completely dissolved. Thus, water, L₃, and Lₐ were present in the final equilibrium state. L₃ is also denoted as D' on phase diagram. (see Figure 5-14) A test tube having 3 wt% surfactant mixtures of 60/40 C₁₂E₈/C₁₀OH showed streaming birefringence and very little water in the bottom at equilibrium. The phase sequences at constant water content near water corner on Figure 5-14 can be shown schematically as:

\[ W_\text{m} \text{ (at low alcohol-to-surfactant ratio)} \rightarrow W+L_1 \rightarrow W+L_1+L_\alpha \rightarrow W+L_\alpha \rightarrow W+L_\alpha+L_3 \rightarrow W+L_3 \rightarrow W+L_3+O_m \rightarrow W+O_m \text{ (at high alcohol-to-surfactant ratio)} \]

The supplementary phase behavior experiments were performed to clarify locations of some of these regions at high water contents and the results are shown schematically as Figure 5-18.

Figure 5-18: Phase Behavior of 3 wt% C₁₂E₈/C₁₀OH at 25°C

- □ indicates the final equilibrium states observed in the dissolution experiments.
- ● indicates the equilibrium phases observed from the phase behavior experiments.

Drops having a C₁₃E₈/C₁₀OH ratio of 50/50 (by weight) also formed myelinal figures initially, but L₃ drops were seen forming seconds later. These L₃ drops coalesced
into a very big drop, and all myelinic figures had dissolved by 9 minutes after initial contact. The large L₃ drop did not dissolve during the remainder of the 90-minute experiment.

When drops having C₁₂E₈/C₁₀OH ratios of 45/55, 40/60, and 30/70 (by weight) were injected into water, myelinic figures were seen initially but were rapidly transformed into the L₃ phase, even while the drops were still attached to the tip of the micropipette. This newly formed L₃ phase surrounded the initial L₂ phase. The volume of the L₂ drop shrunk gradually and that of the L₃ drop increased except for the 30/70 drops where little change in phase volumes was seen. For the other compositions the L₂ drops eventually disappeared, leaving only water and L₃ at the end of the experiment. Several samples having 3 wt% in total of C₁₂E₈/C₁₀OH mixtures were made to observe the equilibrium phases at temperature near 24°C. It showed three phases in the test tube having 30/70 C₁₂E₈/C₁₀OH, and two phases in the ones having 50/50 C₁₂E₈/C₁₀OH.

No myelinic figures were seen when drops with C₁₂E₈/C₁₀OH equal to 20/80 or 15/85 (by weight) were injected into water. The radii of these drops decreased very slowly. A few small water droplets formed inside the main drop in some experiments. However, these droplets eventually coalesced with the external water phase.

The solubility of C₁₀OH in water is negligible. Hence, the compositions of drops initially containing only 15% and 20% surfactant will become even more alcohol rich over time, moving along the coexistence curve of Figure 5-14 toward the alcohol vertex after an initial transient. The radius of such drops was found to vary approximately linearly with the square root of contact time, but not with contact time itself.
Figure 5-19 shows the experimentally determined variation of drop diameter with time for an initial ratio of C_{12}E_8/C_{10}OH equal to 20/80 (by weight) and the corresponding curve calculated using the quasi-steady state diffusion model described in Section 5.1.1. The surfactant is preferentially soluble in alcohol for these conditions and solubility in water is near CMC. The only parameter used in fitting this curve is the product of the diffusion coefficient of surfactant and the weight fraction \( w_{2r} \) of surfactant at the drop surface in the aqueous phase. The composition of the drop when it first reaches the coexistence curve is taken to be that on the line connecting the initial drop composition and pure water on the phase diagram. That is, water is assumed to diffuse into the drop much faster than surfactant diffuses out, which seems to be consistent with the relatively short initial transient period shown in Figure 5-19. Surfactant concentration \( w_{2r} \) at the interface should be below the CMC, which is about 0.0059 wt% [Rosen, 1989]. With this value and the parameter found from the quasi-steady state calculation the diffusivity of surfactant in the aqueous phase was estimated to be about \( 10^{-10} \) m\(^2\)/sec. This value is of the same order of magnitude as the measured value for C_{12}E_8 monomers in water at 25°C, viz., \( 4.7 \times 10^{-10} \) m\(^2\)/sec [Johansson, 1993].

5.3.2 Dissolution of mixtures of C_{12}E_6 and C_6OH or C_{12}E_8 and C_{12}OH

Drops with a ratio of C_{12}E_6/C_6OH equal to 85/15 and 75/25 or C_{12}E_8/C_{12}OH equal to 95/5 by weight were injected into water at temperatures slightly below their respective cloud points measured with aqueous solutions having 2 wt% surfactant mixtures. The cloud point temperatures are 27°C for 75/25 C_{12}E_6/C_6OH, 37°C for 85/15 C_{12}E_8/C_6OH
Figure 5-19: Dissolution of a drop having 20/80 C_{12}E_8 and C_{10}E_0 by weight in water at 25^\circ C

Initial composition before contacting: W_{surf}=0.20, W_{alc}=0.80
Initial contact point along coexistence curve: W_{surf}=0.174, W_{alc}=0.6926

R_0 = 54.7\mu m
W_{alc} = 0.6926 to 0.97
D_2xW_{2r}^{\text{prime}} = 7.65 \times 10^{-15} \text{ m}^2/\text{sec}

- Experimental Data
- Calculation with Quasi-Steady state assumption
and 34°C for 95/5 C_{12}E_6/C_{12}OH. The dissolution behaviors of surfactant drops were observed and compared to the other dissolution experiments.

When a drops with ratio of C_{12}E_6/C_6OH equal to 85/15 were injected into water at 30°C, only few emulsification droplets occurred within the surfactant drops near the end of dissolution experiments and coalesced with the bulk phase. The remaining surfactant drops became elongated in the last stage of dissolution. However, very intriguing phenomena were observed when the dissolution experiments of the surfactant drops having 75/25 C_{12}E_6/C_6OH by weight were conducted at ambient temperature (23°C) and at 25°C. The surfactant drops show the texture of $L_\alpha$ phase under crossed polarizers right after contact with water. In the meantime many small droplets were observed forming on the edge of $L_\alpha$ phase within the surfactant drops, as though in expense of $L_\alpha$ phase. These small droplets coalesced with each other or with the bulk phase (Figure 5-20). The emulsification was even stronger and the dissolution even quicker at 25°C, just 2°C below the cloud point. $n$-Hexanol is soluble in water and, therefore, no slow dissolution was observed near the end of dissolution experiments.

Furthermore, drops with a ratio of C_{12}E_6/C_{12}OH equal to 95/5 were injected into water at 30°C slightly below the cloud point. No or only one small emulsification drop were seen forming inside the surfactant drops. However all the remaining surfactant drops became elongated near the end of dissolution processes.

Drops with a ratio of C_{12}E_6/C_{12}E_3 equal to 85/15 were injected into water at 30 and 33°C slightly below the cloud point (34°C). The surfactant mixtures dissolved in water very quickly and the remaining drops always became elongated. A few water
Figure 5-20: Drop having a ratio of C_{12}E_6/C_6OH equal to 75/25 (by weight) in water at 25°C shows strong emulsifications. (Photo was not taken under crossed polarizers.)
droplets inside the remaining drops were always seen clearly toward the end of the dissolution process.

5.3.3 Dissolution of mixtures of \( \text{C}_8\text{E}_5 \) and \( \text{C}_8\text{OH} \)

Based on the phase diagram (Figure 5-21) [Penders, 1995], surfactant mixtures with different composition ratios of \( \text{C}_8\text{E}_5/\text{C}_8\text{OH} \) (90/10, 75/25, 61/39, 50/50 and 25/75 by weight) were used in dissolution experiments at various temperatures. The solubility of \( \text{C}_8\text{OH} \) at 25°C is 0.054 wt% [Perry’s Handbook, 1984]. The critical micelle concentration of \( \text{C}_8\text{E}_5 \) at 25°C is \( 9.1 \times 10^{-3} \) M (0.32 wt%) [Rosen, 1989].

Drops with a ratio of \( \text{C}_8\text{E}_5/\text{C}_8\text{OH} \) equal to 25/75 (by weight) injected into water at temperatures between 25°C and 35°C behaved in much the same way as alcohol-rich drops in the \( \text{C}_{12}\text{E}_8/\text{C}_{10}\text{OH} \) system discussed above, i.e., they shrank slowly with no intermediate phase formation and minimal spontaneous emulsification of water droplets. Figure 5-22 shows that the radius of such a drop decreased quite linearly with the square root of contact time after a short induction period during which a small increase in radius occurred. Similar results were obtained for drops having an initial \( \text{C}_8\text{E}_5/\text{C}_8\text{OH} \) ratio of 50/50 (by weight) at temperatures between 23°C and 35°C.

More complicated behavior occurred when drops having a \( \text{C}_8\text{E}_5/\text{C}_8\text{OH} \) ratio of 75/25 (by weight) were injected into water at temperatures between 25°C and 35°C. On initial contact with water, myelinic figures grew out from the surface of such a drop, and very bright birefringence was seen in the interior. About a minute after injection, the L₃ phase started to form from the dissolution of the myelins and eventually surrounded the
whole drop. After all the L₁ was converted to L₃, drops of the L₂ phase appeared. Drops of L₁ then formed inside the L₂ drops, so that an L₁/L₂/L₃/L₁ multiple emulsion existed (see Figure 5-23). After some time the L₃ phase dissolved, and the rest of the experiment involved dissolution of the L₂ phase with several episodes of vigorous spontaneous emulsification of L₁ droplets within it. The droplets coalesced with each other and with the surrounding L₁ phase. Complete dissolution occurred in about an hour.

The phase diagram suggested that at slightly higher alcohol contents an intermediate L₃ phase with a higher water content would form. Accordingly, an experiment was performed with a drop initially containing 39 wt% C₈OH at 25°C. Some myelinic figures formed on initial contact, but they were converted to L₃ within a second or two before the drop could be detached from the micropipette. Some 20 seconds after injection spontaneous formation of L₁ droplets occurred within the larger L₃ drop. The droplets rapidly coalesced with each other and with the external aqueous phase. About two minutes after injection another episode of spontaneous emulsification was observed, but this time the dispersed phase was L₂. The droplets did not coalesce with the aqueous phase but instead coalesced with each other to form a single L₂ drop within the larger L₃ drop. The former grew and the latter decreased in volume, ultimately disappearing. Subsequently, the remaining L₂ drop gradually shrank but never completely disappeared. During this time some spontaneous emulsification of L₁ droplets occurred.

The conversion of the drops in the two experiments just described from L₃ to L₂ as they became richer in C₈OH, which is less soluble in water than C₈E₅, is consistent with the phase diagram. Spontaneous emulsification of L₁ occurs when the drops become
Figure 5-21: Phase diagram of C₈E₅/C₈OH/water system [Penders, 1995]

(A) T = 25°C

(B) T = 35°C
Figure 5-22: Dissolution of a drop having 75/25 C₈E₅ and C₈E₀ by weight in water at 30°C

Ro = 58.5 μm
Slope = -8.14 μm/min⁰.⁵
Figure 5-23: Drop having an initial ratio of $C_8E_5/C_8E_0$ equal to 75/25 (by weight) dissolving into water at 30°C shows a $L_1/L_2/L_3/L_1$ multiple emulsion.
supersaturated with water and is more vigorous when the slope is nearly constant alcohol/
surfactant ratio.

When a drop having a 90/10 weight ratio of C₆E₉/C₆OH was injected into water at
30°C, it dissolved completely in a short period. The two initial phases were either miscible
or nearly so, which is generally consistent with the known phase behavior.

5.4 Discussion

As mentioned previously, the diffusion coefficient of the hexagonal phase with
C₁₂E₆/water systems found in this work is in good agreement with that found by Sallen et
al. [1997]. The scheme used in this work was proved to be a simple way to estimate the
diffusivities. From the results the diffusivity of lamellar phase was the greatest and
diffusivities decreased with increasing surfactant concentrations present in the initial bulk
surfactant solution. Increasing the surfactant concentration in the bulk phase increases its
viscosity, as is well known. A decrease in fluidity could also be observed by direct
observation. As one might expect the diffusion coefficient of L₁ phase will decrease as
increasing viscosity of L₁ phase. However, no explanation could be offered here on why
the calculated diffusivities in the other phases also decrease.

The fast motion of the L₂/Lₒ interface was found to cause a minor problem in the
calculation. Therefore a value of Dₗ₂ was often assumed instead of using that from the
results of vertical cell experiments. As explained above, the values of the other diffusivities
are not significantly changed by this procedure.
In addition, the irregular front at the interface also prevented an accurate measurement of the position of the interface. The irregular shape of the front is probably the result of a Mullins-Sekerka instability. Metallurgists have long known that the front between a growing crystal and its melt is unstable above a critical velocity (a few μm/s in general). This instability, first analyzed by Mullins and Sekerka [1964], is caused by the rejection of solute atoms (impurities, most often) from the solid into the liquid, where they pile up in front of the moving interface [Oswald, 1991]. This instability leads to cellular or dendritic patterns. In the present case it is diffusion of water and surfactant, not an impurity, which produces the instability. Oswald et al. [1991] studied the pattern formation during the growth of liquid crystal phases and clearly showed irregular surfaces between liquid crystal and isotropic phases similar to those observed in some of the experiments conducted in this study.

When pure linear ethoxylated alcohols were dissolved in water at temperatures below their cloud point temperatures, the complete dissolution time of surfactant drops with the same initial radius decreased with increasing temperature. However, for commercial nonionic surfactants used in this work, dissolution times increased as temperature approached the cloud point temperatures. The differences in behavior between the commercial and pure surfactants stem from the presence of many individual species in the former. Initially the surfactant drop takes up water into the \( L_2 \) phase and an intermediate \( L_n \) phase which begins to form on initial contact. Simultaneously, the more hydrophilic species diffuse preferentially into the water, leaving the more lipophilic species in the drop. As a result, the cloud point of the surfactant mixture remaining in the drop
may fall below the experimental temperature, and a surfactant-rich L₁ phase may form. The periphery of the drop does indeed appear to become an isotropic liquid during the experiments, in contrast to the situation for the pure surfactants where the outer portion of the drop is always a liquid crystalline phase from the instant of initial contact.

As diffusion continues and the surfactant remaining in the drop continues to become more lipophilic, its ability to solubilize water decreases. Emulsification of water droplets presumably occurs when the solubilization limit falls below the actual water content. Coalescence of some small droplets into larger ones was often observed. Coalescence minimizes total interface area between droplets and L₁ phase and thus minimizes the excess free energy.

The long time required for complete dissolution is likely due to the fact that the rather lipophilic surfactants remaining in the L₁ phase near the end of the experiment do not dissolve in water to any significant extent but must be solubilized in surfactant micelles by a process similar to that described in Chapter 4 for triolein and triolein/fatty acid mixtures, which involves “adsorption” and “desorption” of micelles. More species would have to be solubilized by this mechanism at higher temperatures where the surfactant is more lipophilic, which could explain why dissolution becomes slower just below the cloud point temperature.

It is noteworthy that the emulsification phenomena and the elongated shapes of surfactant drops are often encountered in those systems that are mixtures of hydrophilic and hydrophobic species dissolving in water at temperatures just slightly (few degrees in Celsius) below their cloud points (Figure 5-20). Similar phenomena were also observed in
the system consisting of hydrophobic nonionic and hydrophilic anionic surfactants, which will be presented in Chapter 6. This dissolution process will be explained here using \( \text{C}_{12}\text{E}_8/\text{C}_{10}\text{OH} \) mixtures dissolving in water as an example.

The behavior observed during dissolution of drops of \( \text{C}_{12}\text{E}_8/\text{C}_{10}\text{OH} \) below their cloud points can be explained using the phase diagram. For such drops \( \text{C}_{12}\text{E}_8 \) preferentially diffuses into the aqueous phase while \( n \)-decanol, which has minimal solubility in water, preferentially remains in the drop. If a drop with initial composition IC1 of Figure 5-17, e.g., 95/5 \( \text{C}_{12}\text{E}_8/\text{C}_{10}\text{OH} \) by weight, is injected into water, dissolution is quick, and intermediate \( L_a \) and \( H_1 \) phases (and probably \( V_1 \); see above) are formed, much as for pure \( \text{C}_{12}\text{E}_8 \) at 30°C discussed previously.

If instead alcohol content is increased to IC2, e.g., 85/15, initial dissolution is again fast. As the drop becomes richer in alcohol, the composition path shifts, as observed experimentally and shown on schematic path 2. The composition path of drop reaches the \( L_a \) phase region, but not \( H_1 \) phase. With further contact with water, the drop composition path goes through the \( L_1 \) phase. Since the phase boundaries of Figure 5-14 near the water corner are so narrow, it is very possible that the drop composition path reaches the \( W/L_1 \) coexistence curve. The coexistence curve of \( L_1 \) in equilibrium with water shows that water content of the \( L_1 \) phase decreases rapidly with increasing ratio of alcohol to surfactant. Thus the \( L_1 \) phase can become more supersaturated in water as \( \text{C}_{12}\text{E}_8 \) continues to diffuse into the aqueous phase. The result is spontaneous emulsification of water drops in \( L_1 \), as seen in the experiments. Moreover the solubility of surfactant in the \( W \) phase in equilibrium with \( L_1 \) is much lower than that in the aqueous
phase in equilibrium with $L_a$, so that the overall dissolution rate drops sharply. Indeed, most dissolution after this time may be the result of solubilization into the surfactant micelles formed in the earlier stages of dissolution. Ultimately, the composition of the $L_1$ phase reaches one corner of the $W/L_1/L_a$ three phase triangle, and the lamellar phase (which by now has dissolved in the central part of the drop) forms as an intermediate phase at the drop surface.

The appearance of the lamellar phase is probably responsible for the drop elongation seen in the latter part of dissolution experiments for various mixed surfactant systems just below their cloud points, as well as for the expulsion of small drops (budding) and the emission of jets seen in some of these experiments. It is of interest to explain this unusual behavior, which seems to be related to that observed for large vesicles when heated (see below) and to budding seen previously in this laboratory when drops of pure oleic acid and 75/25 mixtures of oleic acid and triolein were injected into 1 wt% $C_{14}E_6$ at 35°C [Tungsubutra, 1994].

When interfacial tension is low, the shape of vesicles is determined by bending elasticity and curvature. Large vesicles, for example, are known to assume a variety of shapes to minimize the bending energy of their bilayers. Three different routes to shape transformations were found [Lipowsky, 1991; Berndl, 1990]. Study of these exotic shape transformations of vesicles has recently become the focus of considerable research. The shape transformations of vesicles can be induced by the change of control parameter such as temperature since the thermal expansivity of the bilayer is large compared to that of water. The vesicle's area changes more rapidly with temperature than its volume and thus
this change in the area to volume ratio will lead to the various shape transformations [Berndl, 1990; Käs, 1990; Seifert, 1991]. Jülicher et al. [1993] recently reported the domain-induced budding of vesicles by change of another control parameter -- the composition of the lipid bilayers.

Chen et al. [1997] recently reported their study on the theory of fission for two-component lipid vesicles and showed that the coupling of local lipid composition to Gaussian curvature can destabilize the narrow neck in a budded state of lipid vesicles. Depending on the molecular shape of factors of minor component lipids, this coupling can reduce (or increase) the Gaussian rigidity and fission (or fusion) can be enhanced. Perhaps this factor also contributes in our experiments.

In this work the shape transformations were mostly induced by the changes of compositions in the surfactant drops by diffusion and the accompanying spontaneous emulsification. The strong motion of these emulsion droplets, probably provided by the Marangoni effect, might also contribute to the effects. Above all, the bending energies of the vesicles are the most critical to the effects when the interfacial tension is very low. Liquid droplets usually have a spherical shape which is governed by interfacial tension alone. In contrast, it is now generally believed that the shape of vesicles is determined primarily by bending elasticity and, thus, by curvature [Lipowsky, 1991]. Theoretical predictions of the behavior can be obtained from the minimization of the total energy which consists of the bending energies and the edge energy [Jülicher, 1993]. Consider a membrane segment of linear size L. If this segment is planar, it has no bending energy but its boundary has an edge energy arising from the partial contact between water and the
hydrocarbon chains of the lipid. The total edge energy of the segment is proportional to L. On the other hand, if the segment forms a sphere, it has no edge energy but the bending energy is \(4\pi(\kappa^+\kappa_G)\), where \(\kappa\) is the bending rigidity and \(\kappa_G\) is the Gaussian curvature modulus. It does not depend on the linear size L of the membrane. Therefore, for large L, the membrane can always lower its energy by forming a closed surface [Lipowsky, 1991].

The generalized Young-Laplace equation can be written as [Miller, 1985]

\[
\Delta p = -2H\gamma - (4H^2-2K)B
\]

where \(H\) is the mean curvature; \(K\) is the Gaussian curvature; \(\gamma\) is the interfacial tension; \(B\) is the bending stress and equal to \(-A^{-1}(\partial F/\partial 2H)_{r,n,A,K}\). \(F\) is the surface excess Helmholtz free energy. Consider a drop of area \(A\). If the shape of drop is spherical, the volume \(V_s\) is equal to \((A^{23}/6\pi^{1/2})\). However, when the volume-to-area ratio \((V/A)\) of free vesicles is decreased, shape deformations are observed. For a sphere with an interfacial layer having constant spontaneous curvature \(c_o\) and bending modulus \(\kappa\), \(B\) is equal to \(c_o\kappa[1-(c_oR/2)]\). Theory for vesicles predicts (axisymmetric) shape for given values of \((V/V_s), c_o(A/4\pi)^{1/2}\) and with \(\gamma\) assumed to be uniform. Shape is independent of \(\kappa\), but \(\Delta p\) and \(\gamma\) are proportional to \(\kappa\). For \(c_o > 0\), i.e., configurations where outer portion of interfacial layer has larger area than inner portion are favored, equilibrium shapes are generally elongated (prolate). For sufficiently large \(c_o\), budding can occur [Seifert, 1991]. Figure 5-24 shows theoretical prediction of stationary shapes for vesicles with \(\nu=(V/V_s) = 0.8\) and several values of the reduced area difference \(\Delta a\) which is related to spontaneous curvature [Seifert, 1991].
As mentioned earlier in this section, the hydrophilic species in surfactant mixtures dissolve in water more quickly than lipophilic species. When this process leads to formation of an intermediate lamellar phase at the drop surface late in the dissolution process in the manner described previously, the drop resembles a vesicle. Because the drop is more lipophilic than the aqueous solution, the surfactant bilayers will tend to bend toward the lipophilic cores to minimize the free energy. Accordingly the spontaneous curvature is positive. Moreover, if the liquid crystalline layer resists reduction in its area while some material continues to be transferred from drop to aqueous phase, the drop volume $V$ may fall below $V_s$. Thus, all conditions are met for the drop to behave like the vesicles studied by others and become elongated. Budding is expected, according to the theory, if the spontaneous curvature, i.e. $\Delta \sigma$ becomes sufficiently large. Finally, if internal pressure within the drop exceeds the external pressure, a jet is possible if the liquid crystalline layer is broken locally. While admittedly this explanation of the various phenomena is somewhat conjectural, it seems plausible and in qualitative agreement with the vesicle results. Further investigation seems desirable.
Figure 5-24: Stationary shapes \( v=0.8 \) and several values of the reduced area difference \( \Delta a \) [Seifert, 1991]

(a) Symmetric shapes; the rightmost shape is locally unstable \( (v=0.8, \Delta a \) is the parameter).

(b) Asymmetric pear-shaped vesicles; all are locally stable \( (v=0.8, \Delta a \) is the parameter).

The reduced volume \( v = V / [(4\pi/3) \cdot \text{Ro}^3] \), where \( \text{Ro} = (A/4\pi)^{1/2} \)

The reduced area difference \( \Delta a = M / (4\pi \cdot \text{Ro}) \), where \( M \) is the integrated mean curvature.

For a sphere, \( v = \Delta a = 1 \)
Chapter 6: Dissolution of Mixtures of Nonionic and Anionic Surfactants into Water

6.1 Introduction

Drops of the pure nonionic surfactants $C_{12}E_3$ and $C_{12}E_4$ were injected into water at $30^\circ$, $35^\circ$ and $40^\circ$C. Most of these experiments were for conditions where the $L_\alpha$ phase and water coexist at equilibrium in dilute solutions (see Figure 6-1, 6-2 and 6-3) [Mitchell, 1983; Strey, 1996]. Shortly after contact myelinic figures of the lamellar phase were observed growing from the surfaces of the drops. Some additional swelling and development of the myelinic figures was seen, but even after one hour a compact mass of viscous myelinic figures remained (Figures 6-4 and 6-5). For $C_{12}E_3$ in water at $40^\circ$C, where water and the $L_3$ phase coexist at equilibrium, myelinic figures again formed shortly after contact. However, a few minutes later small droplets of the $L_3$ phase appeared at the surface (Figure 6-6) These droplets grew and coalesced until the $L_3$ phase completely surrounded the lamellar phase. Myelinic figures could be seen dissolving into the $L_3$ phase during the experiments. When all the $L_\alpha$ phase had dissolved, a single large $L_3$ drop remained at equilibrium.

As shown in Figure 6-4, a compact mass of viscous myelinic figures grows out and persists when $C_{12}E_3$ contacts water at $35^\circ$C. Clearly, formation of a viscous mass of myelinic figures by a nonionic surfactant would be unfavorable in a washing application. Not only would most of the surfactant not be available for cleaning, but the myelinic figures could possibly entrap solid particles of zeolite or other materials present in the detergent powder and hinder their dispersion in the washing bath. Since hydrophilic
Figure 6-1: Phase diagram of $C_{12}E_3$/water system [Mitchell, 1983]
Figure 6-2: Phase diagram of C_{12}E_{4}/water system [Mitchell, 1983]
Figure 6-3: Phase diagram of C_{12}E_{4}/water system [Strey, 1996]
Figure 6-4: Videoframes of C₁₂E₃ in water at 30°C shows myelin dispersions

(a) Drop of C₁₂E₃ formed a compact of myelinic figures

(b) C₁₂E₃ contacted water at 30°C on vertical cell
Figure 6-5: Videoframes of $C_{12}E_4$ in water at 30°C shows myelin dispersions

(a) Drop of $C_{12}E_4$ formed a compact of myelinic figures

(b) $C_{12}E_4$ contacted water at 30°C on vertical cell
Figure 6-6: Videoframe of a C_{12}E_{3} drop in water at 40°C shows L_{3} droplets
anionic surfactants are present in many detergent formulations, experiments were conducted to determine whether they could reduce or eliminate myelinic figure formation when added to lipophilic nonionic surfactants.

Dissolution experiments were conducted by adding various concentrations of these particles of anionic surfactants to neat nonionic surfactants. The microinjection system described in Section 3.8 was used to inject the resulting dispersions (Figure 6-7).

To reduce formation of myelinic figures upon contact the anionic surfactant sodium dodecyl sulfate (SDS) was purchased from Fisher and used in the experiments described below without further recrystallization. However, based on the suggestion of a Unilever personnel, SDS for dissolution experiments was also purchased from Sigma and recrystallized twice following the procedure given in Section 3.1 to remove any n-dodecanol formed from hydrolysis of the surfactant [Hines, 1997]. In addition, 1-octanesulfonic acid sodium salt with reported purity greater than 99% was purchased from Sigma (St Louis, MO) and used as received without any further recrystallization.

Sieving was used to obtain SDS particles in the desired size range. The fraction of particles caught between a sieve of mesh #170, with mesh size of 90 µm, and a sieve of mesh #325, with mesh size of 45 µm, was used.

6.2. Dissolution of surfactant mixtures using unrecrystallized sodium dodecyl sulfate (SDS)

Phase behaviors of dilute solutions of mixed surfactant systems were studied following the procedures described in Section 3.1. The phase boundary between cloudy
Figure 6-7: A drop having a ratio of $\text{C}_{12}\text{E}_4$/recrystallized SDS equal to 90/10 being injected into water at 30°C with micropipette
and clear phases was determined approximately and the information was used in the drop
dissolution experiments. The dissolution experiments were conducted using microinjection
system described in Section 3-6 for systems with both recrystallized and unrecrystallized
SDS particles.

6.2.1 Dissolution of C\textsubscript{12}E\textsubscript{3}/SDS

Equilibrium experiments were conducted for 2 wt\% C\textsubscript{12}E\textsubscript{3}/SDS solutions at 30° C.
The addition of SDS to C\textsubscript{12}E\textsubscript{3} increased the cloud point temperatures of surfactant
solutions. The samples having 90/10, 85/15 or 80/20 C\textsubscript{12}E\textsubscript{3}/SDS by weight all showed a
clear lower phase and streaming birefringence under crossed polarizers in upper phase at
30° C in contrast to a clear solution containing 75/25 C\textsubscript{12}E\textsubscript{3}/SDS by weight at the same
temperature. Although no sample showing W+L\textsubscript{1} was directly observed in equilibrium
experiments, it should exist since the system exhibits W+L\textsubscript{1} as the final equilibrium in the
dissolution experiments described later in this section. The results are schematically
shown in Figure 6-8

Figure 6-8: Phase Behavior of 2 wt\% C\textsubscript{12}E\textsubscript{3}/SDS (unrecrystallized) solution at 30° C

\[ W-L_\alpha \quad W-L_1-L_\alpha \quad W-L_1 \quad L_1 \]

\[ \text{wt\% of SDS (Sodium Dodecyl Sulfate) in Surfactant Mixture} \]
\[ \square \text{indicates the final equilibrium state observed in the dissolution experiments} \]
\[ \bullet \text{indicates the equilibrium phases observed from the phase behavior experiments} \]
In the drop dissolution experiments, when SDS particles (10 wt%) were added to neat C_{12}E_{3}, myelinic figures grew out from the surface of the surfactant drop immediately upon contact with water, the same phenomena observed in the absence of SDS. However, some of them dissolved gradually and became drops of the surfactant-rich L_1 phase. Both L_α and L_1 could be seen 60 minutes after injection although it appeared that the former was still being slowly converted to the latter.

A dispersion of 20 wt% SDS in C_{12}E_{3} was quite viscous. Myelinic figures still grew very rapidly from the surfaces of drops with this composition upon injection. As before the myelins gradually dissolved as L_1 drops formed, but this time all the lamellar phase eventually disappeared. A single L_1 drop remained at the end of the experiment. Because this phase has a low viscosity and a very low interfacial tension with water, it should, unlike the viscous myelinic figures, be readily dispersed during a washing process. That is, the final equilibrium is W+L_1.

The discrepancy of final states from both experiments might arise from weighing errors when preparing samples for both experiments, especially when the composition is near the phase boundary. Figure 6-8 suggests that the phase boundary between W−L_1 and W+L_1+L_α locates very close to 20 wt% of SDS initially in surfactant mixtures.

Higher concentrations of SDS in C_{12}E_{3} were not investigated because the high viscosities of the dispersions made injection difficult.

6.2.2 Dissolution of C_{12}E_{3}/SDS
Figure 6-9 shows the phase boundaries from equilibrium experiments at 30°C. Since C_{12}E_4 is more hydrophilic (cloud point=8°C) than C_{12}E_3 (cloud point < 0°C), the amount of SDS needed in C_{12}E_4 to make micellar solution at 30°C is less. A mixture of 7 wt% SDS initially present in C_{12}E_4 formed an isotropic solution when equilibrated with excess water, according to experiments conducted in our laboratory. Adding SDS increases the cloud point temperature. The SDS particles were also observed as partially miscible with C_{12}E_4.

Figure 6-9: Phase Behavior of 2 wt% C_{12}E_4/SDS solution (unrecrystallized) at 30°C

\[
\begin{align*}
W+L_\alpha & \quad W+L_1+L_\alpha & \quad W+L_1 & \quad L_1 \\
\square & \quad \square & \quad \square & \quad \square \\
0 & \quad 3\% & \quad 5\% & \quad 7\% & \quad 10\%
\end{align*}
\]

SDS (Sodium Dodecyl Sulfate) in Surfactant Mixtures [wt%]

\[\square\] indicates the final equilibrium states observed in the dissolution experiments. 

\[\bullet\] indicates the equilibrium phases observed from the phase behavior experiments.

When a drop of C_{12}E_4 containing 10 wt% unrecrystallized SDS was injected into deionized water at 30°C or 35°C, myelinic figures were seen but only for a few seconds. The SDS particles were located in the central region of the surfactant drop, surrounded by the L_\alpha phase (see Figure 6-10). Many small droplets of the L_1 phase were observed forming near the edge of the drop and especially near the SDS particles (bright spots in Figure 6-10, which is taken with crossed polarizers.) All the particles dissolved in about 40 seconds. Later the whole surfactant drop became isotropic as all the L_\alpha was converted
Figure 6-10: Drop of $\text{C}_{12}\text{E}_4$ containing 10 wt% unrecrystallized SDS dissolving in water at 30°C
Figure 6-11: Drop of C₁₂E₄ containing 10 wt% unrecrystallized SDS dissolving in water at 30°C showing "protrusion" from remaining drop.
to L₁, but spontaneous formation of droplets, now of water, continued. An intriguing phenomenon was seen about 160 seconds after initial contact when most of the surfactant had dissolved. A conical protrusion developed which emitted a jet (Figure 6-11), behavior similar to that described previously for drops of Tergitol 15-S-7 in water at 30°C or 35°C. Complete dissolution of the entire drop required about 30 minutes.

Similar behavior was observed for drops of C₁₂E₄ containing 5 wt% SDS injected into deionized water at 25°C, 30°C and 35°C. At 25°C the myelinic figures dissolved more slowly. Moreover, after all the SDS particles had dissolved, concentric layers of Lₐ surrounded by L₁ could be seen with the latter growing at the expense of the former. That is, the final equilibrium phase is W+L₁. Dissolution appeared to be complete after about 3 hours in this case compared to about 30 minutes at 30°C and 35°C. It is possible that a small amount of the L₁ phase remained undetected at the end of some of these experiments since separate work indicated that the cloud point of this mixture is near 30°C.

Drops of C₁₂E₄ containing 3 wt% SDS also formed transient myelinic figures when injected into water at 30°C. However, the Lₐ phase never was fully converted to L₁ as in the above experiments. The final state was concentric drops with L₁ surrounding Lₐ. Separate experiments (see Figure 6-9) confirmed that the equilibrium state for this mixture dispersed in water was W+L₁+Lₐ at 30°C.

6.2.3 Dissolution of C₁₂E₅/SDS

The dissolution process in water at 30° and 35°C of a C₁₂E₅ drop containing 10 wt% dispersed SDS was very similar to that described above for a C₁₂E₄ drop with the
same amount of SDS except that dissolution was much faster. This result was expected because C_{12}E_5 is more hydrophilic than C_{12}E_4. Small drops of the C_{12}E_5/SDS mixture comparable in size to those of pure C_{12}E_5 listed in Table 5-1 dissolved so fast that it was not possible to determine dissolution time accurately. A much larger drop dissolved in less than two minutes compared to about six minutes for a comparable drop of C_{12}E_5 with no SDS added.

6.3 Dissolution of surfactant mixtures using recrystallized sodium dodecyl sulfate (SDS)

Sodium dodecyl sulfate is easily hydrolyzed to lauryl alcohol (1-dodecanol) by light and moisture. Accordingly, SDS was doubly recrystallized in 190 and 200 proof ethanol to remove this and other impurities [Hines, 1997]. The use of recrystallized SDS reduces the presence of \( n \)-dodecanol in surfactant mixtures, which tends to decrease the cloud point temperatures of nonionic surfactant solutions as opposed to the addition of SDS, which tends to increase the cloud point temperatures.

6.3.1 Dissolution of C_{12}E_5/SDS

With solutions having a total 2 wt% of C_{12}E_5 and recrystallized SDS mixtures, the phase boundary between clear and cloudy phase at 30°C was carefully determined and located at a ratio very close to 82.5/18.5 C_{12}E_5/SDS by weight initially. That is, one can get complete dissolution when recrystallized SDS is added to a content of slightly more than 18.5 wt% in surfactant mixtures. Less recrystallized than unrecrystallized SDS is needed to make a clear C_{12}E_5 solution since recrystallization minimized the presence of \( n \)-
dodecanol (Figure 6-8 and 6-12). Figure 6-12 shows the schematic phase behavior at 30°C.

In drop dissolution experiments, drops having 75/25 and 70/30 C_{12}E_{3}/SDS by weight were injected into water. Although 2 wt% surfactant mixtures at these ratios exhibit L_{1} phase only in the equilibrium experiments, their final phases present in contacting experiments both showed as W+L_{1} phases. Initially, very thick and compact myelinic figures were seen growing out from the surfaces of drops as before. All myelinic figures dissolved very quickly. The discrepancy of final states from both experiments might stem from the very viscous surfactant mixtures and solid dispersions in mixtures. The liquid in the surfactant mixtures tended to travel faster than the solid in the micropipettes with diameters about 70-100 μm. Consequently unwanted separation of liquid and solid occurred when the surfactant mixtures were driven by high pressured gas in the micropipettes. That is, the injected drops contain less SDS than they would in mixtures. It might be able to be improved by injection of surfactant mixtures with bigger micropipettes into larger glass capillary cells.

Figure 6-12: Phase Behavior of 2 wt% C_{12}E_{3}/SDS solution (recrystallized) at 30°C

<table>
<thead>
<tr>
<th>SDS (Sodium Dodecyl Sulfate) in Surfactant Mixtures [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>□ indicates the final equilibrium state observed in the dissolution experiments.</td>
</tr>
<tr>
<td>Drops of surfactant mixtures having 25 wt% and 30 wt% SDS initially were injected respectively in the dissolution experiments.</td>
</tr>
<tr>
<td>• indicates the equilibrium phases observed from the phase behavior experiments.</td>
</tr>
</tbody>
</table>
6.3.2 Dissolution of \( C_{12}E_4/SDS \)

Figure 6-13 shows the phase diagram of the SDS-water system at different temperatures [Kékicheff, 1987]. At 30°C, this binary system displays micellar phase, hexagonal phase and some polymorphic varieties for the SDS hydrates with increasing SDS content. In the other hand \( C_{12}E_4 \)-water binary system exhibits \( W+L_\alpha, L_\alpha \) and \( L_2 \) phases at the same temperature (Figures 6-2 and 6-3). In contrast, no phase diagram of \( C_{12}E_4 \)-SDS-water system is available. Equilibrium experiments were conducted to determine the phase diagram of this system at 30°C. The schematic phase diagram, which is consistent with results of experiments conducted in the same period by John Walsh et al. of Unilever Research Port Sunlight Laboratory (UK), is shown as Figure 6-14. All the samples were left to equilibrate in the environmental room where the temperature was maintained at constant temperature--30°C, and inspected under crossed polarizers. In this system, many samples contained mixtures of lamellar and hexagonal phases that were really viscous or even gel-like. A few samples were centrifuged but not ultracentrifuged to separate these viscous phases, but not sucessfully. For this reason, it is not possible to accurately determine boundaries of single phase and multiple phase regions containing \( L_\alpha \) and/or \( H_1 \). In this phase diagram, there is an isotropic \( L_2 \) phase near the corner of \( C_{12}E_4 \). It extends to between 8 wt% and 10 wt% SDS in \( C_{12}E_4/SDS \) mixtures. Results from some dissolution experiments using surfactant mixtures with initial compositions located in this region are presented later in this section and in Section 6.5.

Likewise some equilibrium experiments were conducted using 2 wt% \( C_{12}E_4/SDS \) mixtures at 30°C to determine the location of the phase boundary between clear and
Figure 6-13: Phase diagram of SDS/D$_2$O system [Kekicheff, 1989]

\[\text{TEMPERATURE (°C)}\]
\[\text{S.D.S. concentration (wt. %)}\]

$H_\alpha$: Hexagonal Phase
$L_\alpha$: Lamellar Phase
$M_\alpha$: Two-dimensional monoclinic Phase
$R_\alpha$: Rhombohedral Phase
$T_\alpha$: Tetragonal Phase
$Q_\alpha$: Cubic Phase

$C' \chi$: Different polymorphic varieties for the same hydrate
$x$ refers to the number of water molecules associated each SDS molecule in the hydrate
Figure 6-14 (a): Schematic phase diagram of $C_{12}E_4$/SDS/water system at $30^\circ$C

(Sodium Dodecyl Sulfate)
Figure 6-14 (b): Schematic drawing near water-rich corner of phase diagram of $\text{C}_{12}\text{E}_4/\text{SDS}/\text{water}$ system at 30°C

V1 omitted: It must be there since it was seen in dynamic experiments, but its location was unknown since not seen in phase behavior work.
cloudy phases. The results are shown as Figure 6-15. It is noteworthy that Figure 6-15 covers only a tiny region near C_{12}E_{4}/H_{2}O side of phase diagram at 2 wt% surfactant content. Since impurities such as n-dodecanol were removed from SDS by recrystallization, less recrystallized than unrecrystallized SDS is needed to make the same surfactant solution clear (Figures 6-9 and 6-15).

In the dissolution experiments, large drops of surfactant mixtures with diameters about 300 μm or even larger were injected into water or surfactant solutions to observe their dissolution behaviors such as phase changes or whether complete dissolution occurred. Their final states were also compared with those from the equilibrium experiments. Subject to the dimension of glass capillary cells used here, 50×4×0.4mm, smaller drops were injected later to collect the kinetic data on the correlation of the complete dissolution times with the initial radii of the injected surfactant drops. The results are presented as Figure 6-16 and 6-17. Moreover, the effective overall diffusion constants were calculated using the scheme described in Section 5.1.4 and presented as Table 6-1.

Figure 6-15: Phase Behavior of 2 wt% C_{12}E_{4}/SDS (recrystallized) at 30°C

\[
\begin{array}{cccc}
W+L_{\alpha} & W+L_{1}+L_{\alpha} & W+L_{1} & L_{1} \\
0 & 2\% & 2.5\% & 3\% & C_{12}E_{4}/SDS
\end{array}
\]

- □ indicates the final equilibrium states observed in the dissolution experiments.
- ● indicates the equilibrium phases observed from the phase behavior experiments.
Figure 6-16: Dissolution times of drops containing C_{12}E_{4} and recrystallized SDS mixtures in water at 30°C
Figure 6-17: Dissolution times of drops containing C12E4 and 10 wt% recrystallized SDS mixtures in water at 30°C
Table 6-1 Summary of drop dissolution experiments of C_{12}E_{4}/Recrystallized SDS mixtures in water

<table>
<thead>
<tr>
<th>C_{12}E_{4}/SDS [wt% / wt%]</th>
<th>Ro^{2}/time [m^{2}/sec]</th>
<th>D_{eff} [m^{2}/sec]</th>
<th>SDS size [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>95/5</td>
<td>4.2×10^{-11}</td>
<td>1.48×10^{-11}</td>
<td>45 - 90</td>
</tr>
<tr>
<td>92/8</td>
<td>8.2×10^{-11}</td>
<td>2.88×10^{-11}</td>
<td>45 - 90</td>
</tr>
<tr>
<td>90/10</td>
<td>5.6×10^{-11}</td>
<td>1.97×10^{-11}</td>
<td>45 - 90</td>
</tr>
<tr>
<td>90/10</td>
<td>6.6×10^{-11}</td>
<td>2.31×10^{-11}</td>
<td>38 - 45</td>
</tr>
<tr>
<td>85/15</td>
<td>7.2×10^{-11}</td>
<td>2.53×10^{-11}</td>
<td>45 - 90</td>
</tr>
<tr>
<td>Average</td>
<td>5.9×10^{-11}</td>
<td>2.07×10^{-11}</td>
<td></td>
</tr>
</tbody>
</table>

Ro: Initial Drop Radius

When a large drop of C_{12}E_{4} containing 10 wt% recrystallized SDS was injected into deionized water at 30°C, myelinic figures were seen but only for less than a second. Most of an injected surfactant drop dissolved in water very quickly, but the remaining small volume took longer time to complete dissolution. Similar to those with unrecrystallized SDS initially present, many small droplets of the L_{1} phase, were observed forming near the edge of the drops (Section 6.2.). Later the whole surfactant drop became isotropic as all the L_{α} was converted to L_{1}, but spontaneous formation of droplets, now of water, continued. A very small conical protrusion developed which also emitted a jet, behavior similar to that described previously in Section 6.2.2. Complete dissolution of the entire drop required a few minutes.

Drops of C_{12}E_{4} containing 3 wt% recrystallized SDS also formed transient myelinic figures when injected into water at 30°C. The L_{α} phase was soon transformed to concentric drops similar to those described in the experiment of using 85/15 C_{12}E_{5}/unrecrystallized SDS. The final state was surfactant-rich L_{1} drops in water. However, the
equilibrium experiments shows that the phase boundary of $L_1$ and $W+L_1$ is located in the range between 2.5 wt% and 3.0 wt% of SDS initially present. The inconsistency may occur from the very tiny amount of weighing error. But drops of $C_{12}E_4$ containing 5 wt% recrystallized SDS dissolved completely in water. As before, myelinic figures were seen initially right after contact with water and dissolved in only a second.

With the microinjection system (described in Section 3.8), it was possible to record the complete dissolution times and the initial radii of injected surfactant drops. The radii of the injected surfactant drops ranged from 40 to 70 μm and their behavior was recorded from the moment of injection. Consequently the initial radii were measured. The results are summarized as Figures 6-16 and 6-17. Figure 6-16 shows the square of initial drop radii is linear in the complete dissolution time, although the experimental line does not pass through the origin. This might arise from the initial mixing and convection effects of surfactant drops injected by high pressure gas. It often leads to some dark region around surfactant drops and, hence, some uncertainty existed in measurement of the initial drop radii. More likely, the final dissolution of surfactant drops was controlled by solubilization mechanisms of oil drops in surfactant solutions, which were discussed in Chapter 4. It also show the slope rate was the maximum when using surfactant mixtures having 92/8 $C_{12}E_4/SDS$ by weight, which is near the upper solubility of SDS in $C_{12}E_4$. Figure 6-17 also shows smaller SDS particles in surfactant mixtures would also increase slightly the dissolution rates.

The cloud point temperatures were measured for 2 wt% surfactant solutions with various SDS contents. They were measured as 34, 55 and 77°C when initial SDS contents
were 5 wt%, 10 wt% and 15 wt% initially in C₁₂E₄/SDS mixtures. That is, the cloud point temperature is almost linear to the initial composition of SDS present in surfactant mixtures and the equation can be expressed as

\[ T = 4.3S + 12.33 \quad (6.3-1) \]

where \( T \) is the cloud point temperature and in unit of °C; \( S \) is the weight percent SDS in C₁₂E₄/SDS mixtures.

6.4 Dissolution of surfactant mixtures with other anionic surfactants

6.4.1 Dissolution of C₁₂E₄/Sodium Octylsulfonate mixtures

The aggregation number of 1-octanesulfonic sodium salt, sodium octylsulfonate, in water was reported to have a value of 25 at 23°C and its CMC at 40°C is 0.14 M or 3.03 wt%, compared to 71 for the aggregation number of SDS at 23°C and 0.0082 M (0.236 wt%) at 25°C or 0.0086 M (0.248 wt%) at 40°C for the CMC of SDS [Rosen, 1989]. A solution containing 2 wt% this surfactant at 30°C is transparent. The use of this surfactant was intended to minimize the amounts of solid hydrophilic anionic surfactants in C₁₂E₄ drop to have complete dissolution in water and thus to minimize the viscosities of surfactant mixtures, which would be very critical to the injection when using the microinjection system (Section 3.8). That is, it would form micellar solutions for C₁₂E₄ with the minimum amounts of added anionic surfactants at the desired temperatures.

A few experiments were conducted to observe the phase behavior of surfactant solutions having 2 wt% of C₁₂E₄/sodium octylsulfonate mixtures at 30°C. All the samples showed cloudy, W-L₁, even though the content of sodium octylsulfonate in mixtures was
increased to 40%. The reason why the idea mentioned above does not work is probably because of its high CMC -- most is dissolved.

6.4.2 Dissolution of C_{12}E_{5}/Neodol 23-3S

Neodol 23-3S is obtained from the sulfation of Neodol 23-3. Neodol 23-3S used in this study was supplied from Shell (Houston, Texas) in the form of the sodium salt. It was reported as 26.95% active. Neodol 23-3S is viscous fluid, as are mixtures of C_{12}E_{5}/Neodol 23-3S.

When drops of C_{12}E_{5}/Neodol 23-3S mixtures containing 33 wt% Neodol 23-3S were injected into water at 30°C, myelinic figures were seen growing out from the surface of drops. Later the drops became gel-like and never dissolved into water when experiments ended at 90 minutes from injection. Similar initial behaviors was seen for drops having 78/22 C_{12}E_{5}/Neodol 23-3S by weight. However, the myelin dispersions quickly dissolved into L₃ surrounded by L₁. The equilibrium phases were W+L₁+L₃.

6.5 Dissolution of C_{12}E₄ in sodium dodecyl sulfate (SDS) solutions

Dissolution experiments were also performed in which C_{12}E₄ drops were injected into dilute solutions of recrystallized and unrecrystallized SDS -- 0.1 wt%, 0.3 wt% and 1 wt%. The critical micelle concentration (CMC) of SDS in water is about 0.24 wt% for temperatures of interest here [Rosen, 1989]. However, results of dissolution experiments in SDS solutions at 30°C and 35°C all exhibited very great similarity, whether surfactant concentration was above or below the CMC and SDS was recrystallized or not.
Myelinic figures grew outward from the surfaces of the C₁₂E₄ drops immediately upon contact with the SDS solutions. Droplets of a liquid phase started forming among these myelinic figures about 10 seconds after contact. After about one minute, all the myelinic figures had dissolved, and the edge of the surfactant drops became scalloped-shaped (Figure 6-18), presumably W+L₁+Lₐ, except for 0.1 wt% unrecrystallized SDS solution at 30°C, where the shape was more irregular. The scalloped surfactant drops continued shrinking with a few small droplets of the L₁ phase appearing near the edge. Complete dissolution required about 20-30 minutes.

Large drops of 92/8 C₁₂E₄/recrystallized SDS by weight, which were isotropic and about 230 μm in diameter, were also injected into the various concentrations of recrystallized SDS to observe their dissolution behavior. The complete dissolution times were qualitatively compared since the initial sizes of drops were almost the same by using the microinjection system.

When drops were injected into 15 wt%, 20 wt% and 25 wt% recrystallized SDS micellar solutions at 30°C, myelinic figures were all observed growing out from the surfaces of the drops and lasted only for 1 to 2 seconds following the initial contact with water. The whole drops became scallop-shaped similarly to Figure 6-18. However, the drops took long time for complete dissolution. It took about 50 minutes for complete dissolution in 25 wt% SDS solution, 40 minutes in 20 wt% solution and 20 minutes in 15 wt% solution. Later in these experiments the scallop-shaped drops were not very easily distinguished from the surrounding bulk phase, which indicated the values of both refractive indices were very close. It is noteworthy to mention that only few small L₁
drops were observed in the scallop shaped drops and both $V_1$ and $H_1$ phases were observed from the texture under crossed polarizers with injection of two very big drops into 15 wt% SDS solution. $H_1$ dissolves in water more slowly than $L_\alpha$ phase, for example, diffusion coefficient of $H_1$ phase of $C_{12}E_6$/water is about one half of that of $L_\alpha$ phase which is comparable to that of $V_1$ phase. The schematic drawing of phase changes in the drops are shown as

In contrast, quick dissolution (100 seconds) and many spontaneous $L_1$ droplets, faster with SDS, were observed when drops were injected into 5 wt% and 10 wt% recrystallized SDS solutions. As before myelinic figures were seen but quickly degraded in a second after injection. Coalescence of those $L_1$ droplets with the bulk phase was always seen. The remaining drop became elongated and remained so until complete dissolution. A few big drops were injected and observed under crossed polarizers to determine intermediate phases in these drops during the dissolution processes. It was found that only $L_\alpha$ was seen. This dissolution was much faster when no $H_1$ phase was formed.

6.6 Discussion

Addition of small amounts of sodium dodecyl sulfate particles to drops of nonionic surfactants, $C_{12}E_1$ and $C_{12}E_2$, successfully makes drops completely dissolve or prevents the
Figure 6-18: Drop of $\text{C}_{12}\text{E}_4$ dissolving in 0.3 wt% SDS (recrystallized)
at 30°C shows scalloped shape
formation of a persistent compact mass of myelinic figures after initial contact, although some transient formation of myelinic figures was always observed. The myelinic figures dissolved within seconds after initial contact with water or aqueous anionic surfactant SDS solutions, in contrast to the behavior observed in the experiments of neat nonionic surfactants contacting water, where the myelinic figures can persist for hours without noticeable dissolution. Although no complete dissolution was observed in the mixed surfactant systems of C₁₂E₃ and sodium dodecyl sulfate, the myelinic figures dissolved into a surfactant-rich L₁ phase that has low interfacial tension with water when enough SDS was added and can be easily dispersed in the washing solution under some mechanical force such as agitation in washing machines.

The complete dissolution times of C₁₂E₄/SDS in water or aqueous solution are linear in the square of the initial drop radius. This behavior indicates that the dissolution phenomena are diffusion-controlled, which is different from the interface-controlled mechanism found in the solubilization of triglyceride oil or mixtures in aqueous surfactant solutions described in Chapter 4. Nevertheless, the lines on Figures 6-16 and 6-17 do not pass through the origin. It will be discussed later.

The complete dissolution times of C₁₂E₄/SDS in water or aqueous SDS solution were found to be much longer than those of pure nonionic surfactants described in Chapter 5. The overall effective diffusion coefficients in Table 6-1 are about an order of magnitude less than those calculated for neat nonionic surfactants in Table 5-2 at the same or nearly the same temperature. In fact, in most dissolution experiments, most of the surfactant dissolved rather quickly in aqueous phase. However, the remaining small
volumes took a long time to dissolve completely. It is noteworthy that the values of complete dissolution times reported in Chapter 5 and 6 were the averages of at least 10 different runs at the same conditions. The results were reproducible and within 10% from the averages. In these systems, emulsification, elongated (prolate) shapes and even jetting phenomena were observed, the same as those described in Chapter 5.

The effects of size distributions of added SDS particles on the dissolution time was not significant in this study, probably owing to the fact that up to at least 8 wt% SDS was observed to be miscible in C_{12}E_4 and thus might decrease the difference of mean average of SDS particle size distribution in the surfactant dispersions containing 10 wt% SDS as used in this study. In addition, an important factor needs to be considered to interpret the results. That is the experimental error on measurements of initial drop radii, as mentioned earlier in this section. The uncertainty of measurements may be up to 10% of the average.

In contrast, the effects of added amount of SDS initially dispersed in C_{12}E_4/SDS mixtures on the complete dissolution times could be recognized in Figure 6-16. It seems that the slopes in Figure 6-16 are not necessarily decreased by increasing the contents of SDS initially dispersed. This finding is consistent with that found in the systems of dissolution of 92/8 C_{12}E_4/SDS mixture (by weight) in various concentrations of aqueous SDS solutions. In the latter system, it was found an optimum existed for the dissolution of surfactant mixtures for some concentration, between 10 wt% and 15 wt%, of SDS solution. Long dissolution times at high SDS concentration were found to be associated with the formation of H_{1} phase during the dissolution process.
Similar to the explanation of the dissolution behavior of C_{12}E_4/C_{10}OH using phase diagram given in Chapter 5, the behavior observed during dissolution of drops of C_{12}E_4/SDS can be explained using the phase diagram, which has a similar form. If a drop with composition of IC of Figure 6-14 (b), e.g. 92/8 C_{12}E_4/recrystallized SDS by weight, is injected into water, initial dissolution is quick and an intermediate L_α phase is formed. SDS preferentially diffuses into aqueous phase and leaves the more lipophilic C_{12}E_4 in the drop. The composition path of drop will reach a two-phase region of L_1+L_α, shown as schematic composition path 2 of Figure 6-14 (b). As more SDS diffuses out, the composition path shifts from path 2 to path 1 of Figure 6-14(b). The composition path of drop then reaches the cloud boundary, shown as C of Figure 6-14 (b) on the coexistence curve of L_1 in equilibrium with water. Thus, the L_1 phase becomes supersaturated with water as SDS continues to diffuse into the aqueous bulk phase. The result is spontaneous emulsification of water drops in L_1, as observed in the experiments. Similarly the dissolution rate decreases sharply as the solubility of surfactant, C_{12}E_4, in the W phase is low. Finally the composition of the L_1 phase reaches one corner of the W/L_1/L_α three-phase triangle, and, consequently, the lamellar phase forms at the drop surface. Therefore, the elongation of drop is seen as described in Section 5-4.

However, if a drop of C_{12}E_4/SDS is injected into the aqueous SDS solutions with higher surfactant concentration initially present, such as 15 wt% or more, the composition path will change and follow another one like path 3 of Figure 6-14 (b). Intermediate phases, H_1, V_1, L_α, (V_1 not shown on the diagram), develop after initial contact with water. As more water diffuses in and more surfactants diffuse out, the drop reach a two-
phase region of $L_1+H_1$. Thus, small $L_1$ drops are seen forming on the edge of surfactant drop. This behavior is consistent with the observation of equilibrium phase-behavior experiments which showed coexistence of $L_1$ and $H_1$. Finally the whole drop dissolves. The equilibrium phase-behavior experiments showed that the samples of $L_1+H_1$ mixtures were very viscous. Accordingly, the scalloped-shape of drop may be associated with this very viscous mixtures of liquid crystalline phases and $L_1$ phase. It is noteworthy that the location of IC of Figure 6-14 (b) is not drawn to scale. It should be located at a point far below the one shown on the figure. That is, it would be drawn off of the paper if drawn to scale. For the same reason the shape of path 3 is somewhat distorted although it passes through the proper sequence.

With the microinjection system, one can have an almost uniform size of injected drops and can track the drop from the instant of injection. This system was found to be very useful for those experiments with good controlled size of injection drops or for those where size needs to be tracked from the initial moment of contact. However, because injection is driven by high pressure gas (up to 100 psi), some initial mixing upon injection is inevitable. Dark regions surrounding injected drops were often observed, even though they could disappear within a second from the moment of injection. In addition, surfactant drops such as $C_{12}E_6$ will expand slightly upon contact of water as the surfactant concentration on the lower phase boundary of $H_1$ is about 0.4 and the complete injection may take up to 200 ms. These factors might contribute to the measurement errors on the initial size of injection drops. Although they may decreases dissolution time slightly, they do affect the basic mechanisms of dissolution described above. Despite that, the
microinjection system still gives less initial mixing and a better control of injection volume than the use of syringe injection system described in Section 3.3.

It is of great interest to understand how the presence of SDS eliminates or reduces the myelinic structures. Baglioni et al. [1993] reported the structures of mixed micelles of SDS/C_{12}E_{6} and C_{12}E_{6}/DTAC (dodecyltrimethylammonium chloride) surfactants by the application of electron spin echo modulation (ESEM) of x-doxyzlsteoric acid spin probes. They found out that (1) SDS and DTAC solubilize with their head groups in the ethylene oxide region of the nonionic surfactant, and (2) the addition of SDS to C_{12}E_{6} to form mixed micelles opens up the ethylene oxide region to more water penetration in the mixed micelle. This effect depends on the C_{12}E_{6}/SDS mole ratio and it is maximum for the equimolar mixture. Although C_{12}E_{3} and C_{12}E_{4}, not C_{12}E_{6}, were used in this study, the addition of SDS may also open up the ethylene oxide region to more water penetration and thereby increase the cloud point temperature of the systems. Moreover, electrostatic repulsion between micelles may also contribute. One would conclude addition of suitable amount and species of hydrophilic surfactants to these hydrophobic ones may lead to the destruction of the unwanted myelinic dispersions that would be certainly useful in some applications such as the formulation of laundry detergents.
Chapter 7: Summary, Conclusions and Future studies

7.1 Solubilization Rate of Triolein and Triolein/Oleic Acid Mixtures

The rates of solubilization of triolein drops in nonionic surfactant solutions were measured by a novel technique, i.e., observing the decrease in drop radius with time using videomicroscopy. Triolein is solubilized more slowly than \( n \)-hexadecane, which is expected because triolein has a higher relative molecular mass and is solubilized to a lesser extent at equilibrium. However, the triolein rates were lower than would be the case if rates for the two oils were proportional to their respective solubilization capacities. Moreover, solubilization of triolein, but not \( n \)-hexadecane, is much faster when the secondary alcohol ethoxylate Tergitol 15-S-7, whose films are relatively thin and have a rather disordered hydrocarbon chain region, is used instead of surfactants having the same cloud point but with thicker and more ordered films, i.e. pure \( C_{14}E_6 \) and a mixture of pure \( C_{12}E_6 \) with \( n \)-dodecanol. Adding short-chain alcohols also increases film flexibility together with solubilization rates for both triolein and \( n \)-hexadecane.

The mechanisms responsible for this behavior are not completely clear but are associated with "adsorption" and "desorption" of micelles at the interface between the oil and the aqueous solution. In some cases, e.g. the effect of short-chain alcohols, the trends in our results are qualitatively consistent with earlier proposals that shorter micelle dissociation times lead to more rapid adsorption of surfactant molecules by an oil drop. the surfactant later being reemitted as oil-containing micelles. However, no quantitative information is available to conclusively demonstrate the validity of this mechanism. The other possible mechanism is transport between the oil drop and a micelle with which it is
temporarily joined. In this case, film flexibility would facilitate transport of the large triolein molecules through the small neck joining the oil drop and the micelles.

Rapid solubilization of triolein at lower temperature (about 22°C) can be achieved by using an oil-in-water microemulsion phase of the C_{12}E_{4}/n-hexadecane system. However, the problem of initial long “lag” periods needs to be overcome.

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 two. This behavior continues until most of the oleic acid has been solubilized, after which the solubilization rate becomes approximately 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, substantially 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.

7.2 Dissolution of Surfactants
Videomicroscopy was also used to investigate the mechanisms and rates of dissolution of neat, liquid nonionic surfactants. Drops of the pure linear alcohol ethoxylates C₁₂E₅ and C₁₂E₆ dissolved rapidly at temperatures below their cloud points. An intermediate lamellar liquid crystalline phase was always seen, and, at sufficiently low temperatures, intermediate hexagonal and cubic phases as well. Dissolution rates increased with increasing temperature until the cloud point was reached. The results indicated that the process was diffusion controlled. Estimates of effective binary diffusion coefficients in the intermediate phase(s) were obtained by combining their measured growth rates in onedimensional experiments where neat surfactant contacted water with measured dissolution times of surfactant drops. Values of 1.1-2.3 × 10⁻¹⁰ m²/s were found for the liquid crystalline phases at 30°C. They are in good agreement with what Sallen et al. [1997] found for the diffusion coefficients of H₁ and L₁ phases of C₁₂E₆/water at 30°C.

Drops of the commercial nonionic surfactants Neodol 25-7 and Tergitol 15-S-7 required considerable time for complete dissolution at temperatures just below their cloud points. Although initial dissolution of the more hydrophilic species in these surfactants was rapid under these conditions, that of a final small drop rich in rather insoluble lipophilic species was slow. Considerable spontaneous emulsification of water in the surfactant drop was also observed. Moreover, the final small drop frequently became elongated and sometimes formed conical projections that emitted jets. This latter behavior is probably associated with formation of a thin layer of relatively dilute lamellar phase on the surface of the drop.
Similar spontaneous emulsification and some conical projections were seen at temperatures just below the cloud point for the model system C_{12}E_8/n-decanol/water, which was chosen because it was a well-defined system containing both hydrophilic and lipophilic species for which a partial phase diagram was available. The phase diagram was used to help explain the experimental observations.

At 30°C a compact mass of viscous myelinic figures developed and persisted for a long time when a drop of pure C_{12}E_4 was injected into water. However, complete dissolution occurred when 5 wt% of small SDS crystals was added to the drop. Myelinic figures formed upon drop injection but later dissolved, as did the SDS particles. The drop later exhibited considerable spontaneous emulsification, elongation, and some jetting similar to that seen for commercial nonionic surfactants. Complete dissolution also occurred when C_{12}E_4 drops were injected into dilute SDS solutions. Myelinic figures formed on initial contact and later dissolved, but neither spontaneous emulsification nor formation of jets was observed.

7.3 Possibilities for Future Research

There are still some more interesting studies that could be done in the future. The solubilization of triolein in microemulsions such as C_{12}E_4/n-hexadecane systems can be investigated systematically. The rapid solubilization can be applied to those laundry detergents for clothes in need of special cares such as hand-wash only. The rates of solubilization of oils, such as squalane, n-hexadecane and triolein, in micellar solution of
C_{12}E_4/SDS mixtures could also be conducted for comparison with those published data but on different nonionic surfactant solutions, such as C_{12}E_5 and C_{12}E_6 solutions.

The other possible future work would be to extend the C_{12}E_3/SDS system to C_{12}E_3 with more hydrophilic surfactants, such as ones with shorter hydrocarbon chains. C_{12}E_3 is so lipophilic that it forms myelin dispersions at 30°C. Figure 6-8 shows that at least 10 wt% SDS is needed in surfactant mixtures to avoid W+L_α. Even though the maximum amount of SDS is added in such a way to prevent the mixtures from solidifying at 30°C, it still cannot completely dissolve in water in droplet dissolution experiments. If possible, SDS in droplet dissolution experiments of C_{12}E_3 will be replaced by some hydrophilic anionic surfactants.

Jetting or budding phenomena that were observed in the dissolution of commercial nonionic surfactants and linear ethoxylate surfactant mixtures with alcohols are also interesting. Investigation of these phenomena could be conducted to further clarify the possible mechanism. The system of C_{12}E_3/C_{10}OH with precise control of initial composition and the detailed phase diagram will be recommended. More experiments should be conducted to determine the phase boundaries. Consequently, the diffusion path of the injected drop into aqueous solution can be determined and as well as the path leading to the budding phenomena.
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Appendix

Figure A-1: Interfacial tension measurements of triolein with 2 wt% C\textsubscript{12}E\textsubscript{4} at 30\textdegree C

Figure A-2: Interfacial tension measurement of triolein with 2 wt% Tergitol 15-S-7 at 30\textdegree C
Figure A-3: Interfacial tension measurement of n-hexadecane with 2 wt% Tergitol 15-S-7 at 30°C

Figure A-4: Interfacial tension measurement of triolein with 2 wt% Tergitol 15-S-7 and 0.15 wt% C6OH at 30°C
Figure A-5: Variation with time of radius of drop containing 85/15 triolein/oleic acid (by weight) injected into 2 wt% C_{12}E_{6} at 35°C

\[ R_0 = 29.1 \mu m \]
\[ \frac{dR}{dt} = -2.81 \mu m/min \]

Figure A-6: Interfacial tension measurement of triolein with 2 wt% C_{6}OH and added alcohols at 30°C