RICE UNIVERSITY

Dissolution Rates of Surfactants and Granules

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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HOUSTON, TEXAS
APRIL, 2003
ABSTRACT

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A quantitative penetration scan method was used to study rates of dissolution of pure, noncrystalline anionic surfactants in water. The displacement of phase boundaries from initial surface of contact was found to be proportional to the square root of time, indicating the importance of diffusion. For some surfactants studied such as Aerosol OT (AOT) and 7-phenyl tetradecane sulphonate, myelinic figures grew from the initial surface of contact between surfactant and water toward the aqueous phase. A simple model was developed which included both this swelling and diffusion in the rest of the surfactant-containing region. The usual penetration scan method involving semi-infinite phases was supplemented by a novel modified scan in which only a thin layer of surfactant was used. With the combined results it was possible to obtain effective diffusivities of the liquid crystalline phases of AOT and of the two lamellar phases of 7-phenyl tetradecane sulphonate. Values were of order $10^{-10}$ m$^2$/s.

Videomicroscopy was used to investigate the mechanisms and rates of dissolution for a system containing the pure nonionic surfactant C$_{12}$E$_4$ and the soap sodium oleate. A microinjection technique was used to inject drops of surfactants or surfactant mixtures into water. Although C$_{12}$E$_4$ itself does not dissolve in water, dissolution was observed
when drops of its mixtures with sufficient oleic acid were injected into alkaline buffer solutions. Formation of sodium oleate during the dissolution process made the surfactant mixture more hydrophilic and hence soluble. A lamellar phase formed upon injection and dissolved by a shrinking core mechanism.

A hanging drop slide technique was developed and used to study disintegration of single granules consisting of many zeolite particles bound together with liquid nonionic surfactant. For pure nonionic surfactants and their mixtures, granules disintegrated below the cloud point of the pure surfactant or mixture. Disintegration did not occur when the neat surfactant developed viscous myelinic figures upon contact with water. Nor was it observed when an aqueous phase coexisted with a surfactant-rich L₁ phase or L₃ (sponge) phase at equilibrium. Similar behavior was observed for commercial nonionic surfactants and their mixtures.
Acknowledgement

There are many people helped, supported, and inspired me during the completion of my PhD thesis, I would like to take this opportunity to extend my deep gratitude to:

My thesis advisor, Dr. Clarence A. Miller for his invaluable advice and contributions to this work. His insights and high standards have definitely helped to shape this work. Without the support and encouragement of him and his wife, Mrs. Hilary Miller, this work could not have been achieved.

Dr. George J. Hirasaki and Dr. Huey W. Huang, for serving on my thesis committee and their comments on this work.

The faculty and staff of Department of Chemical Engineering at Rice University for their assistance and support. Also, my colleagues at the Interfacial Phenomena Laboratory and at Rice University for making an enjoyable working environment.

This work was funded by Unilever Research of United Kingdom. Special thanks to Dr. John E. Wilson for his support and suggestions on this work and for his help in arranging the trip for me to work at Unilever as a visiting student in summer 2000.

Especially, I would like to give my warmest thanks to my husband, Shijiang Lu whose unconditional love and support enabled me to complete this work.
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Chapter 1: Background

1. Surfactants

Surfactants have long been known to human beings for their application in many aspects of life, for example, washing and cleaning processes. Surfactants perform important functions in cleaning, such as detaching, emulsifying and holding soil in suspension until it can be rinsed away. Other applications of surfactants can be seen in pharmaceutical field such as drug delivery and controlled release systems. Surfactants could be also used in tertiary oil recovery and as wetting and emulsifying agents, e.g., in baking products and mixes, chocolate, cosmetics, dyes and plastics. In recent years the microstructure provided by surfactant aggregates in micellar solutions, microemulsions, and lyotropic liquid crystals has attracted attention due to possible applications in separation processes such as removal of organic and metal contaminants from waste water streams and in enhancing the rates and selectivities of certain chemical reactions. The ability of surfactants to form ordered films at solid-liquid interfaces is also of interest for nanoporous materials.

A surfactant molecule consists of two important parts, a hydrophobic tail and a hydrophilic head group. The tail, usually a long hydrocarbon 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 and Neogi, 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. In this work, we focus on anionic surfactants and nonionic surfactants.

An anionic surfactant carries negative charge on its surface-active portion, for example, RCOO'Na⁺ (soap) and RC₆H₄SO₃Na⁺ (alkylbenzene sulfonate). Anionic surfactants are used in laundry and hand dishwashing detergents, household cleaners, and personal cleansing products. They are generally high sudsing. Linear alkylbenzene sulfonates (LAS), alcohol ethoxysulfates, alkyl sulfates and soaps are the most common anionic surfactants. The neat anionic surfactants are crystalline or amorphous solids.

LAS (R-C₆H₄-SO₃Na) is a mixture of many phenyl isomers and carbon chain homologs. Each carbon chain length homolog contains several phenyl isomers in which the benzene ring is attached to a secondary carbon along the alkyl chain [Stache, 1996]. LAS is the most widely used anionic surfactant in laundry products.

A nonionic surfactant doesn’t bear any charge on its surface-active portion, for example, R(OC₂H₄)ₙOH (linear ethoxylated alcohol) and RC₆H₄(OC₂H₄)ₙOH (polyoxy-ethylenated alkylphenol). 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, C₁₂E₇ and C₁₂E₃, of which CₘEₙ 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 polyoxyethylene 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.

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

1.1 Surfactant Characteristics

1.1.1 Critical micelle concentration (CMC)

A notable feature of Figure 1.1, which shows surface tension as a function of concentration for a particular soap, is the abrupt change in slope at a particular concentration. In the vicinity of this concentration a host of properties of the bulk solution also change their rate of variation with concentration. e.g., surface tension, solubility, light scattering properties, electric resistance or conductance, osmotic pressure, density, detergency, turbidity, self diffusion, etc. Light scattering experiments show that aggregates, which are known as micelles, form beyond this "critical micelle concentration". Further addition of surfactant to the solution beyond CMC gives rise, for the most part, only to more micelles. In micellar form, the hydrocarbon chains are shielded from water and the entire structure, as seen by water, is hydrophilic and compatible with water.
The concentration at which micelles first form in solution is called critical micelle concentration (CMC). CMC can be experimentally determined by measuring the surfactant concentration at which sudden changes of physical properties occur. 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. 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 1.1 Surface tension as a function of surfactant concentration [Roe and Brass, 1954].

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 of the order of $10^{-3}$ mole/liter as electrical repulsion of charged head groups acts against aggregation. As an example of surfactants with comparable chain lengths, the CMC is $6.4 \times 10^{-5}$M for $C_{12}E_5$.
in water at 25°C and $8.2 \times 10^{-3}$ 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.

1.1.2 Krafft point or Krafft temperature

The minimum temperature for micelles to exist is called the Krafft point or Krafft temperature [Miller and Neogi, 1985; Laughlin, 1994] (Figure 1.2). Most anionic 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 the 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 the CMC, below the Krafft temperature, and the solution contains almost no micelles. Above Krafft temperature micelle formation becomes possible. It is noteworthy that surfactants (detergents) are less effective below Krafft point.

1.1.3 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
Figure 1.2: Solubility and CMC curves of the sodium dodecyl sulfate (SDS) in water [McBain and Hutchison, 1955]

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 exception is very near the lower critical solution temperature, where compositions of the two phases are nearly equal. The phase separation is reversible; when the mixture is cooled to temperatures 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 a mixture of two liquid phases when it is raised beyond cloud point
temperature, these phases 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. 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; Carroll et al 1982; O’Rourke et al, 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 et al, 1985a, 1985b].

The temperature at which clouding phenomena occur depends on the structure of polyoxyethylated nonionic surfactants. For example, for nearly pure surfactants, the cloud point temperatures are 10°C for C₁₂E₄, 32°C for C₁₂E₅, 52°C for C₁₂E₆, and 62°C for C₁₂E₇ (Data supplied by manufacturer, Nikko Chemicals, Tokyo, Japan). Huibers et al. [1997] developed a general empirical relationship for estimating the cloud point of pure nonionic surfactants of the alkyl ethoxylate class from their structures.

1.1.4 Phase rule

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

\[ F = C - P + 2 \]

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 the number of equations 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, since no phase is uniform in composition at molecular scales [Smoluchowski, 1908; Buff, 1965, 1989].

1.1.5 Hydrophile-Lipophile-Balance (HLB) and Phase Inversion Temperature (PIT)

In 1949 Griffin made an attempt to classify surface active agents by their hydrophile-lipophile balance (HLB), which was made quantitative in terms of HLB numbers [Griffin, 1949]. The smaller the HLB value, the more oil soluble the surfactant. According to the initial classification, 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 a mixture is the weighted average of the individual HLB numbers.

The phase inversion temperature (PIT) is that where the surfactant phase (D) (see section 1.2.4) has equal interfacial tensions with oil and water. It is also 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 for nonionic surfactants 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]. In commercial polyoxyethylene nonionics, 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, the presence of additives, and the distribution of polyoxyethylene (POE) chain length [Shinoda, 1968; Mitsui and Harusawa, 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 \( \text{C}_i\text{E}_j \) surfactant [Schubert, 1996]. Studies have shown 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 [Raney et al, 1987].

1.2 Phases Involving Surfactant Aggregates

1.2.1 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 concentration reaches CMC, further addition of surfactant into solution only forms an isotropic phase, \( L_1 \) -- a micellar solution (Figure 1.3 and Figure 1.4). The shape of micelles can be spherical, rod-like, long cylindrical, or flexible, thread-like.

Surfactant molecules form micelles because this aggregation largely removes the hydrocarbon chains from contact with water. The conventional explanation is that in this form the hydrocarbon chains are shielded from water and the entire structure, as seen by water, is hydrophilic. Detailed consideration of micelle geometry indicates that the chains are more randomly arranged throughout the micelle interior and that they are not completely shielded by the head groups in typical systems.

At higher temperature or concentration a reversed micellar phase exists as \( L_2 \) in nonionic systems - in contrast to the normal micellar phase \( L_1 \). Both \( L_1 \) and \( L_2 \) can exist
as homogeneous phases or in equilibrium with water phase W depending on the concentration and temperature. L₁+W exists at temperatures above cloud point temperature for nonionic surfactants.

Figure 1.3 Optical properties of liquid crystals. (Result of peripheral evaporation of isotropic solution in sodium 3-undecyl sulphate-water system, showing micellar, hexagonal, cubic and lamellar phases as surfactant concentration increases from left to right in the picture.)

1.2.2. Liquid Crystal Phases

With further substantial amount of surfactant added into a micellar solution of many surfactants a new phase forms -- quite viscous and showing static bright birefringence under crossed-polarizers. This phase is called “liquid crystal”. Surfactant molecules in it 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 \( H_1 \) (Figure 1.3, Figure 1.4 and Figure 1.5). \( H_2 \) 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 favorable and this liquid crystalline phase is known as the lamellar phase - denoted as \( L_\alpha \) (Figure 1.3, Figure 1.4 and Figure 1.5). 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 \( (L_1, L_2 \text{ or } L_3 \text{ phases}) \).

Figure 1.4. Mesophases presented in a surfactant-water system [Lawrence, 1994] in accordance with increasing concentration in a simple binary system of water-surfactant.
Figure 1.5 Temperature-composition phase diagram for \( \text{C}_{12}\text{E}_5 \)/water solutions

[Strey et al, 1990]

Cubic phase, denoted as \( V_1 \) (or \( V_2 \) for its reversed form) (Figure 1.3 and Figure 1.5), is another type of liquid crystalline phase known to exist in many systems containing surfactants [Miller, 1985]. Although they are isotropic under crossed-polarizers, and hence do not exhibit birefringence like the hexagonal and lamellar phases, their microstructures, which cause them to be highly viscous, can be examined by X-ray diffraction.
Under crossed-polarizers the textures of different liquid crystalline phases appear greatly different (Figure 1.3). 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. More photomicrographs of textures of liquid crystalline phases were reported by Rosevear [1954].

1.2.3 Isotropic bicontinuous phase

Another isotropic phase, denoted as L₃, forms at temperatures above those where water and lamellar phase coexist for nonionics (Figure 1.5). It's frequently termed the "sponge phase" because continuous but tortuous water channels are separated by continuous surfactant bilayers whose large-scale morphology resembles that of the solid portion of a sponge, according to electron micrographs. Locally, the bilayers are saddle-shaped with the two radii of curvature having opposite signs.

The main difference between Lₐ and L₃ is that the initially flat bilayers in Lₐ are deformed into saddle-like surfaces in L₃. Freeze fracture electron micrographs of the L₃ phase clearly show that the bilayers are indeed multiconnected and have saddle-shaped microstructures with a negative Gaussian curvature [Strey et al, 1990, 1992; Hoffmann et al, 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 et al, 1992]. That is, the results rule out the isolated disk structure and are consistent with interconnected bilayers.

1.2.4 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 with medium chain alcohols [Hoar *et al.*, 1943]. Since that time many experiments have been performed to determine their structures.

Microemulsions are thermodynamically stable 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 sometimes denoted as W<sub>m</sub> and O<sub>m</sub> 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.

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. Ruckenstein *et al.* recognized the importance of
this effect for microemulsions and developed a suitable analysis to describe it quantitatively [Ruckenstein et al, 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 [Ruckenstein et al, 1978]. Although they occur in ternary systems of some surfactants, 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.

1.3 Dissolution rates of surfactants

For surfactants used in aqueous washing process to be effective, they must dissolve completely in the washing bath in a time period much shorter than the washing time. The mechanisms and rates of dissolution of neat, liquid nonionic surfactants were investigated in previous project [Chen, 1998; Chen et al, 2000]. Drops of the pure linear alcohol ethoxylates C_{12}E_5 and C_{12}E_6 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 one-dimensional experiments where neat surfactant contacted water with measured dissolution times of surfactant drops. Values of 1.1-2.3\times10^{-10} \text{m}^2/\text{s} were found for the liquid crystalline phases at 30^\circ\text{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.

Emulsification phenomena, i.e., spontaneous formation of drops of a liquid phase, are often encountered in those systems that are mixtures of hydrophilic and hydrophobic species dissolving in water at temperatures just slightly below their cloud points [Chen, 1998; Chen et al. 2001], i.e. the dissolution of Tergitol 15-S-7, a commercial secondary alcohol ethoxylate, at 30°C (Figure 1.6). Similar phenomena were also observed in the system consisting of hydrophobic nonionic and hydrophilic anionic surfactants, i.e., C₁₂E₄/SDS (sodium dodecyl sulfate) system. In Chen's work, it was found that 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

Figure 1.6 Drop of Tergitol 15-S-7 in water at 30°C shows emulsification.
was rapid under these conditions, that of a final small drop rich in rather insoluble lipophilic species was slow. Considerable spontaneous emulsification in the surfactant drop was also observed. Moreover, the final small drop frequently became elongated and sometimes formed conical projections that emitted jets (Figure 1.7). This latter behavior is probably associated with formation of a thin layer of relatively dilute lamellar phase and maybe also L₃ phase on the surface of the drop although this behavior is not yet completely understood.

Similar spontaneous emulsification and some conical projections were seen at temperatures just below the cloud point for the model system C₁₂E₈/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. Key features of the behavior observed during dissolution of drops of C₁₂E₈/C₁₀OH below their cloud points can be explained using the phase diagram (Figure 1.8). To determine the actual set of compositions formed on contact, i.e., the initial diffusion path for a drop initially containing 95/5 C₁₂E₈/C₁₀OH by weight, composition IC₁ of Figure 1.8, one would need to know exact phase boundaries and tie lines, as well as diffusion coefficients [Ruschak and Miller, 1972]. Although this information is not available, the dotted line connecting IC₁ with the water corner provides some insight and suggests that intermediate lamellar and hexagonal phases should form on initial contact, as was, in fact observed experimentally. Since C₁₂E₈ is more soluble in water than is decanol, the decanol content of the drop increased during the experiment, so that the small drop, which dissolved slowly at the end of experiment was presumably a decanol-rich phase.
The other dotted line in Figure 1.8, which starts at point IC2, represents behavior of a drop initially containing 15 wt% decanol, a mixture which has a cloud point of approximately 37°C. In this case, the dotted line suggests that L_α is the only intermediate phase expected on initial contact, in agreement with the experimental results. Here too the drop becomes richer in decanol with increasing time, at some point exceeding its cloud point composition with the result that L_1 becomes an intermediate phase between L_α and water. If L_1 is nonwetting, it forms as individual drops or lenses as observed. As the alcohol-to-surfactant ratio of the drop increases further, Fig 1.8 suggests that the L_3 phase should also appear, which may also account for some of the emulsification observed. It should be noted, however, that equilibration among these dilute phases is known to be slow. Thus, even relatively small volumes of different phases in contact during the experiment may not be in or even close to equilibrium.

Figure 1.7 Drop of Tergitol 15-S-7 in water at 30°C shows elongated shape and jetting phenomena.
In Chen's work, it was found that when a drop of pure \( \text{C}_{12} \text{E}_4 \) was injected into water at 30°C, a compact mass of viscous myelinic figures developed and persisted for a long time. 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. Chen's work on C_{12}E_4/SDS system will be further discussed in Chapter 5.

2. Detergency

The main components of powder detergent formulations are surfactants and builders. Heavy-duty laundry powders also often contain bleach systems. Furthermore, antiredeposition and fluorescent whitening agents, fragrances and enzymes are incorporated [Showell, 1998].

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 et al, 1993].
2.1 Surfactants in detergent powder

Surfactants are the most important component in detergent powders. Their main function in the washing machine is assisting in the soil removal process. In many cases, the surfactant performs the role of binding the other powder ingredients together. Hence, the physical properties of the surfactant can play a key role in the formulation process as well as the finished product [Showell, 1998].

It is noteworthy that LAS is too hydrophilic to form bicontinuous microemulsions for typical washing conditions with nonpolar soils such as mineral oil. We need to mix LAS with nonionic which is less hydrophilic. A powder detergent or granule may have both solid anionic and liquid nonionic surfactants which are incorporated along with zeolite.

2.2 Builders in detergent powder

Builders such as zeolites are the backbone of the detergent because they enhance or build the washing efficiency of the surfactants and other components. Builders have to meet a wide range of requirements. In particular, they must inactivate the water hardness ions, calcium and magnesium, from the washing liquor, thus preventing them from interacting with the surfactants. Some builders are also a source of alkalinity and buffer the pH of the wash water at ~10. That supports the action of the other detergent ingredients to dislodge dirt and stains and to prevent dissolved dirt from resettling on fabrics [Showell, 1998].
Zeolites have been replacing phosphates as builder system for fabric washing products for a number of years. This move has been prompted by environmental concerns over the use of phosphates.

The change from phosphates to zeolite, although originating in Europe and the US, is now a global phenomenon. As a result, zeolite is now being used over an ever increasing range of wash conditions. The Ca ion-exchange properties of zeolite A are known to be sensitive to temperature. The zeolite types used in this study are: commercial detergent grade 4A sample which is non-swelling and zeolite A24 which is swelling. The typical size of zeolite powder is around 2~5 μm.

Due to these beneficial properties builders contribute well to detergency performance. As powder detergents are better built than heavy-duty liquid detergents, they often show better cleaning results, which means that builders are one of the keys to the dominance of powders over liquids.

Since zeolites are commonly used as "builders" for ion exchange to remove Ca\(^{2+}\), Mg\(^{2+}\) from water and since nonionics are liquids, one way of including nonionics in a powder product is to incorporate them in "granules" with zeolite. The preparation of granules requires mixing the components, usually a solid carrier and a liquid binder, under high shear conditions. Surfactant takes up 20~30wt% and zeolite takes up 70~80wt% in the granule. The diameter of the granules is typically around 250~1000 μm.

To be effective, the granules should disperse quickly in the washing bath. One objective of this thesis is to combine information on surfactant dissolution with experiments on granule dispersion to understand the process.
Chapter 2: Project Scope and Objectives

This study is to develop fundamental understanding of dissolution process for surfactants and surfactant mixtures and disintegration of granules made up of inert solids such as zeolite and liquid surfactant.

The first objective is to study the dissolution of anionic surfactants, a topic about which little is currently known. The anionic surfactants are typically crystalline solids or highly viscous liquid crystalline phases near ambient temperature. Study of dissolution of crystalline solid is not easy since compacts of crystalline materials are subject to wetting along grain boundaries and disintegration, making interpretation of results questionable. A method to study dissolution of liquid crystalline phase, the linear penetration scan method, was developed. Anionic surfactants such as AOT, 7-phenyl tetradecane sulphonate and 5-phenyl undecyl sulfonate have been studied, as discussed in Chapter 4.

A second objective is to understand the role of soap in nonionic surfactant dissolution. From previous study [Chen, 1998], we know that a droplet of pure nonionic surfactant C12E4 swelled and formed myelinic figures when it was immersed in water and that a compact mass of viscous myelinic figures remained for a long time. The formation of a viscous mass of myelinic figures would be unfavorable in a washing process because most of surfactant would not be available and 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.

It has been reported that swelling and mesophase formation are inhibited when relatively small amounts of soap, ca. 10%, are added to granules containing nonionic
surfactant. One suggestion is that the soap forms a continuous network within the nonionic, thus providing a "structuring" effect. However, the mechanism by which the soap acts is not well understood. When added to C₁₂E₄, it may simply promote dissolution by producing a surfactant mixture which is more hydrophilic than C₁₂E₄. One part of the study described in Chapter 5 was designed to provide further information on these systems.

Another important objective is to get fundamental understanding of disintegration of granules. To be effective, the granules should disperse quickly in the washing bath. It seems likely that the behavior of granules in a washing machine depends on the rate of formation and dissolution of surfactant mesophases, which act as a glue to hold granules together in a compact glob. Then information on surfactant dissolution should be combined with experiments on granule dispersion to understand the process.

Necessary background information on surfactants, detergent powders and granules was provided in Chapter 1. Experimental procedures and all equipment set-ups are described in Chapter 3.

Chapter 4 focuses on the rates of dissolution of anionic surfactants. For highly soluble anionic surfactants, such as 5-phenyl undecyl sulfonate, dissolution was controlled by diffusion. For the insoluble anionic surfactant with large miscibility gap, such as pure AOT and 7-phenyl tetradecane sulfonate, myelins formed during the dissolution. When diffusion controls and equilibrium phase behavior is known, the diffusivities of intermediate phases of surfactant-water systems can, in principle, be obtained by combining the use of semi-infinite and thin layer vertical contacting experiments. In the latter a thin layer of anionic surfactant is brought into contact with a
large volume of water. However, when myelinic figures develop, convection in the liquid phase and swelling of the lamellar phase must be incorporated into the model. A first step in this direction is described in Chapter 4.

The dissolution processes of C_{12}E_{4}/soap system are presented in Chapter 5. Dissolution behavior of C_{12}E_{4}/oleic acid in buffer solutions and water and of C_{12}E_{4}/sodium oleate in water was studied. Formation of soap during the dissolution process made the overall surfactant mixture more hydrophilic, causing the lamellar phase which developed immediately upon injection to dissolve. Oleic acid can also promote dissolution of the lamellar phase of C_{12}E_{4}. But the isotropic phase formed is L_{3} or L_{2} phase. Sodium oleate can promote the dissolution of the lamellar phase of C_{12}E_{4} by different mechanisms. With high concentration of sodium oleate (i.e. 15% or 17%), 'shrinking core' mechanism dominated. In contrast, with low concentration of sodium oleate (i.e. 7% or 10%), the lamellar phase was converted to a surfactant-rich phase fairly early and spontaneous emulsification occurred. The dissolution time was greater in this case. Dissolution of some commercial surfactants is also described in Chapter 5.

Chapter 6 discusses the dissolution of neat surfactants and corresponding granules. Our results for pure nonionic surfactants and their mixtures show that granules disintegrated below the cloud point of the pure surfactant or mixture. Disintegration did not occur when the neat surfactant developed viscous myelinic figures upon contact with water. Nor was it observed when an aqueous phase coexisted with a surfactant-rich L_{1} phase or L_{3} (sponge) phase at equilibrium. Similar behavior was observed for commercial nonionic surfactants and their mixtures although there were a few exceptions, presumably
owing to the presence of many individual isomers and broad distributions of ethylene oxide chain lengths.

Chapter 7 summarizes the current findings of this work and the directions of future work.
Chapter 3: Materials and Research Methodology

1. Materials

Sodium bis (2-ethylhexyl) sulfosuccinate, also known as Aerosol OT (AOT) has a molecular weight of 444.56 and at 30°C, a density of 1.13 g/cm³. AOT used in this study, of purity greater than 96%, was purchased from TCI America, Portland OR.

Several linear alkylbenzene sulfonate (LAS) samples were supplied by Unilever Research. 5-phenyl undecyl sulfonate and 5-phenyl decyl sulfonate are highly viscous liquid crystalline phases while 6-phenyl dodecane sulphonate, 2-phenyl dodecane sulphonate, 7-phenyl tetradecane sulphonate, 2-phenyl tetradecane sulphonate, 2-phenyl decyl sulfonate are crystalline.

Water used for experiments was doubly distilled with a Barnstead Glass Still and deionized with NANOpure II system. The resistivity of deionized water was at least 16.7 MΩ/cm measured at the ambient temperature near 20°C.

The pure linear alcohol ethoxylates $C_{12}E_3$, $C_{12}E_4$, $C_{12}E_5$, $C_{12}E_6$, $C_{12}E_8$, and $C_{14}E_6$, were purchased 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 25-3, 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 3.0 moles respectively per mole of surfactant. They were supplied by Shell Chemical Company (Houston, Texas). pH=9, 10, 11, 12 buffer solutions and oleic acid with a purity of greater than 95% were purchased from Fisher
Scientific Company. Sodium oleate with a purity of 99% was purchased from Sigma-Aldrich company.

Commercial surfactants Vista 1012-62, Neodol 23-6.5, Neodol 91-5, Synperonic A7, Lialet 111-5.5, Neodol 25-3 and Neodol 1-5 were supplied by Unilever research. Neodol and Dobanol (shown as below) are both Shell trade names and the products are similar. For example, Neodol 23-6.5 has an average EO number of 6.5 and carbon number between 12 and 13. Vista, Synperonic, Lialet are all trade names from different companies. For example, Synperonic A7 has an average EO number of 7.

The preparation of granules requires mixing the components, usually a solid carrier and a liquid binder, under high shear conditions. Some of granules used in this study were supplied by Unilever. Granules were made in Unilever's Port Sunlight laboratory using a Sirman C6 mixer, which is a commercial high shear food mixer that can be used to prepare granules on a small (~0.5kg) scale. The mixer consists of a stainless steel vessel and a removable motor driven blade assembly which is centrally located close to the base of the spindle. A Perspex lid is fitted on top of the vessel and is held in place by a simple arm and clamp unit.

The solid materials are normally added to the bowl and motor started. The liquid is then introduced via the opening in the lid. The rate of mixing is either fixed or can be adjusted as appropriate.

Granules made in this way are listed below:

(1) Lialet 111-5.5, zeolite 4A

(2) Lialet 111-5.5, zeolite A24
(3) Lialet 111-5.5, zeolite A24, sodium stearate

(4) Lialet 111-5.5, zeolite 4A, sodium stearate

(5) Dobanol 6.5, zeolite A24

(6) Dobanol 6.5, zeolite A24, FAES (Fatty Acid Ester Sulphonate)

(7) Dobanol 6.5, zeolite 4A, FAES

(8) Dobanol 7, zeolite 4A, PAS (Primary Alkyl Sulfate)

(9) Dobanol 7, zeolite A24, PAS

Other granules used in this study were made at Rice. The procedure used the same principles but on an even smaller scale (~10g). A mortar and a pestle were used. The solid materials (i.e., Zeolite 4A) were added to the mortar, then the liquid (i.e. surfactant or surfactant mixture) was introduced. The pestle was used to mix the solid materials and the liquid. A scraper was used to scrape the materials that stuck to the wall of the mortar and mix them with the drier materials in the mortar. The ratio of the solid materials and the liquid could be adjusted as appropriate, but was typically around 70:30 by weight.

Granules made in this way are listed below:

(10) Pure C_{12}E_3, Zeolite 4A

(11) Pure C_{12}E_5, Zeolite 4A

(12) Pure C_{12}E_6, Zeolite 4A

(13) C_{12}E_4,C_{12}E_6, Zeolite 4A

(14) C_{12}E_3,C_{12}E_7, Zeolite 4A
(15) C_{12}E_2, C_{12}E_8, Zeolite 4A
(16) C_{12}E_8, C_{10}OH, Zeolite 4A
(17) Neodol 91-5, Zeolite 4A
(18) Neodol 23-6.5, Neodol 91-5, Zeolite 4A
(19) Neodol 25-3, Neodol 25-7, Zeolite 4A
(20) C_{12}E_4, Sodium Oleate, Zeolite 4A
(21) Tergitol 15-S-7, Zeolite 4A

2. Phase behavior

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 a temperature controlled environmental room. The polarizing light screening system was used for determining phase states. This technique provides information about the isotropy, anisotropy, and scattering of the solutions. Diffuse light was transmitted from the back side and through a polarizer. While samples were located between the polarizer and the analyzer, the analyzer plate was rotated to position its optical axis 90° with respect to the polarizer. Liquid crystalline (L_α) phases were easily distinguished by the birefringence displayed in this arrangement. L_1 phases normally resided at the bottom of the tubes and were clear or slightly bluish micellar solutions or O/W microemulsions. L_2 phases
normally resided at the top of the tubes and were clear or slightly bluish micellar solution or W/O microemulsions.

Some information on phase diagrams of the LAS samples, which were not available, were determined in our lab. The linear penetration scan method helped to distinguish the intermediate phases, and then samples with different concentration of the surfactant were prepared. The polarizing light screening system described above was used to determine the phase boundaries. A centrifuge was used to determine the boundaries of the two-phase L₁/L₂ region. The rotation speed of the centrifuge was 3500 rpm and the radius was 13.5cm. It was found that a separation into two layers was achieved after only a few minutes. However, phase boundaries involving two liquid crystalline phases could not be determined by this method.

3. 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 [Chen, 1998](Figure 3.1).

The microscope used for nonionic 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, allowing 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 scales. 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 a 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 utilized 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 can be 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 and picture slides could be done with NeXT workstation and photomodule camera (Dunn Instruments, Inc.)
Figure 3.1: Schematic Drawing of Video Microscope System

Panasonic AG7650P
S-VHS Video Player

Panasonic AGA-750
Video Editor

Bio-Electronics TC-3
Time Code Generator

Panasonic BT-S901Y
Video Monitors

to NeXT

Panasonic AG7750P
S-VHS Video Recorder/Player

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
4. Research methodology:

4.1 Linear penetration scan method.

Direct observation of the dynamic interfacial phenomena was made possible with use of a vertically mounted microscope where comparable volumes of water and surfactant were employed (Figure 3.2). The microscope can be viewed as a conventional transmission microscope that has been taken apart and reassembled on its side. The image is sent directly through an extension tube to the camera and VCR system.

Sample cells (50mm×4mm, Vitro Dynamics Inc., Cat. No.2540) with the denser phase in the bottom half were placed on the microscope stage in a controlled temperature environment. The lighter phase was then carefully injected from the top of the cell by use of a syringe 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 formation, and small-scale instabilities. In some cases where the interfaces are not planar, we measured several regions of cell and used the average value.

Thin layer experiment has been developed in this study, where a thin layer of surfactant is brought into contact with a large volume of water. The reason for using this technique will be explained in Chapter 4.

4.2 Surfactant droplet dissolution experiment

Rectangular optical glass capillaries (50mm×4mm, Vitro Dynamics Inc., Cat. No. 2540) were used to contain water. The water or buffer solution was imbibed into the glass

cell by capillary action. Then the glass cell was sealed at one end and attached to a standard microslide (3 inch by 1 inch) with photopolymer adhesive (Norland Products Inc. Adhesive No. 63, New Brunswick, NJ) which was cured with ultraviolet light of 250-380nm by a fiber optical gun (Norland Products Inc. New Brunswick, NJ). The cell was then transferred to the thermal stage, Mettler FP-5, mounted on Nikon Optiphot-Pol microscope.
Microinjection system (Picospritzer II) was used to inject small drops of surfactants having diameters of 50-150μm. Picospritzer II is a system with a high speed solenoid valve that supplies repeatable pressure pulses. Nitrogen was used as driving gas.

Micropipettes were pulled from capillaries with outside diameters of 1mm, purchased from Drummond Scientific Co. of Broomall, PA (Catalog number: 1-000-0300), and had inside diameters from 50-150μm. 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 paper clip 3/4" in length. Micropipettes with longer shanks are more convenient when injecting surfactant drops into bulk liquids 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.

With highly viscous liquids, i.e. mixtures of C₁₂E₄/Sodium oleate, micropipettes with a bigger diameter of 200-300μm were made and rectangular optical glass capillaries (0.6×6.0 I.D., Vitro Dynamics Inc., Cat. # 4806-100) were used to contain water.

After the droplet of surfactant was injected, the dissolution behavior was recorded by VCR (Figure 3-3). This technique was basically that used by Chen [1998] in former study.
4.3. Granule dissolution experiment.

Two techniques were developed during this work for visualizing granule disintegration.

- Single Granule Dissolution Experiment

Single granules or pairs of granules were placed on a hanging drop slide. (Fisher, 76×26mm, 1.4~1.6mm thick. The well was 18mm in diameter, 0.5mm or 1.5~1.95mm deep. Figure 3-4.) Granule was stuck in the well by adhesive, water was injected by syringe, and then coverslip was put on the well to prevent water evaporation. Dissolution experiment was videotaped (See Figure 3-4).

- Vertical Cell Contacting Experiment

Rectangular glass capillary tubing (Vitro Dynamics Inc., path length×width =0.4mm×4mm, Cat # W2540) was used and mounted in vertical orientation. Granules were put at the bottom of the cell to form a powder bed with a thickness of one granule and height 3~5mm. Water was injected into the cell by syringe. Contacting experiment was videotaped.
Figure 3.3: Schematic Diagram of Microinjection System

Driving pressure

Compressed air

TO VCR AND IMAGE ANALYSIS

Surfactant drop (Radius = 50–150 μm)

Glass microslide filled with water or other solution

400 μm

Micropipette and holder

Pressure in Pressure out
Figure 3.4: Hanging drop slide used in single granule disintegration experiments

1. Hanging drop slide
2. The well
3. Cover slip
4. Single granule
Chapter 4: Dissolution of Anionic Surfactants

1. Introduction

A videomicroscopy system was used to investigate the mechanism and rates of dissolution of pure, neat, liquid nonionic surfactants in water in previous research [Chen, 1998; Chen et al 2000]. The results indicated that the process was diffusion controlled. Estimates of effective binary diffusion coefficients in the intermediate liquid crystalline phases were obtained by combining their measured growth rates in a one-dimensional quantitative penetration experiment where neat surfactant contacted water with measured dissolution times of surfactant drops.

The mechanism and rates of dissolution of anionic surfactants are presently unknown. This chapter describes initial work on this topic using the quantitative linear penetration scan method. Anionic surfactants such as AOT, 7-phenyl tetradecane sulfonate and 5-phenyl undecyl sulfonate have been studied. The last two of these are pure isomers of the types typically found among the mixture of isomers in commercial linear alkylbenzene sulfonates (LAS), which are widely used in household laundry and other cleaning applications.

2. Diffusion path analysis

2.1 Diffusion equation in one dimensional Cartesian coordinates with moving boundary.

Consider mass transport in a binary surfactant/water system with a planar moving interface. At time zero, two semi-infinite uniform phases are brought into contact at the
interface, \( x=0 \), in absence of any convection. Diffusion coefficients are taken as independent of composition within any phase. The further assumption is made that the moving planar interface is at local equilibrium, i.e., diffusion through bulk phases is much slower than adsorption and desorption at the interface.

The density of the whole system is constant if the density of water and that of surfactant are close to each other. In the form of Fick's First Law \( n_A - w_A(n_A + n_B) = -\rho D_{ab} \nabla w_A \) [Bird et al, 1960], \( n_A + n_B = 0 \) is applicable for such a system in the absence of imposed convection. There is no convection term in the equation. This is a very good assumption for nonionic surfactant since the density of nonionics is very close to that of water. For anionic surfactant, such as AOT whose density is around 1.1g/cm\(^3\), this assumption is also reasonable.

With these assumptions the diffusion equations can be expressed as

\[
\frac{\partial w_j}{\partial t} = D_j \frac{\partial^2 w_j}{\partial x^2} \quad j = 1,2
\]

(1)

\( x \) is the distance from the initial surface of contact, \( t \) is the time, \( w_j \) is the local mass fraction in phase \( j \). \( D_j \) is the binary diffusion coefficient in phase \( j \).

2.2 Semi-infinite case.

When two large quantities of liquids of uniform concentrations are brought into contact without convection at an interface in a one-dimensional configuration, the boundary conditions are that \( w_j \) at infinity is equal to its value before contact. Then equations (1) have similarity solutions [Carslaw and Jaeger, 1959].
\[ w_j = a_j + b_j \text{erf}(\eta_j) \quad \text{where} \quad \eta_j = \frac{x}{\sqrt{4D_j t}} \] (2)

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

Equation (2) also applies when the system has intermediate phases. If locations of interfaces in each phase are known from experiment, i.e., if \( \frac{x}{\sqrt{t}} \) has a known constant value for each interface, there are three unknown variables, \( a, b, D \), for each phase \( j \). Supposing that compositions at both ends of each phase are known from phase diagram, there is only one degree of freedom in each phase. 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.

\[ -\rho_{S^+}D_{j}^{S^+}(dw_j^{S^+}/dx)|_{S^+} + \rho_{S^-}w_{j}^{S^-}(dx/dt)|_{S^-} = -\rho_{S^+}D_{j}^{S^+}(dw_j^{S+}/dx)|_{S^+} + \rho_{S^-}w_{j}^{S^-}(dx/dt)|_{S^-} \] (3)

Where \( S^+ \) and \( S^- \) denote both sides of interface.

If the composition is continuous at interfaces, such as \( L_a/V_1 \) and \( V_1/H_2 \) interfaces in the phase diagram of Figure 4.2 for AOT-water system, equation (3) can be further simplified as
\[
\sqrt{D_j} \ b_j \ exp\left(-\frac{x^2}{4D_j t}\right) = \sqrt{D_j} \ b'_j \ exp\left(-\frac{x^2}{4D_j t}\right)
\]

(4)

Notations with prime and without prime denote different sides of the interface.

If the composition is discontinuous at interfaces, such as L/L\(_\alpha\) interface for AOT-water system, the following equation applies:

\[
(D_j \ \frac{\partial w_j}{\partial x})_e - (D'_j \ \frac{\partial w'_j}{\partial x})_e = [w'_j(\varepsilon) - w_j(\varepsilon)] \frac{d\varepsilon}{dt}
\]

(5)

Where \(\varepsilon\) is the interfacial position. These equations are consistent with the solutions (2) if the interfacial position \(\varepsilon\) varies with time according to

\[
\varepsilon = \gamma \sqrt{t}
\]

(6)

2.3 Thin-layer vertical contacting experiment

The number of interfaces where equation (4) or (5) applies is one less than the number of phases, so that semi-infinite experiment is not sufficient to find effective diffusivities for all phases. Values for all the diffusivities can, in principle, be obtained if the results of this experiment are combined with those of an experiment where a thin layer of surfactant is brought into contact with a large volume of water. Such an experiment was not used by Chen [1998] who instead measured the time for dissolution of a spherical drop of neat (liquid) nonionic surfactant. Besides the impracticality of using a drop experiment for a solid surfactant, the novel thin layer method proposed here provides more information because the positions of all interfaces can be measured as a function of time.
For the thin layer experiment illustrated below the following boundary and initial conditions apply (see accompanying diagram):

\[
\begin{align*}
\frac{\partial w_j}{\partial x} &= 0 \quad x = 0 \quad (7) \\
\frac{\partial w_j}{\partial x} &= 0 \quad x = l \quad (8) \\
I.C. \quad w_j = f(x) &= \begin{cases} 0 & 0 < x < l \\ 1 & l < x < d \end{cases} \quad (9)
\end{align*}
\]

If a value is chosen for the diffusivity in one phase selected as a reference, the other values can be calculated from semi-infinite experiment. Then equation (1) can be solved numerically for the thin layer experiment using these values. Among the solutions with different reference diffusivities, the best is that which most closely matches variation of interfacial positions with time as measured experimentally.

A. Analytical solution

A quick estimate of the average diffusivity of the system can be obtained by assuming that all diffusivities are equal and that concentration is continuous at all
interfaces. In this case the solution for a general function \( f(x) \) is given by [Slattery, 1990].

\[
w = 2 \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{\cos \alpha_n x}{\alpha_n l} \int f(x) \alpha_n \cos \alpha_n x dx + \frac{1}{l} \int f(x) dx \quad \text{where } \alpha_n = \frac{n\pi}{l} \quad n = 1,2,\ldots
\]  

(10)

For the particular \( f(x) \) given in equation (9), one has

\[
w = 2 \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{\cos \alpha_n x}{\alpha_n l} (\sin \alpha_n l - \sin \alpha_n l) + \frac{l-l_1}{l}
\]  

(11)

B. Numerical solution

Numerical solution is needed if different diffusivities are taken in different phases for thin layer case. One possibility is to use it with ratios from semi-infinite experiment as mentioned above and discussed in detail later.

When dissolution of surfactant into water 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. 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 one dimensional Cartesian coordinates can be expressed as:
\[
\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial w}{\partial x} \right) \quad (12)
\]

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 (12) which turned out to be

\[
\frac{w_i^{j+1} - w_i^j}{\Delta t} = \frac{A_{i+\frac{1}{2}}^j - A_{i-\frac{1}{2}}^j}{\Delta x} \quad \text{where} \quad A_{i+\frac{1}{2}}^j = D_{i+\frac{1}{2}} \cdot \frac{w_{i+1}^j - w_i^j}{\Delta x} \quad (13)
\]

The Courant number, \( D_{i+\frac{1}{2}} \Delta t / (\Delta x)^2 \), must be less than 0.5 to get stable solutions. \( w_i^j \) denotes the concentration \( w \) at spatial point \( i \) and at time step \( j \). The concentration \( w_i^{j+1} \) can be calculated from equation (13) with all known concentrations \( w_i^j \). It is noteworthy that the Courant stability requirement is needed in applying the explicit forward-time-center-block finite difference scheme to integrate equation (12). 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.

For surfactant where there is a discontinuity in composition at interface, we need to use mass balance equation to update the interface position at each time step. Equation (5) can be written as (see accompanying diagram):

\[
D_s \frac{w_{i+1}^j - w_-}{(1.5 - \eta) \Delta x} - D_s \frac{w_- - w_{i-1}^j}{(0.5 + \eta) \Delta x} = (w_- - w_+) \frac{x_{i+1}^{j+1} - x_i^j}{\Delta t} \quad (14)
\]

where \( \eta \) is the distance from the interface to the boundary of the block. \( w_- \) and \( w_+ \) are the surfactant concentrations of the interface at left and right sides respectively.
By Equation (14), one can calculate the discontinuous interface position at time step \( t+1 \) from the known variables at time step \( t \). In the block where the interface is located, the expression in equation (13) should be:

\[
A_{i+\frac{1}{2}}^j = D_{i+\frac{1}{2}} \cdot \frac{w_{i+1}^j - w_i^j}{(1.5 - \eta)\Delta x} \quad \text{and} \quad A_{i-\frac{1}{2}}^j = D_{i-\frac{1}{2}} \cdot \frac{w_i^j - w_{i-1}^j}{(0.5 + \eta)\Delta x}
\] (15)

The Courant number, \( D_i \Delta t / (\Delta x)^2 \), must be less than 0.5 to satisfy the stability condition. In this calculation, we made \( \Delta t = \frac{0.4 \cdot (\Delta x)^2}{D_{\text{max}}} \) where \( D_{\text{max}} \) is the largest value of all the diffusivities. Then the Courant number is equal to \( \frac{0.4 \cdot D_i}{D_{\text{max}}} \) which is less than 0.5 and the stability condition is satisfied.
3. Dissolution of AOT in water

3.1 Introduction

Aerosol OT, also known as AOT or sodium bis(2-ethylhexyl) sulfosuccinate, is a widely used anionic surfactant. It has been used as a model surfactant by investigators to obtain a fundamental understanding of surfactant systems, especially microemulsions. One of the reasons is that its hydrophilic and lipophilic properties are nearly balanced. Further, since microemulsions form without requiring the presence of any cosurfactant such as alcohol, the phase behavior is considerably simplified.

During the swelling and dissolution of a surfactant lamellar phase instabilities can be observed at the interface. These instabilities, known as myelinic figures or myelins, were first observed in lipids by Virchow [Virchow, 1954] and have been seen by many others since that time. They form as water permeates into the lamellar phase, causing it to swell. This requires surfactant backflow. If the surfactant in the swollen phase cannot easily dissolve into pure water, this backflow takes the form of myelins [Buchanan et al, 1998]. That is, myelins are observed only when surfactant solubility is low and a wide miscibility gap exists between lamellar and micellar phases. It has been found that myelins are formed when phosphatidylcholine (PC) and AOT are contacted with water [Haran et al, 2002, Dave et al, 2003]. Myelins consist of multilamellar tubules (typically of order 10μm in diameter) consisting of concentric alternating amphiphile bilayers and water layers with a core axis of water (Figure 4.1) [Haran et al, 2002, Buchanan et al, 2000]. Most myelin studies have focused on their growth and late timescale behavior.
[Warren and Buchanan, 2001]. However, The mechanism for myelin formation is still incompletely understood.

Figure 4.1 Myelin description [Haran et al, 2002]

3.2 Method

Vertical cell contacting experiments were conducted. Pure AOT, which is highly viscous H₂ phase, was pushed into the bottom of the cell and the cell was then sealed by adhesive. The water was carefully injected from the top of the cell. The position of each
phase boundary was recorded with time. Thus, the growth rate of each phase and the velocity of each interface were known.

3.3 Semi-infinite experiment

The phase diagram of AOT (Figure 4.2) shows that at 25°C two liquid crystalline intermediate phases should develop between the aqueous phase L₁ and reverse hexagonal phase H₂ [Franses and Hart, 1983]. They are the lamellar liquid crystal Lₐ and a bicontinuous cubic phase V₁. It also indicates that there is a discontinuity in composition at L₁/ Lₐ interface. There is little difference in phase behavior between 25°C and 30°C for AOT/water system. The reported CMC value for AOT at 25°C is 9.0×10⁻⁴ M (around 0.04 wt%) [Sanchez et al, 1997]

Figure 4.2. Phase diagram for AOT/water system at 25°C

```
0  0.014  0.12  0.77  0.8  1.0
```

AOT composition

L₁: micellar solution phase, Lₐ: liquid crystalline phase, V₁: viscous isotropic solution

H₂: reversed hexagonal phase

Video frames of a semi-infinite experiment of AOT contacting with water are shown in Figure 4.3. All four phases mentioned above are seen. The circles with bright centers and dark edges are air bubbles trapped in the viscous liquid crystalline phases.
Above the lamellar phase, vesicle-like structures are formed by the extensive coiling of myelins, as observed by the magnified micrographs (Figure 4.4). The same phenomena were also observed by Haran et al [2002]. In our experiments, the boundary between the remaining portion of the lamellar phase and myelins is located at initial surface of contact within experimental error.

Figure 4.3. Video frames of AOT vertical contacting experiment at 30°C
Figure 4.4 Myelins formed in AOT vertical contacting experiment with water

Figure 4.5 shows that interfacial positions and the thickness of intermediate phases in this experiment were proportional to the square root of the contact time.

Buchanan *et al.* [2000] studied myelinic growth mechanism by use of tracer particles and suggested that water enters the lamellar phase at the roots of the myelins and feeds them, causing them to grow backward into the surrounding water phase. They have shown that during the swelling process, dopant particles continually move from the aqueous phase toward the roots of the myelins and accumulate there. The particles mark the point of entry by the water into the lamellar phase. The particles are not observed to accumulate at the myelin tips or in channels between myelins. Myelin growth mechanism is fluid flow down channels (Figure 4.6). Dave and coworkers [2003] support the idea of surfactant back-flow mechanism of myelin growth introduced by Buchanan *et al*.: the essential mechanism of myelin growth is the back-flow of surfactant, to make way for water entering the lamellar phase as it swells.
For the interface geometry, only a small fraction of the cross-sectional area is occupied by channels, whereas the remainder forms myelins. The myelin fraction of the cross-sectional area, $f$, is constant. If the myelins are considered to be close-packed tubes, $f = 0.907$. Besides, there is essentially no concentration gradient of water within the myelinc zone. Instead there is a pressure gradient that drives the observed fluid motion of the water.

As we mentioned before, the base of myelins doesn't move during the experiment and is located at initial surface of contact ($x=0$). We assume that all surfactant in the region above the initial contact surface is in the myelins. We also assume that surfactant in $L_1$ region which flows to base of myelins is negligible. Surfactant concentration is assumed uniform along the myelins since they are of nearly uniform diameter and equal to $w_0$, the concentration at $x=0$.

Results shown in Figure 4.5 suggest that transport in the liquid crystalline phases can be modeled by ordinary diffusion. The previous similarity analysis applies in region below the myelins (equation (2) in section 2.2). The concentration in $L_\alpha$ phase has the form

$$w_\alpha = a_3 + b_3 \text{erf} \frac{x}{\sqrt{4D_{l,\alpha} t}} \quad (16)$$

Similar equations apply for the $V_1$ and $H_2$ phases. From equation (16), the concentration at $x=0$ has the form $w_0 = a_3 \quad (17)$

The mass balance equation at $x=0$ is

$$D_{l,\alpha} \frac{dw_\alpha}{dx} = \frac{d}{dt}(\varepsilon_3 \sqrt{f w_0 f}) \quad (18)$$
The left side of this equation represents the flux of surfactant at \( x = 0 \) from the portion of the lamellar phase below the myelinic figures. On the right side of the equation, \( \varepsilon_3 \) is the slope of a plot of interface position of \( L_1/myelin \) versus square root of contact time, \( f \) is the fraction of area occupied by myelins. Term \( (\varepsilon_3 \sqrt{t w_0 f}) \) is total surfactant in the myelinic zone per unit area at \( t \).

Combining equations (16)(17)(18), finally we have the mass balance equation at \( x=0 \)

\[
\sqrt{D_{L_1 a} b_3} = \frac{a_3 f \varepsilon_3}{2}
\]  

(19)

For the \( L_\alpha/V_1 \) and \( V_1/H_2 \) interfaces, the mass balance equation can be obtained from equation (4), given in section 2.2. The whole system still has one more degree of freedom in order to be completely determined because the number of interfaces and thus the number of mass balances is one less than the number of phases. If the value of diffusivity in one phase is assumed, those in the other phases can be calculated. Here we assume the value of diffusivity in lamellar phase \( D_{L\alpha} \), and calculated values of diffusivity in cubic and reversed hexagonal phases, \( D_{V1} \) and \( D_{H2} \). The results are shown in Figure 4.7. They suggest that for plausible values of \( D_{L\alpha} \), values of \( D_{V1} \) and \( D_{H2} \) are comparable in magnitude.

It appears that while some diffusion of surfactant into the aqueous phase probably occurred in our experiments described above, swelling and formation of myelinic figures dominated. Evidence for this conclusion is that if the data of Figure 4.5 are analyzed assuming no myelins and diffusion control in all phases, for plausible values of \( D_{L\alpha} \) of
order $10^{-10}$ m$^2$/sec, the values found for $D_{L1}$ are of order $10^{-8}$ m$^2$/sec, far above any reasonable value (Table 4.1). This result indicates that convection is present in the L$_1$ phase, which is consistent with the existence of flow of water to the roots of the myelins. We rule out the existence of significant flow due to natural convection since the experiment was conducted in a cell only 400 μm thick in a room where temperature was maintained at 30°C. In addition the top of the cell was sealed to prevent evaporation, which could promote natural convection.

It's noteworthy that the experimental results are reproducible, i.e., we could get the same slope of interfacial positions vs square root of contact time within experimental error from another independent experiment.

Table 4.1. Calculated diffusivities of intermediate phases of 100% AOT at 30°C

<table>
<thead>
<tr>
<th>$D_{L\alpha}$ (m$^2$/s)</th>
<th>$D_{L1}$ (m$^2$/s)</th>
<th>$D_{V1}$ (m$^2$/s)</th>
<th>$D_{H2}$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.9 \times 10^{-10}$</td>
<td>$8.4 \times 10^{-9}$</td>
<td>$1.2 \times 10^{-10}$</td>
<td>$1.9 \times 10^{-12}$</td>
</tr>
<tr>
<td>$1.2 \times 10^{-10}$</td>
<td>$3.0 \times 10^{-8}$</td>
<td>$1.8 \times 10^{-10}$</td>
<td>$0.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>$2.0 \times 10^{-10}$</td>
<td>$1.8 \times 10^{-7}$</td>
<td>$3.3 \times 10^{-10}$</td>
<td>$6.0 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Figure 4.5. Growth rates of intermediate phases of AOT/water at 30°C

a. The change of position of L_1/Myelin interface with contact time

![Graph](image)

Slope = 0.0953 mm/min^{1/2}

b. The growth rate of lamellar phase excluding myelins

![Graph](image)

Slope = 0.1066 mm/min^{1/2}
c. The growth rate of $V_1$ phase

\[
\begin{array}{c}
\text{Slope}=0.0229 \text{mm/min}^{1/2} \\
\end{array}
\]
Figure 4.6 Myelin growth mechanism; the mechanism is fluid flow down channels (A), not diffusion of water onto myelin tips (B) [Buchanan, 2000]
Figure 4.7 Calculated diffusivities of intermediate phases of AOT at 30°C
3.4 Thin-layer vertical contacting experiment

In the thin layer experiment, a thin layer of AOT is brought into contact with a large volume of water. The base of myelins didn’t move and was located at the initial contacting surface. Besides, the interface position of L\textsubscript{1} and myelins is proportional to the square root of time with almost the same slope, as shown in Figure 4.8. A more complete analysis of the data making use of results of Section 3.3 can also be carried out.

If a value is chosen for the reference diffusivity D\textsubscript{Lα}, the other values can be estimated from Figure 4.7. Then equation (1) can be solved numerically using the model described above which accounts for formation of myelinic figures. With these diffusivities, one finds the dissolution time where the concentration at the bottom of the cell is that of the V\textsubscript{1}/H\textsubscript{2} phase boundary. The calculated dissolution time is compared with experimental dissolution time at which the H\textsubscript{2} phase disappeared. One repeats this calculation process until agreement between calculated and experimental dissolution times is obtained.

The experimental and calculated results for AOT/water thin layer experiment are shown in Figure 4.9. Diffusivities used in numerical solution are: D\textsubscript{H2}= 0.36\times10^{-10} m\textsuperscript{2}/sec, D\textsubscript{Lα} =1.31\times10^{-10} m\textsuperscript{2}/sec, D\textsubscript{V1}= 1.70\times10^{-10} m\textsuperscript{2}/sec. Basically, one can choose different values of D\textsubscript{Lα} and get other diffusivities from Figure 4.7 as a starting point, then find a set of diffusivities that fit all of the thin layer data, i.e., both motion of interfaces and time for H\textsubscript{2} phase to disappear. Figure 4.9 shows that numerical solution provides good agreement between measured and calculated positions of the V\textsubscript{1}/H\textsubscript{2} and L\textsubscript{α}/V\textsubscript{1} interfaces as a function of time. It should be noted that the myelinic figures were
far enough from the bottom of the cell that their base remained at the initial contact surface within experimental error and that their growth rate was virtually the same as in the semi-infinite experiment. Presumably, surfactant mass fraction at the base of the myelins also remained nearly constant at the calculated value of 49.7 wt%. However, it would change eventually if the experiment were continued for a much longer time.

Figure 4.8 AOT thin layer experiment: interface position of L₁/myelins as a function of square root of time
Figure 4.9 AOT thin layer vertical contacting experiment, the difference between experimental value and calculated value.
3.5. Semi-infinite experiments for 60%, 50% and 34% AOT

Vertical contacting experiments were also conducted for 60%, 50% and 34% AOT with water. According to phase diagram of AOT, these samples are all in the region of lamellar phase.

When 60% AOT was contacted with water, myelins were observed (Figure 4.10). The base of myelins is at the point of initial contact. The interface position of $L_1$ and myelins is proportional to the square root of contact time. The growth rate is 0.102 mm/min$^{0.5}$, which is equal to the growth rate of myelins in pure AOT contacting experiment (Figure 4.8). Because the $V_1$ and $H_2$ phases were not present, it was not possible to perform a thin layer experiment and extract values of effective diffusivities from the time of disappearance of the $H_2$ phase.
Figure 4.10: Myelin formation in 60% AOT vertical contacting experiment with water

a: Image with low magnification

b. Image with high magnification

When 50% AOT was contacted with water, only a thin layer of myelins was observed. After around 50 minutes, the myelins disappeared gradually (Figure 4.11).
Figure 4.11: Video frames of 50% AOT vertical contacting experiment with water

a. Myelin formation at the beginning of the experiment

b. Myelins disappeared gradually after 50 minutes
When 34% AOT was contacted with water, no myelins were observed even immediately after initial contact (Figure 4.12). The $L_1/L_\alpha$ interface position is proportional to the square root of contact time. The slope is 0.0813 mm/min$^{1/2}$. If we assume the value of $D_{L\alpha}$, the ratios of $D_{L1}$ to $D_{L\alpha}$ obtained from the semi-infinite analysis are shown in Table 4.2. It shows that reasonable values of $D_{L1}$ are obtained for values of $D_{L\alpha}$ less than or equal to that found previously using the myelin model ($1.31\times 10^{-10}$ m$^2$/s). Hence a diffusion controlled process is suggested although some convection in the $L_1$ phase may occur.

Table 4.2. Calculated diffusivities of intermediate phases of 34% AOT at 30°C

<table>
<thead>
<tr>
<th>$D_{L\alpha}$ (m$^2$/s)</th>
<th>$D_{L1}/D_{L\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.2\times 10^{-10}$</td>
<td>1.7</td>
</tr>
<tr>
<td>$1.31\times 10^{-10}$</td>
<td>3.5</td>
</tr>
<tr>
<td>$1.44\times 10^{-10}$</td>
<td>6.2</td>
</tr>
<tr>
<td>$2\times 10^{-10}$</td>
<td>19.1</td>
</tr>
</tbody>
</table>

When the concentration of starting AOT phase decreases from 60% to 34%, the driving force for the myelin growth decreases. Then the role of swelling decreases while the role of diffusion increases. No myelins were observed in 34% AOT contacting experiment. The data analysis also indicated that diffusion dominates. However, it should be emphasized that whether and how myelinic figures develop depend on the structure of the lamellar phase at the scale of microns, e.g., the number and type of defects. Buchanan et al [1998] found in their work with the AOT/NaCl brine system that no myelins formed if the lamellar phase was subjected to extensive shear before contact with
brine, generating a microstructure of nearly spherical particles (onions). In our experiments with pure AOT, the lamellar phase was not present initially but nucleated near the initial surface of contact. It is not known what defect structure arose during this process, but lamellar microstructures involving concentric cylinders are well known. If present, these could presumably be extruded during the swelling process. Further studies to investigate such matters would be of interest.

Figure 4.12: Video frame of 34% AOT vertical contacting experiment with water

3.6 Summary

Dissolution behavior of anionic surfactant AOT was studied. It seems to be intermediate in behavior between surfactants such as C_{12}E_{4} or phospholipids, which virtually always forms myelins at room temperature because surfactant concentration in the L_{1} phase is very low, and other compounds such as C_{12}E_{5} where there are no myelins and surfactant concentration in the L_{1} phase at the transition to the lamellar phase is high. Myelins formed when 100% AOT was contacted with water. In contrast,
ordinary diffusion apparently dominated the dissolution process when 34% AOT was contacted with water.

For pure AOT, a model has been developed which was used to obtain effective diffusivities in the \( L_\alpha \), \( V_1 \), and \( H_2 \) phases as well as the composition of the myelinic figures which grew from the initial surface of contact toward the aqueous phase. Reasonable values of these quantities were obtained. This model is similar in some respects to that suggested by Buchanan et al [2000]. Key differences are that we have included diffusion in the liquid crystalline phases below the base of the myelins and combined results of the semi-infinite and thin layer penetration experiments. As a result, we are able to estimate the effective diffusivities. We have not assumed that the myelins are fully swollen, i.e., have the composition of the lamellar phase in equilibrium with the \( L_1 \) phase (12 wt% for AOT). Instead myelin composition is calculated as part of the data analysis. Moreover, the analysis neglects diffusion of surfactant from the myelins into the aqueous phase. This neglect is entirely appropriate when solubility of the surfactant is very low, as for PC, \( C_{12}E_3 \). However, it may not be as good for ionic surfactants with higher solubilities. For AOT with 1.4% solubility, this model is apparently still reasonable for dissolution of pure AOT.

In these experiments we have not followed behavior until dissolution was complete. For AOT this occurs in solutions which are dilute, i.e., contain less than 1.4% AOT, but still in the range of practical interest. For other more lipophilic surfactants such as PC and \( C_{12}E_3 \), solubility is very low, and complete dissolution is not expected for conditions of interest in applications. Of course, dissolution of such lipophilic surfactants is possible if they are mixed with more hydrophilic surfactants, as shown in Chapter 5.
4. Dissolution of linear alkylbenzene sulfonate (LAS)

Linear alkylbenzene sulfonates are the surfactants most widely used in detergency. Commercial products are mixtures of various isomers. Seven pure LAS samples, 5-phenyl C11, 5-phenyl C10, 2-phenyl C10, 2-phenyl C12, 2-phenyl C14, 6-phenyl C12, 7-phenyl C14 were synthesized by Unilever Research and provided for this study. The carbon number varies from 10 to 14 and the phenyl position from 2 to 7, which are in the interesting range for detergent formulations. We will see how dissolution rates of these samples vary with structure of LAS. Most experiments were conducted at 30°C, a typical temperature for warm-water washing.

It has been found that an equilibrium between two lamellar phases exists in the binary system 5-phenyl C12 LAS/water (Figure 4.13) [Ockelford, 1993]. There is an upper consolute temperature at around 40°C above which only one lamellar phase is present. They also observed similar behavior in other LAS/water systems. We expect such an upper consolute temperature to exist for the LAS isomers that we are studying, having similar structure, i.e., with the aromatic ring attached near the center of the chain.

4.1 Dissolution of 7-phenyl C14 LAS

Small angle X-Ray experiments were carried out to determine the phase diagram of 7-phenyl C14 LAS at University of Manchester Institute of Science and Technology, U.K. [Tiddy and Richards, 2002]. Their initial results show that two lamellar phases co-exist between approximately 35 wt% and 70 wt% of pure 7-phenyl C14 in water at 21°C. The X-ray data for the 80% sample show that only a single lamellar phase is present. Above 85% surfactant is a region in which the X-ray data indicate multiple
Figure 4.13 Partial phase diagram of 5-phenyl C12 LAS in water.

phases or complex phase behavior, possibly involving crystalline phases. No samples containing less than 30 wt% surfactant were investigated.

At Rice, we determined surfactant composition for the lower limit of the $L_1+L_{\alpha 1}$ region to be approximately 1 wt% using the polarizing light screening system. The upper boundary of this region was found to be approximately 9 wt% by separation of the sample using a centrifuge. As mentioned in Chapter 3, the rotation speed of the centrifuge is 3500 rpm and the radius is 13.5 cm. The approximate phase diagram is shown in Figure 4.14 (The dashed lines indicate uncertainty). We estimate the surfactant concentration for the lower and upper boundaries of $L_{\alpha 1} + L_{\alpha 2}$ region to be approximately 40% and 65% since 2-phase region should be slightly narrower at 30°C than at 21°C as indicated in Figure 4.13.

Pure 7-phenyl C14 seems to be largely crystalline at 30°C. After adding 10% water or more, we could get an amorphous solid. To avoid complicated phase behavior
indicated by the X-ray studies, we conducted vertical contacting experiments of 80% 7-phenyl C14 LAS with water. Video frames of a semi-infinite experiment are shown in Figure 4.15. Myelins could be observed above the lamellar phase, as shown in Figure 4.16. The results of the semi-infinite experiment are shown in Figure 4.17. It shows that interface positions are proportional to the square root of contact time.

It was found that the $L_{\alpha 1}/L_{\alpha 2}$ interface became fuzzier after we heated the experimental cell used in Figure 4.15 to 50°C for about 1 hour, presumably since only a single lamellar phase exists at this temperature.

If we ignore formation of myelins and neglect convection, and further assume that all the interfaces are in equilibrium, we can use the theory described in section 2.2 to get effective diffusivity ratios. If we assume the value of diffusivity in lamellar phase $D_{L_{\alpha 1}}$, other diffusivities can be calculated from semi-infinite experiment. The results are shown in Table 4.3. Unrealistically large apparent values of $D_{L_{11}}$ are found, which is consistent with the observed formation of myelins involving permeation of water into the lamellar phase, causing it to swell.
Figure 4.15. Video frames of semi-infinite experiment at 30°C, 80% 7-phenyl C14 LAS with water (Width of the cell is 4mm)
Figure 4.16 Myelins formed in the vertical contacting experiment of 80% 7-phenyl C14 LAS with water.

Table 4.3 Calculated diffusivities of intermediate phases of 80% 7-phenyl C14 LAS at 30°C assuming all the phases are in equilibrium.

<table>
<thead>
<tr>
<th>$D_{L11}$ (m²/s)</th>
<th>$D_{L21}$ (m²/s)</th>
<th>$D_{L22}$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.1 \times 10^{-10}$</td>
<td>$4.4 \times 10^{-9}$</td>
<td>$2.4 \times 10^{-11}$</td>
</tr>
<tr>
<td>$1.44 \times 10^{-10}$</td>
<td>$2.6 \times 10^{-8}$</td>
<td>$2.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>$2.0 \times 10^{-10}$</td>
<td>$8.0 \times 10^{-8}$</td>
<td>$7.4 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Figure 4.17. Semi-infinite experiment at 30°C, 80% 7-phenyl C14 LAS with water

The roots of myelins were located at the initial surface of contact in the semi-infinite experiment within experimental error. We can use the same method to analyze this system as we have used for AOT. i.e., we assume that all surfactant in the region
above the initial contact surface is in the myelins and that transport below this surface is by diffusion. The mass balance equation at $x=0$ can be obtained from equation (19) (section 3.3). The mass balance equation at $L_{a1}/L_{a2}$ interface can be obtained from equation (5) (section 2.2). Boundaries of the $L_{a1}+L_{a2}$ region are taken as those in Figure 4.14. The results are listed in Table 4.4. They suggest that for plausible values of $D_{La1}$, values of $D_{La2}$ are comparable in magnitude, a reasonable result.

Table 4.4 Calculated diffusivities of intermediate phases of 80% 7-phenyl C14 LAS at 30°C with the model of myelins

<table>
<thead>
<tr>
<th>$D_{La1}$ (m²/s)</th>
<th>$D_{La2}$ (m²/s)</th>
<th>Myelin composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.9 \times 10^{-10}$</td>
<td>$1.24 \times 10^{-10}$</td>
<td>0.314</td>
</tr>
<tr>
<td>$1.0 \times 10^{-10}$</td>
<td>$1.37 \times 10^{-10}$</td>
<td>0.321</td>
</tr>
<tr>
<td>$1.44 \times 10^{-10}$</td>
<td>$1.78 \times 10^{-10}$</td>
<td>0.341</td>
</tr>
<tr>
<td>$2 \times 10^{-10}$</td>
<td>$2.1 \times 10^{-10}$</td>
<td>0.359</td>
</tr>
</tbody>
</table>

A thin layer experiment of 80% 7-phenyl C14 LAS with water was also conducted. The base of myelins didn’t move and was located at the initial contacting surface. Besides, the interface position of $L_1$ and myelins is proportional to the square root of time as shown in Figure 4.18 and the growth rate of myelins was virtually the same as in the semi-infinite experiment.

If a value is chosen for the reference diffusivity $D_{La1}$, the value of $D_{La2}$ can be estimated from Table 4.4. Then equation (1) can be solved numerically using the same method we have used for AOT. With these diffusivities, one finds the dissolution time where the concentration at the bottom of the cell is that of the $L_{a1}/L_{a2}$ 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.

The experimental and calculated results for 80% 7-phenyl C14 LAS/water thin layer experiment are shown in Figure 4.19. For the thin layer of surfactant with a thickness of 0.55 mm, it took 4200 seconds for $L_{\alpha 2}$ phase to disappear in the experiment. It was found that diffusivities of $D_{L\alpha 1} = 1.90 \times 10^{-10}$ m$^2$/sec and $D_{L\alpha 2} = 2.05 \times 10^{-10}$ m$^2$/sec fit all of the thin layer data, i.e., both motion of interface and time for $L_{\alpha 2}$ phase to disappear. Figure 4.19 shows that numerical solution provides good agreement between measured and calculated positions of the $L_{\alpha 1}$/ $L_{\alpha 2}$ interface as a function of time. Surfactant mass fraction at the base of myelins remained nearly constant at the calculated value of 34%. In comparison, the calculated time for $L_{\alpha 2}$ phase to disappear from another set of diffusivities: $D_{L\alpha 1} = 1.8 \times 10^{-10}$ m$^2$/sec and $D_{L\alpha 2} = 2.0 \times 10^{-10}$ m$^2$/sec is around 4400 second, which is longer than the experimental result.
Figure 4.18: 80% 7-phenyl C14 LAS thin layer experiment: interface position of L1/myelins as a function of square root of time

Figure 4.19: 80% 7-phenyl C14 LAS thin layer vertical contacting experiment, the difference between experimental and calculated values of the L_{α1}/L_{α2} interface
4.2 Dissolution of 5-phenyl undecyl sulphonate

It's likely that the phase diagram of 5-phenyl C11 LAS follows the same pattern as 5-phenyl C12 LAS (Figure 4.13). No X-ray data are currently available for this isomer, but differential scanning calorimeter results indicate that the lamellar phase extends to 100% surfactant [Tiddy and Richards, 2003]. We can study it using the same method as we have used for AOT. The consolute temperature for this isomer may be less than the 40°C cited above for 5-phenyl C12 LAS, but the extent of the $L_{\alpha 1}+L_{\alpha 2}$ region at the experimental temperature of 30°C is unknown.

Initial observation using the polarizing light screening system indicated a surfactant composition of approximate 31 wt% for the upper limit of the $L_1$ region. We also have determined the upper boundary of the two-phase region ($L_1+L_{\alpha 1}$) by separation of the sample using a centrifuge. A preliminary phase diagram is shown in Figure 4.20 (the dashed lines indicate uncertainty).

Figure 4.20 Phase diagram of 5-phenyl C11 LAS at 30°C

\[
\begin{array}{|c|c|c|c|}
\hline
L_1 & L_{1}+L_{\alpha 1} & L_{\alpha 1} & L_{\alpha 1}+L_{\alpha 2} & L_{\alpha 2} \\
\hline
0 & 0.31 & 0.65 & 1.0 \\
\hline
\end{array}
\]

Composition of 5-phenyl C11 LAS
Video frames of a semi-infinite experiment of 5-phenyl C11 LAS with water are shown in Figure 4.21. The large dark portion of the $L_{\alpha 1}$ region in the second video frame is an area where the lamellar phase has "annealed" to a lower energy state with all bilayers parallel to the upper and lower surfaces of the rectangular cell. There is no birefringence when this orientation exists.

Vertical contacting experiment showed that the interface position of $L_{\alpha 1}/L_{\alpha 2}$ and $L_{1}/L_{\alpha 1}$ moved linearly with respect to the square root of time (Figure 4.22), which means the process is diffusion controlled. There is no formation of myelins since 5-phenyl C11 LAS is a soluble surfactant. Instead, the lamellar phase $L_{\alpha 1}$ dissolved directly into the micellar phase $L_1$, which is consistent with high solubility of surfactant in phase $L_1$ (31%). Further analysis of the data is not possible in the absence of information on boundaries of the $(L_{\alpha 1} + L_{\alpha 2})$ region.
Figure 4.21 Video frames of a semi-infinite experiment at 30°C, 5-phenyl undecyl sulphonate with water
Figure 4.22 Results of the semi-infinite experiment at 30°C, 5-phenyl undecyl sulphonate with water
4.3. Dissolution of 6-phenyl C12 LAS

Preliminary phase diagram was determined using the same method as described before. No information is available on boundaries of $L_{\alpha 1}+L_{\alpha 2}$ or $L_{\alpha 2}$ region. The preliminary phase diagram is shown in Figure 4.23 (the dashed lines indicate uncertainty).

Figure 4.23 Phase diagram of 6-phenyl C12 LAS at 30°C

<table>
<thead>
<tr>
<th></th>
<th>$L_{\alpha 1}$+L$_{\alpha 2}$</th>
<th>L$_{\alpha 1}$</th>
<th>L$<em>{\alpha 1}$+L$</em>{\alpha 2}$</th>
<th>L$_{\alpha 2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.08</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Composition of 6-phenyl C12 LAS

Pure 6-phenyl C12 LAS seems to be largely crystalline at 30°C. After adding 10% water or more, we could get an amorphous solid. Video frames of a semi-infinite experiment of 90% 6-phenyl C12 LAS with water are shown in Figure 4.24. A lamellar phase developed after contacting. There is no formation of myelins as indicated by the higher magnification micrograph (Figure 4.25). The results of the semi-infinite experiment are shown in Figure 4.26. It shows that interface positions are proportional to the square root of contact time, which suggests a diffusion controlled process. Here too analysis of the results must await further information on phase behavior at high surfactant concentrations.
Figure 4.24. Video frames of a semi-infinite experiment at 30°C, 90% 6-phenyl C12 LAS with water
Figure 4.25. Video frames with higher magnification, 90% 6-phenyl C12 LAS with water
Figure 4.26. Results for the semi-infinite experiment at 30°C, 90% 6-phenyl C12 LAS with water.
4.4 Dissolution of 5-phenyl C10 LAS

Currently the sample is a liquid, which is not expected. It may be caused by absorbing water from the air. The composition of the sample is uncertain. The results of a semi-infinite experiment are shown in Figure 4.27. (Note: The density of the sample is less than that of water, so the sample was injected from the top of the cell.)

Figure 4.27 shows that the interface positions are proportional to the square root of contact time, which suggests a diffusion controlled process. There is no myelin formation during the experiment, the expected result since, like the 5-phenyl C11 LAS isomer discussed earlier, solubility in water should be high.
Figure 4.27. Results for the semi-infinite experiment at 30°C, 5-phenyl C10 LAS with water.
4.5 Dissolution of 2-phenyl C10 LAS

2-phenyl C10 LAS is a crystalline material. When 32% 2-phenyl C10 LAS was contacted with water at 30°C, nothing happened even after several hours. We expect that the other similar isomers, 2-phenyl C12 LAS and 2-phenyl C14 LAS, which have even longer chains will also not dissolve at 30°C. The isomers having long, straight chains with only slight branching at one end form crystalline structures more readily than those having two chains of nearly equal length.

When 75% 2-phenyl C10 LAS was contacted with water at 70°C, 3 intermediate phases developed: H₁, V₁, L₀. No phase diagram was determined at this time. This temperature is well above that for practical application.

5. Concluding remarks

Dissolution of anionic surfactants such as AOT, 7-phenyl C14 LAS, 5-phenyl C11 LAS etc was studied. For soluble anionic surfactants, such as 5-phenyl C11LAS and 6-phenyl C12 LAS, there is no formation of myelins and dissolution is controlled by diffusion. For relatively insoluble anionic surfactants with large miscibility gaps, such as pure AOT and 7-phenyl C14 LAS, myelins formed during the dissolution. For AOT, transition from myelins to ordinary diffusion controlled dissolution occurred when concentration of initial starting phase decreased to 34%.

A model was developed which included the swelling of myelins and diffusion occurring in the rest of the surfactant-containing region. It was possible to obtain effective diffusivities by combining the semi-infinite and thin layer experiments. The data of AOT and 7-phenyl C14 LAS were analyzed and diffusivities were of order $10^{-10}$ m²/s.
Chapter 5: Dissolution of Nonionic Surfactant/Soap and Commercial Surfactants

1. Dissolution of nonionic surfactant/soap

1.1 Introduction

From previous study [Chen, 1998], we know that a droplet of pure nonionic surfactant C_{12}E_4 swelled and formed myelinic figures when it was immersed in water and that a compact mass of viscous myelinic figures remained indefinitely. The formation of a viscous mass of myelinic figures would be unfavorable in a washing process because most of surfactant would not be available and 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.

In Chen's work, dissolution of C_{12}E_4/SDS system was studied. Adding SDS increased the cloud point temperature of C_{12}E_4. The SDS particles were observed to be partially miscible with C_{12}E_4. 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. Many small droplets of the L_1 phase, were observed forming near the edge of the drop and especially near the SDS particles. All the particles dissolved in about 40 seconds. Later the whole surfactant drop became isotropic as all the L_\alpha was converted to L_1, but spontaneous formation of droplets, now of water and/or L_3, 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, behavior similar to that described previously for drops of Tergitol 15-S-7 in water at 30°C and 35°C (see Figure 1.4 in Chapter 1). Complete dissolution of the entire drop required about 30 minutes.

Soaps are also hydrophilic surfactants which can promote dissolution of C_{12}E_{4} and other nonionics too lipophilic to dissolve in water. However, it is not clear if the mechanism by which soap acts is the same as for SDS, especially when the soap is formed in situ instead of being present as particles initially. The work described herein was to provide further information on these systems.

Mixtures of C_{12}E_{4} and stearic acid, which is a solid at 30°C, are very viscous which makes injection difficult. In this study, oleic acid which is a liquid at 30°C, was used instead of stearic acid. When a drop of C_{12}E_{4} containing oleic acid was injected into buffer solution, soap could be made in situ. Samples having different ratios of C_{12}E_{4} to oleic acid were prepared to study the dissolution of soap/nonionic mixtures. Besides, dissolution behavior of C_{12}E_{4} containing oleic acid in water and C_{12}E_{4}/sodium oleate in water was also studied.

Drop dissolution experiments were conducted to study the dissolution behavior of C_{12}E_{4}/soap system.

1.2 Results and discussion

1.2.1. Dissolution of mixtures of C_{12}E_{4} and oleic acid in buffer solutions

From the phase diagram of C_{12}E_{4} shown in Figure 5.1 [Mitchell et al, 1983], we know that there is no formation of a micellar solution (L_{1}) at room temperature. The
phase present at room temperature is $L_\alpha$ which initially appears in the form of myelins when neat $C_{12}E_4$ is contacted with water (Figure 5.2).

Figure 5.1. Phase diagram of $C_{12}EO_4$-water system

![Phase Diagram](image)

Figure 5.2. Image of a droplet of pure $C_{12}E_4$ between crossed polars showing the formation of myelins at 30°C

![Image of Droplet](image)

Pure $C_{12}E_4$ injected into buffer solution also showed myelins which remained for a long time. This means that buffer solution doesn’t significantly change phase behavior of pure $C_{12}E_4$.

Drop dissolution experiments were conducted for different samples. Phase behavior after equilibrium was reached is shown in Figure 5.3 as a function of oleic acid
content of the drop and pH of the buffer solution (See Table 5.1). However, exact boundaries are uncertain. The symbols shown in Figure 5.3 are defined as follows:

- Complete dissolution of the Lα drop required about 1 minute.
- Complete dissolution of the Lα drop required about 8 minutes.

- Final phase behavior is L1.
- Final phase behavior is W+L1.
- Final phase behavior is W+Lα+L1.
- Final phase behavior is W+Lα.

When a drop with an initial radius of 120~130μm of C12E4 containing 20% oleic acid was injected into pH=10 buffer solution at 30°C, myelinic figures were seen after contact. Shortly thereafter many small droplets of L1 phase were observed forming near the edge of the drop. These droplets grew and later coalesced (Figure 5.4). Myelinic figures could be seen dissolving into L1 phase during the experiment. When all the Lα phase had dissolved, a single large L1 drop remained at equilibrium. That is, the final equilibrium was W+ L1. Complete dissolution of the Lα phase required several minutes. Because the L1 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.
Figure 5.3. Phase behavior of C$_{12}$E$_4$/oleic acid in buffer solution at 30°C (ratio of mixed surfactant to buffer solution is about 1%).

Figure 5.4. Droplet of C$_{12}$E$_4$ containing 20% oleic acid in pH=10 buffer solution 30°C.

(Distance between vertical dotted lines is about 200μm.)
Figure 5.5 Graph of square root of the complete dissolution times of the lamellar phase vs initial droplet radii for drops of C_{12}E_{4} containing 20% oleic acid in pH=10 buffer solution at 30°C.

A plot of the square root of the total time required to reach the equilibrium state versus the initial drop radius for several drops is shown in Figure 5.5. It can be seen that the square root of dissolution time increases with initial drop radius, which suggests that the dissolution process is diffusion controlled.

When pH value of buffer solution was increased, the droplet dissolution rate of C_{12}E_{4} containing 20% oleic acid was increased. A droplet with an initial radius of 100 μm of C_{12}E_{4} containing 20% oleic acid also showed myelinic figures after it was injected into pH=11 buffer solution. The L_{1} phase boundary could be seen around the L_{α} phase (Figure 5.6). But after a while, the L_{1} phase boundary disappeared and all the L_{α} phase was converted to isotropic phase. That is, the final equilibrium is L_{1}. Complete dissolution of the entire drop required about 8 minutes.
Figure 5.6. Droplet of C_{12}E_{4} containing 20% oleic acid in pH=11 buffer solution at 30°C

(Scale is same as Figure 5.4).

When pH=12 buffer solution was used instead of pH=11, myelinic figures were converted to L_{1} phase during the dissolution process (Figure 5.7), but the dissolution was faster and complete dissolution of the drop with an initial radius of 105\mu m required only about 1 minute. The shrinking core mechanism dominated the whole process.

Figure 5.7. Droplet of C_{12}E_{4} containing 20% oleic acid in pH=12 buffer solution at 30°C

(Scale is same as Figure 5.4).

From these results, it can be seen that adding oleic acid can improve the dissolution of C_{12}E_{4} in alkaline solutions. The shrinkage of the droplet occurred with a phase transition from usual myelinic region, W+ L_{\alpha} phase to L_{1} phase or W+ L_{1} phase. When drops of C_{12}E_{4} containing 20% oleic acid were injected into buffer solution, the
soap was made in situ. The transformation to a more favorable micellar region can be attributed to the soap inducing an upward shift of phase boundaries on the phase diagram of C_{12}E_4 (Figure 5.1), thereby causing a micellar solution to be present at temperatures where there is usually an immiscible two phase region. This is brought about by an introduction of charge on the surface of the micelles. An electrostatic repulsion between the micelles opposes phase separation.

There exist two equilibria in oleic acid and buffer solution system.

\[ HA + OH^- \leftrightarrow A^- + H_2O \]

\[ HA \leftrightarrow H^+ + A^- \]
Figure 5.8. Graph of square root of the complete dissolution times vs. initial droplet radii for drops of C₁₂E₄ containing different concentration of oleic acid in pH=12 buffer solution at 30°C

When pH value of buffer solution was increased, H⁺ concentration decreased and OH⁻ concentration increased. These two factors can both increase A⁻ concentration or soap concentration, then dissolution rate can be enhanced.

When concentration of oleic acid was increased, the dissolution rate could be enhanced, too. From Figure 5.8, it can be seen that dissolution rate of droplets of C₁₂E₄ containing 25% oleic acid is greater than for droplets of C₁₂E₄ containing 20% oleic acid. The lines from the plots do not pass through the origin, maybe due to initial mixing and convection effects accompanying the rapid introduction of the droplet to the bulk solution.
The above experiments show that the lamellar phase persists in the drop throughout the dissolution process for a drop of C₁₂E₄/oleic acid in buffer solution, i.e., lamellar phase dissolution is by the shrinking core mechanism. In contrast, the lamellar phase is converted to a surfactant-rich L₁ phase fairly early in the dissolution process for drops of C₁₂E₄/SDS in water, as discussed previously. In the former case pH and the fraction of the acid that is ionized probably change rapidly within the lamellar phase near its outer boundary. In the latter case the central part of the drop becomes more hydrophilic as soon as the SDS dissolves, and the Lₐ phase is converted to L₁ phase. Then SDS dissolves preferentially in aqueous phase so that the drop becomes more lipophilic and reaches composition above the cloud point where solubility in the aqueous phase is low, producing slow dissolution. For C₁₂E₄/oleic acid there seems to be no such final stage of slow dissolution. Hydroxide ions initially diffuse in to convert some acid to soap and form concentrated Lₐ. Some soap dissolves in L₁ phase but more soap keeps forming so Lₐ never becomes so lipophilic that its solubility in the aqueous phase is low.

1.2.2. Dissolution of mixture of C₁₂E₄ and oleic acid in water

The previous study shows that soap has a beneficial effect on the rate of dissolution of C₁₂E₄. To understand how oleic acid affects the dissolution of C₁₂E₄, drops of C₁₂E₄ containing 25% oleic acid, C₁₂E₄ containing 20% oleic acid, C₁₂E₄ containing 15% oleic acid were injected into water, and dissolution behavior was observed. After a drop of C₁₂E₄ containing 25% oleic acid was injected into water, myelinic figures could be seen at first. Then the drop was converted to an isotropic phase completely in about one minute (Figure 5.9). This phase kept swelling during the experiment, but remained immiscible with water.
Figure 5.9. Dissolution of droplet of C_{12}E_{4} containing 25% oleic acid in water at 30°C

(Distance between vertical dotted line is about 240\mu m.)

A drop of C_{12}E_{4} containing 20% oleic acid also showed myelins (Figure 5.10) after it was injected into water, but the myelins were converted to the isotropic phase slowly (more than 10 minutes). A drop of C_{12}E_{4} containing 15% oleic acid exhibited the same phenomena after it was injected into water, but dissolution of the myelins was even slower (Complete dissolution required more than 40 minutes).
Figure 5.10. Dissolution of droplet of C_{12}E_{4} containing 20% oleic acid in water at 30°C.

From these experiments, we conclude that oleic acid can promote dissolution of the lamellar phase of C_{12}E_{4} even when the aqueous phase is not alkaline. But oleic acid and soap promote dissolution by different mechanisms. Forming soap by injecting into a solution with high pH makes nonionic surfactant more hydrophilic and induces an upward shift of cloud point and other phase boundaries. But when injecting into water with neutral pH, little soap is formed and oleic acid makes nonionic surfactant more lipophilic and induces a downward shift of the phase boundaries. The final isotropic phase formed may be L_{3} or L_{2} phase. Both have low viscosities in water and should be readily dispersed during a washing process.

1.2.3 Dissolution in C_{12}E_{4}/Sodium Oleate system

Particles of sodium oleate were sieved in screens with a mesh size of 38μm, then particles with a diameter less than 38μm were weighed into a small tube to mix with C_{12}E_{4}. The mixture was rotated until the solid was homogeneously dispersed. Mixtures of C_{12}E_{4}/Sodium oleate are very viscous, so micropipettes with a diameter of 200–300μm were made and rectangular optical glass capillaries (0.6×6.0, Vitro Dynamics Inc., Cat. # 4806-100) were used to contain water.
The mixtures studied were

93wt% / 7wt%, 90wt% / 10wt%, 85wt% / 15wt%, 83wt% / 17wt%  C_{12}E_4/Sodium oleate

Drops of mixtures of C_{12}E_4 / Sodium Oleate could dissolve completely to an isotropic phase at 30°C if the concentration of sodium oleate in the mixture was at least 7%. Besides, drops of C_{12}E_4+7% sodium oleate and C_{12}E_4+10% sodium oleate showed emulsification in their dissolution processes. It is similar to that described in Chapter 1 and to that of C_{12}E_4/SDS mixtures discussed earlier in this chapter. Complete dissolution of a drop of C_{12}E_4+7% sodium oleate required about 28 minutes while that a similar drop of C_{12}E_4+10% sodium oleate required about 10 minutes.

No emulsification was observed in the dissolution processes of C_{12}E_4+15% sodium oleate and C_{12}E_4+17% sodium oleate. Complete dissolution of drop of C_{12}E_4+15% sodium oleate required about 1~2 minutes while that of C_{12}E_4+17% sodium oleate required about 0.5~1 minute.

The experimental results showed that sodium oleate had a beneficial effect on the dissolution of C_{12}E_4. With high concentration of sodium oleate (i.e. 15% or 17%), the lamellar phase remained in the central part of the drop throughout the dissolution process and ‘shrinking core’ mechanism dominated as shown in Figure 5.11.
Figure 5.11 Shrinking core mechanism in the dissolution process of $C_{12}E_4/15\%$ (or above) sodium oleate

With low concentration of sodium oleate (i.e. 7\% or 10\%), the dissolution behavior was like $C_{12}E_4/SDS$ system: the lamellar phase was converted to a surfactant-rich phase fairly early and spontaneous emulsification occurred as shown in figure 5.12.

Figure 5.12. Spontaneous emulsification mechanism in the dissolution process of $C_{12}E_4/7\%$ (or below) sodium oleate

Besides, dissolution of drops of pure $C_{12}E_4$ in sodium oleate solution was also studied far above CMC of sodium oleate which is $4.7 \times 10^{-5}$ mol/l [Theander and Pugh, 2001] at 30$^\circ$C. It was found that drops of pure $C_{12}E_4$ could dissolve completely if the sodium oleate concentration was higher than 1\% by weight. No emulsification was observed in the dissolution process. ‘Shrinking core’ mechanism dominated. Complete dissolution of $C_{12}E_4$ drop with an initial radius of 120$\mu$m in 1\% sodium oleate solution required about 4–5 minutes.
1.3 Summary

Dissolution of C₁₂E₄ containing oleic acid in alkaline buffer solutions and water and of C₁₂E₄ containing sodium oleate particles in water was studied. Formation of soap at alkaline pH had a beneficial effect on the rate of dissolution of the insoluble ethoxylated alcohol. The lamellar phase dissolved to form the L₁ phase. When the amount of oleic acid present and the pH were sufficiently high, the L₁ phase was miscible with water and ‘shrinking core’ mechanism dominated. Even when this was not the case, the L₁ phase had low viscosity and should be readily dispersed. Oleic acid can also promote dissolution of the lamellar phase of C₁₂E₄. But the isotropic phase formed is L₃ or L₂ phase. Sodium oleate can promote the dissolution of the lamellar phase of C₁₂E₄. With high concentration of sodium oleate (i.e. 15% or 17%), ‘shrinking core’ mechanism dominated. While with low concentration of sodium oleate (i.e. 7% or 10%), the lamellar phase was converted to a surfactant-rich phase fairly early and spontaneous emulsification occurred. All the phenomena observed can be explained in terms of hydrophilic and lipophilic properties and corresponding equilibrium phase behavior of the surfactant/acid/soap system. No special “structuring” effect of the soap needs to be invoked.
2. Dissolution of commercial nonionic surfactants

Dissolution of commercial nonionic surfactants was examined using the same microinjection system as described before. This information will be useful for the granule disintegration study which will be described in Chapter 6. In Chen's work, dissolution behavior in a ternary system was examined, i.e., C_{12}E_{8}-C_{19}OH-H_{2}O. It is noteworthy that the emulsification phenomena and the elongated shapes of surfactant drops are often encountered in these systems that are mixtures of hydrophilic and hydrophobic species dissolving in water at temperatures just slightly (few degrees in Celsius) below their cloud points. The dissolution of commercial surfactants is similar.

![Droplet Dissolution Results](image)

The above chart shows the dissolution times at 30°C of droplets with average size of 100 microns (droplet radius of Neodol 25-3EO is about 40 microns). The two samples whose dissolution times were shown going off the scale at 20 minutes actually didn't
dissolve. Final states of these two samples in test tube experiments were both W+Lα. Commercial surfactants Vista 1012-62, Neodol 23-6.5, Neodol 91-5, Synperonic A7 dissolved in water fast while Lialet 111-5.5, Neodol 25-3 and Neodol 1-5 didn’t.

A plot of square root of the total time of dissolution versus the initial droplet radius for several commercial surfactants is shown in Figure 5.13. It can be seen that the initial droplet radius decreases linearly with the square root of the total dissolution time. This suggests that the dissolution process is diffusion controlled. The lines from the plot do not pass through the origin, perhaps due to initial mixing and convection effects accompanying the rapid introduction of the droplet to the bulk solution. It shows that surfactant with least EO number dissolved most slowly.

Figure 5.13. Graph of the square root of the complete dissolution times vs initial droplet radii for drops of Vista 1012-62, Neodol 91-5, Neodol 23-6.5.
A droplet of Lialet 111-5.5 showed myelinic figures after it was injected into water. Later additional swelling was seen (Figure 5.14), but viscous myelinic figures remained even after 50 minutes.

Figure 5.14. Droplet of Lialet 111-5.5 dissolving in water at 30°C

Phase separation was observed after a droplet of Neodol 1-5 was injected into water. It couldn’t dissolve even after an hour.

It's found that different commercial products with similar average composition sometimes have very different behaviors, presumably due to different EO distributions. i.e., Neodol 91-5 could dissolve fast in water while Neodol 1-5 couldn't.

Tables 5.2 and 5.3 list dissolution times of different surfactants or surfactant mixtures which were studied in this work and previous project [Chen, 1998]. We have already shown that the complete dissolution time of the surfactant varies linearly with the square of the initial drop radius. Estimated dissolution times of different surfactants in Table 5.3 were calculated using this result. That is, actual dissolution times for drops of various sizes shown is Table 5.2 were converted to a drop radius of 100µm for Table 5.3 in an effort to compare all the surfactants on the same basis.

Table 5.3 shows that, dissolution is faster for more hydrophilic surfactants. Drops of the pure linear alcohol ethoxylates $C_{12}E_3$ and $C_{12}E_6$ and commercial surfactants such as
Neodol 23-6.5 and Neodol 25-7 dissolved rapidly at temperatures below their cloud points where a shrinking core mechanism was seen with little spontaneous emulsification. Large dissolution times are seen for mixtures such as \( C_{12}E_4/SDS=90/10 \), \( C_{12}E_4/Sodium oleate=90/10 \) and Neodol 91-5 where there was spontaneous emulsification but not a shrinking core mechanism. As discussed previously, diffusion of more hydrophilic species into the aqueous phase early in the dissolution process leaves a drop enriched in the more lipophilic species, which dissolves slowly.

In terms of phase behavior, dissolution of a drop is rapid if a lamellar phase \( L_{\alpha} \) forms which is in equilibrium with an aqueous phase \( L_1 \) having a high concentration of surfactant. For example, Figure 1.5 in chapter 1 shows that at 28°C the \( L_1 \) phase of \( C_{12}E_5 \) extends to more than 50 wt% surfactant before being transformed to \( L_{\alpha} \). The large surfactant solubility in \( L_1 \) provides a large concentration gradient in the aqueous phase leading to rapid dissolution, as shown in Table 5.3. In contrast, if composition of the drop is above its cloud point either initially or owing to preferential dissolution of more hydrophilic species, surfactant concentration in the aqueous phase in equilibrium with \( L_{\alpha} \) or surfactant–rich \( L_1 \) is low (See figure 1.5) and dissolution is slow. Examples are \( C_{12}E_4/SDS \) and \( C_{12}E_4/sodium oleate \) containing 90% of the nonionic surfactant (Table 5.3).
Table 5.1. Phase behavior of C_{12}E_{4}/oleic acid in buffer solution at 30°C

<table>
<thead>
<tr>
<th></th>
<th>pH=9</th>
<th>pH=10</th>
<th>pH=11</th>
<th>pH=12</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12}E_{4} +10% oleic acid</td>
<td>W+L_{1} + L_{α}</td>
<td>W+L_{1} + L_{α}</td>
<td>W+L_{1}</td>
<td>W+L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4} +15% oleic acid</td>
<td>W+L_{1} + L_{α}</td>
<td>W+L_{1}</td>
<td>W+L_{1}</td>
<td>W+L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4} +20% oleic acid</td>
<td>W+L_{1}</td>
<td>W+L_{1}</td>
<td>L_{1}</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4} +25% oleic acid</td>
<td>W+L_{1}</td>
<td>W+L_{1}</td>
<td>L_{1}</td>
<td>L_{1}</td>
</tr>
</tbody>
</table>
Table 5.2 Average time for dissolution at 30°C of mixtures of C_{12}E_{4} with oleic acid and sodium oleate

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Solution</th>
<th>Ini. Radius (µm)</th>
<th>Diss. Time (Min)</th>
<th>Final Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12}E_{4}/Oleic acid=80:20</td>
<td>pH=10 buffer solution</td>
<td>140~145</td>
<td>3.6*</td>
<td>W+L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=80:20</td>
<td>pH=11 buffer solution</td>
<td>105~110</td>
<td>8.8</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=80:20</td>
<td>pH=12 buffer solution</td>
<td>110~120</td>
<td>1.3</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=75:25</td>
<td>pH=11 buffer solution</td>
<td>130~135</td>
<td>11.2</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=75:25</td>
<td>pH=12 buffer solution</td>
<td>150~160</td>
<td>1.05</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=85:15</td>
<td>pH=12 buffer solution</td>
<td>165~170</td>
<td>0.98*</td>
<td>W+L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=80:20</td>
<td>water</td>
<td>140~145</td>
<td>1.35*</td>
<td>W+L_{3} or L_{2}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=85:15</td>
<td>water</td>
<td>165~175</td>
<td>10.5*</td>
<td>W+L_{3} or L_{2}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Sodium oleate=93:7</td>
<td>water</td>
<td>195~205</td>
<td>28</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Sodium oleate=90:10</td>
<td>water</td>
<td>200~210</td>
<td>10</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Sodium oleate=85:15</td>
<td>water</td>
<td>168~175</td>
<td>1.15</td>
<td>L_{1}</td>
</tr>
<tr>
<td>C_{12}E_{4}/Sodium oleate=83:17</td>
<td>water</td>
<td>160~170</td>
<td>0.98</td>
<td>L_{1}</td>
</tr>
</tbody>
</table>

* denotes the dissolution time for the lamellar phase.
Table 5.3 Average time for complete dissolution of surfactants with initial radius of 100μm at 30°C

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Solution</th>
<th>Diss. Time (Min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12}E_{5} (28°C)</td>
<td>water</td>
<td>0.37</td>
</tr>
<tr>
<td>C_{12}E_{4}/Sodium oleate=85:15</td>
<td>water</td>
<td>0.40</td>
</tr>
<tr>
<td>C_{12}E_{6}</td>
<td>water</td>
<td>0.43</td>
</tr>
<tr>
<td>Neodol 25-7 (35°C)</td>
<td>water</td>
<td>0.45</td>
</tr>
<tr>
<td>Neodol 23-6.5</td>
<td>water</td>
<td>0.50</td>
</tr>
<tr>
<td>Tergitol 15-S-7</td>
<td>water</td>
<td>0.67</td>
</tr>
<tr>
<td>C_{12}E_{4}/Oleic acid=80:20</td>
<td>pH=12 buffer solution</td>
<td>0.98</td>
</tr>
<tr>
<td>Neodol 91-5</td>
<td>water</td>
<td>1.5</td>
</tr>
<tr>
<td>C_{12}E_{4}/Sodium oleate=90:10</td>
<td>water</td>
<td>2.4</td>
</tr>
<tr>
<td>C_{12}E_{4}/SDS=90:10</td>
<td>water</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Chapter 6: Dissolution of Neat Surfactants and Corresponding Granules

1. Introduction

As mentioned in Chapter 1, the use of granules is one way of incorporating liquid nonionic surfactants into powder detergents. Key components of the granules are zeolite and liquid nonionic surfactants. Sometimes solid anionics such as alkyl sulfates are also included. Both single granule dissolution experiments and vertical contacting experiments have been carried out for granules approximately 500µm in diameter containing some 30% nonionic surfactant and 70% small (<10µm in diameter) zeolite particles.

Previous work has suggested that the behavior of granules in a washing machine depends on the rate of formation and dissolution of surfactant mesophase, which acts as a glue to hold granules together in a compact glob. The shear forces in a washing machine do not appear to be sufficiently strong to break up such a glob in which the glue is highly viscous. Therefore one has to rely on surfactant dissolution.

2. Single granule experiments: granules made from pure surfactants

2.1. Disintegration of granules of pure C₁₂E₃/Zeolite 4Å:

Myelinic figures of the lamellar phase were observed shortly after a droplet of C₁₂E₃ was contacted with water at 30°C. Behavior was similar to that shown in Figure 5.4
for C_{12}E_{4}. The L_\alpha phase and water coexisted at equilibrium. For C_{12}E_{3} in water at 40°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 L_3 phase appeared at the surface. 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 [Chen, 1998].

Disintegration of individual granules of pure C_{12}E_{3}/Zeolite 4A was studied at 30°C and 40°C respectively [Bai et al, 2003]. As we expected, the granule couldn't disintegrate in water at 30°C. Lamellar phase formed and grew at the surface of the granule. The formation of a coherent L_\alpha phase inhibited the granule disintegration, and few zeolite particles were released after 20 minutes (Figure 6.1).

At 40°C, it was observed that some lamellar phase was converted to L_3 phase at the surface of the granule after a minute (Figure 6.2). Twenty minutes after contact, only a few particles had been released. The lamellar and L_3 phases still held the granule together.
Figure 6.1 Disintegration of granule of pure C$_{12}$E$_{3}$/Zeolite 4A at 30°C (In this and subsequent case, the time code indicates time after the initial contact of the granule and water. Here 7 min and 59 s)

Figure 6.2 Disintegration of granule of pure C$_{12}$E$_{3}$/Zeolite 4A at 40°C
2.2 Disintegration of granules of pure C_{12}E_{5}/Zeolite 4A

Neat surfactant dissolution of C_{12}E_{5} was studied at 28°C and 35°C. At 28°C which is below its cloud point (32°C), the surfactant dissolved completely in water by a shrinking core mechanism (Figure 6.3), as found previously by Chen [1998], the only intermediate phase being L_α. During dissolution, the L_2 phase shrank as it was converted to the L_α phase and eventually disappeared. Meanwhile L_α was converted to L_1 at the boundary between these phases and also ultimately disappeared. A drop with an initial radius of 100μm took only 22 seconds to dissolve. At 35°C, which is above its cloud point, two intermediate phases were observed, the lamellar phase which appeared

Figure 6.3. Shrinking core mechanism during dissolution of pure nonionic surfactants below their cloud points.

immediately upon injection of a surfactant drop and the surfactant-rich L_1 phase, which was visible later at the interface between the L_α phase and water although presumably present in small amounts from the time of initial injection. Eventually, the L_α phase dissolved, leaving a single drop of the L_1 phase in equilibrium with the aqueous phase.
For a drop with an initial radius of 100μm, it took 23 seconds for the Lα phase to dissolve completely.

The disintegration of granules of pure C_{12}E_{5}/Zeolite 4A was studied at 28°C and 35°C. There was a short induction period which was around 10–15 seconds for the granule at 28°C. After the induction period, the disintegration of the granule was very fast and was complete within 1–2 minutes (Figure 6.4).

Granules didn’t disintegrate at 35°C. The L₁ phase held the granule together, and only a few particles were released from the liquid phase boundary (Figure 6.5).

2.3 Disintegration of granules of pure C_{12}E_{6}/Zeolite 4A

Pure C_{12}E_{6} has a cloud point of 52°C. At 30°C, three liquid crystalline intermediate phases developed between the neat surfactant (L₂) and the aqueous phase (L₁). These were lamellar liquid crystal (L-α), a bicontinuous cubic phase (V₁), and the normal hexagonal phase (H₁). A drop with an initial radius of 100μm took 26 seconds to dissolve (Table 5.3).

The corresponding granule disintegrated very rapidly in 1–2 minutes at 30°C (Figure 6.6). There was no lag time. This result confirms that complete dissolution of surfactant allows the zeolite particles to be released.

Table 6.1 summarizes disintegration behavior of granules made from pure nonionic surfactants in water.
Figure 6.4 Disintegration of granule of pure C$_{12}$E$_5$/Zeolite 4A at 28°C.

Figure 6.5 Disintegration of granule of pure C$_{12}$E$_5$/Zeolite 4A at 35°C.
Figure 6.6 Disintegration of granule of pure C\textsubscript{12}E\textsubscript{6}/Zeolite 4A at 30\textdegree C.

Table 6.1. Disintegration Behavior of Granules Made from Pure Surfactants

<table>
<thead>
<tr>
<th>Neat surfactants</th>
<th>Temp.</th>
<th>Final equilibrium phase in water of the neat surfactant</th>
<th>Disintegration of corresponding granules</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{12}E\textsubscript{3}</td>
<td>30\textdegree C</td>
<td>W+L\textsubscript{a}</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td></td>
<td>40\textdegree C</td>
<td>W+L\textsubscript{3}</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>C\textsubscript{12}E\textsubscript{5}</td>
<td>28\textdegree C</td>
<td>L\textsubscript{1}</td>
<td>Rapid, 1<del>2 minutes. (10</del>15 seconds lag time)</td>
</tr>
<tr>
<td></td>
<td>35\textdegree C</td>
<td>W+L\textsubscript{1}</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>C\textsubscript{12}E\textsubscript{6}</td>
<td>30\textdegree C</td>
<td>L\textsubscript{1}</td>
<td>Rapid, 1~2 minutes.</td>
</tr>
</tbody>
</table>
3. Single granule experiments: granules made from pure surfactant mixtures

Some granules made of species with varying difference in EO numbers were studied to compare with pure surfactant results described above. One objective was to make nonionic surfactant mixtures with equal cloud points but varying the breadth of the distribution and to see how this difference affects granule disintegration.

3.1 Disintegration of granules of C_{12}E_{4}/C_{12}E_{6}/Zeolite 4A:

Neat surfactant mixtures having C_{12}E_{4}/C_{12}E_{6} ratios of 50/50, 45/55, 40/60, 34/66 by weight were prepared. The observed phase behavior for 1.5 wt% C_{12}E_{4}/C_{12}E_{6} solutions at 30°C is listed below:

<table>
<thead>
<tr>
<th>C_{12}E_{4}/C_{12}E_{6} weight ratio</th>
<th>C_{12}E_{4}/C_{12}E_{6} molar ratio</th>
<th>Final phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>55.4/44.6</td>
<td>W+L_{1}</td>
</tr>
<tr>
<td>45/55</td>
<td>50.4/49.6</td>
<td>W+L_{1}</td>
</tr>
<tr>
<td>40/60</td>
<td>45.3/54.7</td>
<td>L_{1}</td>
</tr>
<tr>
<td>34/66</td>
<td>39.0/61.0</td>
<td>L_{1}</td>
</tr>
</tbody>
</table>

Drop dissolution experiments were conducted for C_{12}E_{4}/C_{12}E_{6} ratios of 50/50, 45/55 and 40/60. The result was consistent with the phase behavior experiment. Drops of C_{12}E_{4}/C_{12}E_{6} (50:50, by weight) formed lamellar phase shortly after contact. After the lamellar phase dissolved by the shrinking core mechanism, a single L_{1} drop coexisted
with the aqueous phase at equilibrium. For a drop with an initial radius of 150\( \mu \)m, it took 1.3 minutes to get the final state. A drop of C\(_{12}E_4/C_{12}E_6\) (45:55, by weight) showed similar phenomena although the dissolution was a little faster. Drops of C\(_{12}E_4/C_{12}E_6\) (40:60, by weight) also formed lamellar phase shortly after contact. However, the lamellar phase dissolved completely. For a drop with an initial radius of 100\( \mu \)m, it took 0.6 minute (36 seconds) to dissolve completely. No spontaneous emulsification such as that observed for some commercial nonionic surfactants and other pure nonionic surfactant mixtures [Chen, 2001] was observed during the dissolution of these mixtures.

Granule disintegration was studied at 30\(^\circ\)C. The disintegration of a C\(_{12}E_4/C_{12}E_6\)(40:60, by weight)/Zeolite 4A granule was fast and took 1~2 minutes. The granule of C\(_{12}E_4/C_{12}E_6\)(50:50, by weight)/Zeolite 4A didn't disintegrate and was held together by the liquid phase although it did expand to some extent. Thus, the concentrated L\(_1\) phase can hold the granule together, the same as found for pure C\(_{12}E_5\) above its cloud point.

### 3.2 Disintegration of granules of C\(_{12}E_3/C_{12}E_7\)/Zeolite 4A

The drop dissolution experiment of C\(_{12}E_3/C_{12}E_7\) (50:50, by weight) was conducted. After the drop was injected into water, the lamellar phase could be observed, then many L\(_1\) droplets formed on outer surface of the lamellar phase, grew and later coalesced. Finally, there existed one L\(_1\) drop, surrounding the remaining lamellar phase, the final phases present being W+L\(_1\)+L\(_{\alpha}\).
Disintegration of the granule of C₁₂E₉/C₁₂E₇ (50:50, by weight)/Zeolite 4A didn't occur. Some L₁ drops with big contact angle formed at the surface of granule. The granule was still held together after 20 minutes.

3.3 Disintegration of granule of C₁₂E₂/C₁₂E₈/Zeolite 4A

Neat surfactant mixtures having C₁₂E₂/C₁₂E₈ ratios of 34/66, 30/70 26/74, 20/80 were prepared. The observed phase behavior for 1.5 wt% C₁₂E₂/C₁₂E₈ solutions 30°C is listed below:

<table>
<thead>
<tr>
<th>C₁₂E₂/C₁₂E₈ weight ratio</th>
<th>C₁₂E₂/C₁₂E₈ molar ratio</th>
<th>Final phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>34/66</td>
<td>50.3/49.7</td>
<td>W+L₁</td>
</tr>
<tr>
<td>30/70</td>
<td>45.7/54.3</td>
<td>W+L₁</td>
</tr>
<tr>
<td>26/74</td>
<td>40.8/59.1</td>
<td>L₁</td>
</tr>
<tr>
<td>20/80</td>
<td>32.9/67.1</td>
<td>L₁</td>
</tr>
</tbody>
</table>

Drop dissolution experiments of C₁₂E₂/C₁₂E₈ (20:80, by weight) were conducted at 30°C. Shrinking core mechanism dominated during the dissolution process and no spontaneous emulsification was observed. At the end of the experiment the drop dissolved completely. In contrast, drops of C₁₂E₂/C₁₂E₈ (26:74, by weight) showed spontaneous emulsification in the dissolution process and dissolved completely. Drops of C₁₂E₂/C₁₂E₈ (30:70, by weight) showed spontaneous emulsification during the dissolution
process, and a single L₁ drop coexisted with the aqueous phase at final state. Dissolution of drops of C₁₂E₂/C₁₂E₈ (34:66, by weight) showed similar behavior.

Granule disintegration was studied at 30°C. Disintegration of a C₁₂E₂/C₁₂E₈ (20:80, by weight)/Zeolite 4A granule was fast and took 1~2 minutes. Disintegration of a C₁₂E₂/C₁₂E₈ (26:74, by weight)/Zeolite 4A granule was also fast and took 1~2 minutes, even though the mechanism of surfactant dissolution was different, as indicated above. The processes were similar to those observed for granules made with other surfactants below their cloud points. The granule of C₁₂E₂/C₁₂E₈ (34:66, by weight)/Zeolite 4A didn't disintegrate and was held together by the liquid phase, as observed for other surfactants above their cloud points.

3.4. Disintegration of granule of C₁₂E₈/ C₁₀OH/ Zeolite 4A

A surfactant mixture of C₁₂E₈/C₁₀OH (85:15, by weight) has a cloud point of 37°C. At slightly lower temperatures neat surfactant showed emulsification and formation of protrusions and batonnets during dissolution as observed by Chen et al [Chen 2001]. Dissolution was faster at 30°C than at 35°C though in both cases the total dissolution time was greater than for pure C₁₂E₅ and C₁₂E₆ at 30°C.

Granule disintegration was studied at 30°C, 35°C and 45°C. It was found that the granule of C₁₂E₈/ C₁₀OH / Zeolite 4A is easy to disintegrate at 30°C and 35°C although it is slightly faster at 30°C. Granule disintegration was complete in less than 1 minute at 30°C, 1~2 minutes at 35°C, about the same as for other surfactant mixtures below the cloud point discussed above. Granule disintegration didn't occur at 45°C, i.e., above the cloud point the granule was held together by the liquid phase.
3.5 Disintegration of granules of C_{12}E_4/ Sodium Oleate/ Zeolite 4A

As reported in Chapter 5, dissolution of the neat surfactant mixture C_{12}E_4/Sodium Oleate=90/10 is dominated by "spontaneous emulsification" mechanism, while dissolution of neat surfactant mixture C_{12}E_4/Sodium Oleate=85/15 is dominated by "shrinking core" mechanism. The dissolution is faster in the latter case.

Granule disintegration was fast with both surfactant mixture C_{12}E_4/Sodium Oleate=90/10 and surfactant mixture C_{12}E_4/Sodium Oleate=85/15. Granule disintegration was complete in 1~2 minutes for both of them. It was hard to tell which one was faster.

Table 6.2 summarizes disintegration behavior of granules made from pure nonionic surfactant mixtures in water.
Table 6.2. Disintegration Behavior of Granules Made from Pure Surfactant Mixtures

<table>
<thead>
<tr>
<th>Neat surfactants</th>
<th>Ratio (by weight)</th>
<th>Temp (°C)</th>
<th>Final equilibrium phase in water of the neat surfactant (dilute solution)</th>
<th>Disintegration of corresponding granules</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12}E_4/C_{12}E_6</td>
<td>40:60</td>
<td>30°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes.</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>30°C</td>
<td>W+L_1</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>C_{12}E_3/C_{12}E_7</td>
<td>50:50</td>
<td>30°C</td>
<td>W+L_1+L_α</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>C_{12}E_2/C_{12}E_8</td>
<td>20:80</td>
<td>30°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes</td>
</tr>
<tr>
<td></td>
<td>26:74</td>
<td>30°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes</td>
</tr>
<tr>
<td></td>
<td>34:66</td>
<td>30°C</td>
<td>W+L_1</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>C_{12}E_8/C_{10}OH</td>
<td>85:15</td>
<td>30°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes</td>
</tr>
<tr>
<td></td>
<td>85:15</td>
<td>35°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes</td>
</tr>
<tr>
<td></td>
<td>85:15</td>
<td>45°C</td>
<td>W+ L_1</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>C_{12}E_4/Sodium Oleate</td>
<td>85:15</td>
<td>30°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes</td>
</tr>
<tr>
<td></td>
<td>90:10</td>
<td>30°C</td>
<td>L_1</td>
<td>Rapid, 1~2 minutes</td>
</tr>
</tbody>
</table>
4. Vertical contacting experiments: granules made from pure surfactants and surfactant mixtures

Vertical contacting experiments were carried out at 30°C to test the disintegration behavior of granules that were packed in a cell. Such experiments provide some insight into behavior which might be expected when water contacts a bed of granules in a powder detergent. The granule sizes were uniform causing large void spaces between them when packed together. Granules of pure C₁₂E₃/Zelite 4A, pure C₁₂E₆/Zelite 4A, pure C₁₂E₆/Zelite 4A, C₁₂E₄/ C₁₂E₆ (40:60 and 50:50, by weight)/ Zeolite 4A, C₁₂E₈/ C₁₀OH (85:15, by weight)/ Zeolite 4A were tested respectively.

When water was injected into beds of most granules, the dissolution of surfactant made the granules disintegrate. Bubbles consisting of air initially in the void space tended to rise, carrying along small particles or clusters of particles released from the granules. The remaining particles tended to settle because their density was larger than that of water. As a result, a bed with much smaller pores and porosity and having a flat upper surface formed. Above it convection existed owing to the upward motion of air bubbles and downward motion of particles released at the liquid/air interface when the bubbles coalesced. When granules mentioned above (except for granules of C₁₂E₃/Zelite 4A and C₁₂E₄/ C₁₂E₆ (50:50, by weight)/ Zeolite 4A) were contacted with water at temperatures below their cloud points, the granules fell apart and pore space disappeared almost immediately. The bed surface became flat within two minutes. Figure 6.7a and 6.7b show one typical experiment for granules of pure C₁₂E₃/Zelite 4A. In contrast, granules made of C₁₂E₃/Zelite 4A exhibited different phenomena when they were contacted with water.
at 30°C, i.e., some void space could still be seen after 50 minutes and the upper surface of the bed was irregular. Myelinic figures developed at the surface of the granules and held them together (Figure 6.7c and 6.7d). The liquid L₁ phase developed at the surface of granules made of C₁₂E₄/ C₁₄E₆ (50:50, by weight)/ Zeolite 4A. Although the pore space disappeared due to the swelling of the granules, it didn't form a flat surface layer even after 40 minutes. These experiments confirm that granules disintegrate completely below the surfactant cloud point, thereby complementing the single granule experiments, where initial disintegration behavior could be seen clearly but the large number of opaque zeolite particles sometimes obscured the latter stages of the process.
Figure 6.7. (a)(b) Vertical contacting experiment of granules of pure C_{12}E_{3}/Zeolite 4A with water at 30°C.

(c)(d) Vertical contacting experiment of granules of pure C_{12}E_{3}/Zeolite 4A with water at 30°C.
5. Vertical contacting experiments: granules with commercial surfactants supplied by Unilever.

Similar vertical contacting experiments were carried out at 30°C as an initial screening test of the dissolution behavior of granules made with zeolite particles and commercial nonionic surfactants. The granule sizes were uniform causing large void spaces when they were packed together (Figure 6.8a).

When water was injected into beds of most granules, the dissolution of surfactant made the granules disintegrate. As in the experiments with pure surfactants described above, air bubbles tended to rise carrying along small particles or clusters of particles released from the granules. The remaining particles tended to settle because their density was larger than that of water. As a result a bed with much smaller pores and porosity formed. Above it convection existed owing to the upward motion of air bubbles and downward motion of particles released at the liquid/air interface when the bubbles coalesced. For example, when granules made of Lialet 111-5.5, zeolite A24 and sodium stearate were contacted with water, the granules fell apart immediately and pore space disappeared after only one minute (Figure 6.8).

Granules made of Lialet 111-5.5 and zeolite A24 with no sodium stearate were an exception. They formed a white surface layer after being contacted with water and didn’t fall apart. Pore space could still be observed after 15 minutes (Figure 6.9).

Figure 6.8 and Figure 6.9 show that dissolution of granules is dependent on surfactant dissolution. Lialet 111-5.5 did not dissolve completely in water, as observed
Figure 6.8 (a, b). Vertical contacting experiment of granules made of Lialet 111-5.5, zeolite A24, sodium stearate

Figure 6.9. Vertical contacting experiment of granules of Lialet 111-5.5, zeolite A24

a. Before contacting. b. 15 minutes after contacting. c. Individual granule hanging in the middle of the cell.

previously (Chapter 5). This behavior helps explain the above observation that granules of Lialet 111-5.5 and zeolite A24 can’t disintegrate easily. Adding sodium stearate to Lialet 111-5.5 made the surfactant mixture more hydrophilic and promoted dissolution of the nonionic surfactant, just as adding sodium oleate promoted dissolution of C_{12}E_{4} as described in Chapter 5. As a result, the granule of Lialet 111-5.5, Zeolite A24 and sodium stearate could fall apart easily, and void space in the bed disappeared rapidly. For the same reason, disintegration of granules with Zeolite 4A, Lialet 111-5.5 and sodium stearate was observed to be more rapid than that of granules with Zeolite 4A and Lialet 111-5.5 alone.
Disintegration also occurred, though very slowly, for granules with Lialet 111-5.5 and zeolite 4A. In this case, disintegration was not complete as a small amount of porosity remained even after 20 minutes. So considerable disintegration occurred with zeolite 4A but virtually none with zeolite A24. These results show that granule dissolution is influenced by both surfactant composition and the type of zeolite. In particular, a swelling zeolite can prevent granule disintegration.

Adding anionic surfactants FAES or PAS (see Chapter 3) made Dobanol 6.5 and Dobanol 7 more hydrophilic and promoted dissolution of the nonionic surfactants. The result is that disintegration of granules No. (6) (7) (8) (9) (see Table 6.3) are more rapid than granule No. 5, which contains Dobanol 6.5 alone.

6. Single granule experiments: granules made from commercial surfactants supplied by Unilever.

The dissolution experiment with one or a small number of individual granules seems most promising for identifying the chief mechanisms of granule breakup and of interaction between adjacent granules. Such experiments were conducted with all the granules supplied.

The ranking of relative activity (Table 6.3) was consistent with results from the vertical cell contacting experiments. Figure 6.10 shows the dissolution behavior of a granule made of Lialet 111-5.5, zeolite A24. The lighter region around the particle is presumably the same as the white regions shown in the granule bed experiment in Figure 6.9. It may be Lα phase around the undissolved interior of the granule, possibly mixed with zeolite particles.
Figure 6.10. Single granule dissolution, made of Lialet 111-5.5 and zeolite A24

a. 10× magnification.  
b. 20× magnification.

In contrast, Figure 6.11 shows behavior of a granule made of Lialet 111-5.5, zeolite 4A. The granule had the tendency to shed both clumps of particles and some individual particles. The large clump breaking off near the bottom of Figure 6.11b suggests that granule disintegration may not always be axisymmetric, i.e., it may not always follow the shrinking core mechanism. In this case it may also be incomplete.

Figure 6.11. Single granule dissolution, made of Lialet 111-5.5 and zeolite 4A

a. 10× magnification.  
b. 10× magnification.

Granules (6) (7) (8) (9), which are all active, can disintegrate in water in less than 1 minute. Granules (3) (4) can disintegrate in water in 1-2 minutes. All of them (initial radii are about 150-250 microns) fell apart completely.
7. Single granule experiments: Granules made from commercial nonionic surfactants at Rice.

7.1 Granule disintegration of Neodol 23-6.5/Neodol 91-5/Zeolite 4A series:

As described in section 3, disintegration of granules made from pure surfactant mixtures was studied. One objective was to make nonionic surfactant mixtures with equal cloud points but varying the breadth of the distribution and to see how this difference affected granule disintegration. It was found when the neat surfactant dissolved in water completely but with different mechanisms, little difference in granule disintegration was seen. Similarly, disintegration of granules made from commercial surfactants was also studied. The objective was to see the difference in granule disintegration behavior when we varied the composition ratio of the commercial surfactants.

As we showed in Chapter 5, dissolution of Neodol 23-6.5 was fast at 30°C. Granules of Neodol 23-6.5/zeolite A24 (Unilever granule) disintegrated rapidly. There was spontaneous emulsification during dissolution process of neat Neodol 91-5, and its dissolution rate was slower than Neodol 23-6.5 (Table 5.3) but still relatively fast. For a granule of Neodol 91-5/zeolite 4A (made at Rice), most particles were released shortly after contact, although several clusters remained after 5 minutes when the experiment was stopped. Probably these clusters eventually disintegrated as well.

Dissolution of neat surfactant mixtures having Neodol 23-6.5/Neodol 91-5 ratios of 80/20, 60/40, 40/60, 20/80 was studied. All these mixtures dissolved completely. It was found that spontaneous emulsification occurred during the dissolution process if
there was more than 60% Neodol 91-5 in the surfactant mixture. Otherwise dissolution occurred more rapidly and without emulsification.

Disintegration of corresponding granules didn't show much difference. Granules of approximately the same size (0.02 gram, 500–600 µm) all took 2~3 minutes to disintegrate. This result is consistent with those of section 3 for mixtures of pure nonionic surfactants in that, granules disintegrated rapidly when the neat surfactant dissolved in water completely, whether or not spontaneous emulsification occurred during dissolution of neat surfactant. Further comment on this behavior is given below.

7.2 Granule disintegration with Neodol 25-3 and Neodol 25-7

Granule disintegration for mixtures of Neodol 25-3 and Neodol 25-7 in different ratios was studied. These surfactants have very different distributions of polyoxyethylene chain length.

It was found that for the mixture of Neodol 25-3 /Neodol 25-7= 10/90, spontaneous emulsification occurred during the dissolution process of the neat surfactant, but there was still a relatively small amount of surfactant remaining after a long time in the form of the lamellar liquid crystal. The corresponding granule disintegration was very fast. Most particles were released shortly after contact. There might have been a very small part of a granule that didn’t disintegrate.

The mixture of Neodol 25-3 / Neodol 25-7=20/80 showed similar behavior. The neat surfactant didn't dissolve completely in water. Disintegration of the corresponding granule was not very fast. Myelins could be observed after contact, few particles were
released after 1 minute. After that, the granule began to disintegrate. There might have been a very small part of a granule that didn’t disintegrate.

The mixture of neat surfactant Neodol 25-3 / Neodol 25-7=50/50 didn't dissolve completely. Myelinic figures could be observed during the dissolution process. There was a relatively large amount of myelins remaining after long time. A granule of this mixture didn't disintegrate. The lamellar phase formed and grew at the surface of the granule. Few particles were released from the granule, even after 30 minutes.

7.3 Granule dissolution of Tergitol 15-S-7 / Zeolite 4A

Commercial surfactant Tergitol 15-S-7 has a cloud point of 37°C. Granule disintegration was studied 30°C, 35°C and 45°C. It was found that the granule of Tergitol 15-S-7/zeolite 4A is easy to disintegrate at 30 and 35°C although it is slightly faster at 30°C. Granule disintegration was complete in 1~2 minute. At 45°C, when a drop of the neat surfactant was injected into water, spontaneous emulsification within the aqueous drop was observed. At the end of experiment, a single L₄ drop coexisted with water. For the granule disintegration experiment, particles began to be released after contact. After 2 minutes, there was little further change for the granule. It's hard to tell whether the whole granule disintegrated or not.
Table 6.3: The activities based on single granule experiments of the granules with commercial nonionic surfactants and mixtures of nonionic and anionic surfactants at 30°C.

<table>
<thead>
<tr>
<th>Granule</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Lialet 111-5.5, zeolite 4A</td>
<td>Not active.</td>
</tr>
<tr>
<td>(2) Lialet 111-5.5, zeolite A24</td>
<td>The granule didn't disintegrate.</td>
</tr>
<tr>
<td>(3) Lialet 111-5.5, zeolite A24, sodium stearate</td>
<td>Rapid, 1~2 minutes.</td>
</tr>
<tr>
<td>(4) Lialet 111-5.5, zeolite 4A, sodium stearate</td>
<td>Rapid, 1~2 minutes.</td>
</tr>
<tr>
<td>(5) Dobanol 6.5, zeolite A24</td>
<td>Rapid, 1~2 minutes.</td>
</tr>
<tr>
<td>(6) Dobanol 6.5, zeolite A24, FAES</td>
<td>Rapid, less than 1 minute.</td>
</tr>
<tr>
<td>(7) Dobanol 6.5, zeolite 4A, FAES</td>
<td>Rapid, less than 1 minute.</td>
</tr>
<tr>
<td>(8) Dobanol 7, zeolite 4A, PAS</td>
<td>Rapid, less than 1 minute.</td>
</tr>
<tr>
<td>(9) Dobanol 7, zeolite A24, PAS</td>
<td>Rapid, less than 1 minute.</td>
</tr>
<tr>
<td>Neodol 23-6.5, Neodol 91-5, Zeolite 4A</td>
<td>Granules can disintegrate in 2~3 minutes when Neodol 23-6.5 content of the surfactant mixture in this granule is greater than 20wt%.</td>
</tr>
<tr>
<td>Neodol 25-3, Neodol 25-7, Zeolite 4A</td>
<td>Granules can disintegrate when Neodol 25-3 content of the surfactant mixture in this granule is less than 20wt%.</td>
</tr>
<tr>
<td>Tergitol 15-S-7, Zeolite 4A</td>
<td>Disintegrate in 1~2 minutes at 30 or 35°C, disintegrate to some extent even above its cloud point at 45°C.</td>
</tr>
</tbody>
</table>
8. Discussion and concluding remarks

8.1. Disintegration of granules made from pure surfactant and surfactant mixtures

Some interesting dissolution behavior of neat surfactants and corresponding granules has been observed. It has been found if the neat surfactant is below its cloud point, the corresponding granule disintegrates relatively fast. If the neat surfactant forms an L₃ or L₁ phase that is immiscible with water, the zeolite particles remain in the surfactant-rich phase or at the interface, and the corresponding granule doesn't disintegrate in our experiment where there is no agitation. Evidently the particles are not strongly wet by the external aqueous phase. However, since the L₃ and L₁ phases have low viscosity and low interfacial tension with water, the granule might be able to disperse in the washing bath under high shear forces. Disintegration of granules didn't occur when the neat surfactant developed viscous myelinic figures upon contact with water. The lamellar phase has very high viscosity, and the granule should not be able to disperse even under high shear forces.

In the previous study of commercial nonionic surfactants and mixtures of pure nonionic surfactants [Chen, 2001] it was found that dissolution of a neat surfactant drop was rapid at temperatures far below its cloud point and closely resembled the dissolution process for pure nonionic surfactants. However, at temperatures just below the cloud point, preferential dissolution of the more hydrophilic component(s) raised the cloud point of the surfactant mixture remaining in the drop above the temperature of the experiment. As a result, intriguing phenomena such as "spontaneous emulsification" of L₁ and/or L₃ phases occurred and sometimes drop elongation to highly nonspherical
shapes, the latter apparently caused by anisotropic expansion of a dilute lamellar phase as it took up water. When such phenomena occurred, most of the drop dissolved rapidly, but a small amount, presumably enriched in the more lipophilic species, took longer to dissolve.

While the previous work showed that transition to the more complex dissolution mechanism occurred as the cloud point was approached, it did not include investigation of the effect of differences in solubility of the surfactants in a mixture, e.g., differences in EO number for a given hydrocarbon chain length. The results presented in section 3 provide some insight on this question. A C_{12}E_{4}/C_{12}E_{6} mixture has a cloud point of 30°C when the former is present at a concentration slightly less than 45 wt% (50.4 mol%). When C_{12}E_{4} content falls to 40 wt% (45.3 mol%), dissolution occurs without emulsification or elongation. For C_{12}E_{2}/C_{12}E_{8} mixtures the cloud point is 30°C when C_{12}E_{2} content is just below 30 wt% (45.7 mol%). When C_{12}E_{2} content drops to 26 wt% (40.8 mol%), complete dissolution occurs but is accompanied by emulsification. That is, emulsification is observed when the EO difference between surfactants is large but not when it is small for comparable composition changes from the cloud point. This result would be expected because the multiphase regions of the ternary phase diagram are presumably larger for larger differences in EO number.

As reported above, little difference in granule disintegration rate was seen for a C_{12}E_{4}/C_{12}E_{6} mixture containing 40 wt% C_{12}E_{4} and a C_{12}E_{2}/C_{12}E_{8} mixture containing 26 wt% C_{12}E_{2} even though the mechanism of dissolution of the neat surfactant drops was different in the latter case. Also total dissolution time t_d in the latter case was longer, even accounting for the differences in initial drop radius r_0 by assuming that t_d is
proportional to $r_0^2$. The reason is likely that, as indicated above, most of the surfactant dissolved rapidly even for mixtures where emulsification was observed. If a final, small portion of the granule disintegrated somewhat more slowly, it would have been hard to detect by the present techniques and is likely of little practical interest in any case. The same argument explains the rapid disintegration of C$_{12}$E$_8$/C$_{10}$OH (85:15, by weight) granules at 30°C and 35°C, where extensive emulsification and drop elongation were observed during dissolution of the neat surfactant mixtures.

Additional vertical contacting experiments were performed to try to understand why there was lag time for granules of C$_{12}$E$_5$/Zeolite 4A but not for those of C$_{12}$E$_6$/Zeolite 4A below the cloud point as reported in sections 2.2 and 2.3. Surfactant containing 5–10 wt % zeolite 4A was injected from the top of the cell and contacted with water (Figure 6.12). Since surfactant is in upper part of the cell, one would expect zeolite particles to settle as they are denser than both surfactant and water.

When such an experiment was performed for C$_{12}$E$_5$ at 30°C, a single, coherent lamellar (L$_\alpha$) intermediate phase formed at the surface of contact and prevented zeolite particles from entering the water, as shown schematically in Figure 6.12. In contrast, for C$_{12}$E$_6$ at 30°C, where lamellar, cubic, and hexagonal intermediate phases all developed, particles were able to pass through the liquid crystalline layer at a few sites and streamed downward there through the aqueous phase, as indicated in Figure 6.12. It may be that particles were unable to pass through the lamellar phase in the former case because they became trapped at nodes of the defect structure, as has been reported for 9.5 μm latex particles in the lamellar phase of an anionic surfactant [Basappa et al., 1999]. It is not clear why behavior is so different for C$_{12}$E$_6$. The lack of a coherent liquid crystalline
layer apparently allows particles to settle into the aqueous phase in the vertical cell experiment and to be released from the granule immediately in the granule disintegration experiment.

Figure 6.12 Schematic diagram of vertical contacting experiments of surfactant containing 5~10 wt% zeolite 4A particles with water.

Case 1: $C_{12}E_5$

Surfactant + 5~10 wt% zeolite 4A particles

Water

Case 2: $C_{12}E_6$

Particles distributed in all 3 intermediate phases

Particles streamed downward in the aqueous phase.
The trapping of particles within a coherent lamellar phase may be responsible for the lag time observed before disintegration of the C\textsubscript{12}E\textsubscript{5}/Zeolite 4A granule began. An approximate equation describing dissolution of a spherical drop of surfactant in water was obtained using Laplace transforms [Crank, 1975] and presented previously [Chen, 2000]:

$$u(r, t) = \frac{1}{2} \left[ \text{erf} \left( \frac{r + r_0}{\sqrt{4Dt}} \right) - \text{erf} \left( \frac{r - r_0}{\sqrt{4Dt}} \right) \right] + \frac{\sqrt{Dt}}{r\sqrt{\pi}} \left[ e^{-\left( r + r_0 \right)^2/4Dt} - e^{-\left( r - r_0 \right)^2/4Dt} \right]$$

(1)

where \( t \) is contact time, \( r_0 \) is initial radius of the spherical drop, \( r \) is radial position, \( D \) is the binary diffusion coefficient which is assumed to be independent of composition, \( \omega_\infty \) is the bulk composition at very large \( r \), \( \omega_0 \) is the initial concentration of the neat surfactant and \( u = \left( \omega - \omega_0 \right)/(\omega_0 - \omega_\infty) \).

By setting \( u \) equal to its value at the boundary between lamellar and aqueous (\( L_1 \)) phases, where surfactant concentration is 54 wt\%, one can predict the motion of this boundary as a function of time. The average diffusivity \( D \) will be smaller in the granules with their high solid content than in the solid-free surfactant/water system. Taking \( D = 1.0 \times 10^{-10} \text{ m}^2/\text{s} \), one finds from equation (1) that \( L_1/L_\infty \) boundary moves from 250 \( \mu \text{m} \) to 237.3 \( \mu \text{m} \) in 10 seconds. That is, the observed lag time of 10–15 seconds is the same order of magnitude as the time required to dissolve the lamellar phase in the pore space of first few layers of particles.

Figure 6.13 shows the predicted ratio of the radius of a C\textsubscript{12}E\textsubscript{5}/Zeolite 4A granule at 28°C to the initial radius as a function of time for various effective diffusivities. Since
granule disintegration appeared to be substantially complete in approximately two minutes in the experiments, this figure suggests an effective diffusivity of order $10^{10}$ m$^2$/s. The neat surfactant dissolution results [Chen, 2002] indicate an effective diffusivity of $2 \times 10^{10}$ m$^2$/s for the intermediate L$_{\alpha}$ phase in this system. As expected, it is slightly larger than when particles are present.

Figure 6.13 The ratio of granule radius of C$_{12}$E$_5$/Zeolite 4A at 28°C to the initial granule radius (250 μm) as a function of time.

8.2. Disintegration of granules made from commercial surfactants

Behavior for granules made with commercial nonionic surfactants and their mixtures is generally similar to that seen for pure surfactants and their mixtures, but there are a few exceptions, where disintegration occurred to a large extent even though dissolution of the neat surfactant is incomplete. i.e., mixture of Neodol 25-3 / Neodol 25-7=20/80 didn't dissolve completely in water, but disintegration of the corresponding
granules occurred to some extent. Granules made with Tergitol 15-S-7 also showed some
disintegration above cloud point. When we use commercial surfactants with broader and
more complex EO distribution than mixtures of pure surfactants, the behavior is not
simple and shows some difference.

It was found from study of the Unilever granules (item 1–9 in Table 6.3) that
addition of a solid, anionic surfactant such as PAS, FAES or sodium stearate can
significantly increase the rate of granule disintegration. Since the anionic surfactant
particles represent part of the solid content of the granules, their dissolution increases
granule porosity, which itself promotes granule disintegration. That is, making the
surfactant mixture more hydrophilic is not the only effect of using anionic surfactants in
granules. This behavior is of interest but was not explored further here. Granule
disintegration rate is also influenced by the type of zeolite, although this matter was also
not studied extensively in this work.
Chapter 7: Summary and Future Work

1. Dissolution rates of pure anionic surfactants.

The technique developed in the previous project at Rice in which interfacial positions were measured as a function of time during a penetration scan in a vertical cell was applied to several pure noncrystalline anionic surfactants. For highly soluble anionic surfactants, such as 5-phenyl undecyl sulfonate, dissolution was controlled by diffusion. For rather insoluble anionic surfactants with large miscibility gaps, such as pure AOT and 7-phenyl tetradecane sulfonate, myelins formed during the dissolution. When diffusion dominates, values for all the diffusivities can be obtained by combining results from the semi-infinite experiment with those of an experiment where a thin layer of surfactant was brought into contact with a large volume of water. When myelins form, a model including convection in the liquid phase and the swelling of the lamellar phase was developed. With this model, it was found that $D_{L\alpha} = 1.31 \times 10^{-10} \text{m}^2/\text{sec}$, $D_{V1} = 1.70 \times 10^{-10} \text{m}^2/\text{sec}$, $D_{H2} = 0.36 \times 10^{-10} \text{m}^2/\text{sec}$ for lamellar, viscous isotropic, and reversed hexagonal phases respectively of AOT by combining semi-infinite and thin layer vertical contacting experiments. Similarly, it was found that $D_{L\alpha 1} = 1.90 \times 10^{-10} \text{m}^2/\text{sec}$ and $D_{L\alpha 2} = 2.05 \times 10^{-10} \text{m}^2/\text{sec}$ for the two lamellar phases respectively for experiments in which 80% 7-phenyl tetradecane sulfonate contacted water. For 5-phenyl undecyl sulfonate and 6-phenyl dodecane sulfonate, effective diffusion coefficients can be obtained when the complete phase diagrams become available.
2. Dissolution behavior of surfactant mixtures and commercial surfactants

Drops of C_{12}E_4/oleic acid mixtures were injected into various alkaline buffer solutions at 30°C. Complete dissolution occurred at pH 11 and 12 when oleic acid content of the drop was at least 20wt%. Dissolution appeared to be diffusion controlled in both cases but was faster for pH 12. At pH 10 and the same oleic acid content the viscous lamellar phase, which persisted when pure C_{12}E_4 was injected into water, dissolved to form a surfactant-rich L_1 phase of low viscosity which coexisted with the aqueous phase at equilibrium. Formation of soap during the dissolution process made the overall surfactant mixture more hydrophilic, causing the lamellar phase which developed immediately upon injection to dissolve. While the same basic concept of making the surfactant mixture more hydrophilic was also responsible for the complete dissolution of C_{12}E_4/SDS mixtures observed in the previous project, the behavior here was, owing to different phase behavior and different dynamics involving continuous formation of soap, somewhat different involving a shrinking core mechanism with no spontaneous emulsification.

Drops of C_{12}E_4/oleic acid mixtures were injected into water. Lamellar phase was converted to L_3 or L_2 phase when oleic acid content was 25wt% and 20wt%. This conversion was much faster for 25wt% than that for 20wt%.

Dissolution behavior of C_{12}E_4/sodium oleate in water was also studied. Complete dissolution occurred when sodium oleate content was higher than 7wt%. With high concentration of sodium oleate (i.e. 15wt% or 17wt%), 'shrinking core' mechanism dominated. With lower concentrations of sodium oleate (i.e. 7wt% or 10wt%), the
lamellar phase was converted to a surfactant-rich phase with low solubility in water fairly early and spontaneous emulsification occurred, resulting in longer dissolution times. Thus, dissolution rates are highest when composition of the undissolved surfactant mixture remains below its cloud point and maintains a high solubility in water.

Dissolution of drops of various commercial nonionic surfactants was observed with results similar to those of previous work at Rice and Unilever.

3. Dissolution of neat surfactants and disintegration of corresponding granules.

A hanging drop slide technique was developed and used to observe behavior of individual granules contacted with water. The difference in observed behavior between granules made from swelling and nonswelling zeolites with non-ionic (but no anionic) surfactant was striking.

A practical way to make granules on a small scale was developed which made studies with pure nonionic surfactants feasible. Disintegration of granules made with such surfactants was studied to get better understanding of the relation between the dissolution of neat surfactant and corresponding granule. Our results show that disintegration occurred for surfactants or mixtures which dissolved completely in water. In particular, granules disintegrated below the cloud point of the nonionic surfactant or mixture. Little differences in disintegration time were seen for various systems. However, disintegration did not occur when the neat surfactant developed viscous myelinic figures upon contact with water. Nor was it observed when an aqueous phase coexisted with a surfactant-rich L₁ phase or L₃ (sponge) phase at equilibrium. Similar behavior was observed for granules
made with commercial nonionic surfactants and their mixtures, but there were a few exceptions, presumably due to broad and complex EO distribution, where disintegration occurred to a large extent even though dissolution of the neat surfactant was incomplete.

When two-dimensional beds of granules containing non-ionic surfactants and zeolites, i.e., beds only one granule thick, were contacted with water in a vertical cell, the granules rapidly disintegrated and the porosity of the original bed disappeared. An exception was the behavior of granules of $C_{12}E_2$/zeolite 4A and granules containing the swelling zeolite A24 etc, where void space between adjacent granules persisted. Disintegration was faster for more hydrophilic surfactants and surfactant mixtures, e.g., when some anionic surfactant was added.

4. Possibilities for future research

There are still some more interesting studies that could be done in the future. Further investigation of pure LAS isomers is of interest as complete phase behavior becomes available. More quantitative analysis for 7-phenyl tetradecane sulfonate and 5-phenyl undecyl sulfonate etc. could be obtained.

Dissolution of mixtures of linear alkylbenzene sulfonates is another interesting topic. During the dissolution of mixtures of nonionic surfactants, emulsification phenomena, are often encountered in those systems that are mixtures of hydrophilic and hydrophobic species dissolving in water at temperatures just slightly below their cloud points, i.e, commercial surfactant Tergitol 15-S-7 and pure surfactant mixtures $C_{12}E_2/C_{12}E_8$. Dissolution behavior of mixtures of pure LAS isomers could be studied to compare with dissolution of mixtures of nonionics.
Moreover, dissolution of mixture of a nonionic surfactant and LAS could be studied in the future, i.e., mixture of \( \text{C}_{12}\text{E}_4 \) with 5-phenyl undecyl sulfonate. To get good mixing, we can heat the sample to a high temperature, then cool it down and contact with water or maybe start with \( L_\alpha \) phase containing substantial water as in some liquid detergents.

Myelin formation could be observed for insoluble surfactants with wide miscibility gap between lamellar phase and micellar solution. Investigation of these phenomena could be conducted to further clarify the possible mechanism. For example, determination of myelin composition, perhaps by X-ray diffraction, would be of interest. So would further examination of the dependence of growth of myelins on initial defect structure in a lamellar phase and on details of the experimental technique such as the thickness of the cell used.
Reference


Chen, B H., PhD Thesis (Rice University, Houston, USA), 1998.


Faculty of engineering, Yokohama National University, *Oil Chemistry* 28, 627 (1979)


