



CHAPTER II

LITERATURE REVIEW

A middle-phase microemulsion can be produced by altering the HLB of the surfactant system by varying one of several system variables (e.g., electrolyte, temperature, surfactant, cosurfactant, and oil). Adjusting the system salinity while holding other variables constant is known as salinity scan. More details of methods for promoting phase changes have been described (Bourrel *et al.*, 1988). Due to the ultralow interfacial tension and super-high solubilization of middle phase microemulsion systems, this technique has been exploited in many applications such as enhanced oil recovery, surfactant enhanced subsurface remediation, biotechnology, pharmaceutical field and cosmetics (Solans and Kunieda, 1997).

2.1 Microemulsion Formation in Ionic and Nonionic Surfactant System

Shiau *et al.*, (1994) demonstrated that middle phase microemulsion formation by utilizing the mixtures of bis-ethylhexyl sulfosuccinate (AOT) and ethoxylated sorbitan esters with sodium mono- and dimethylnaphthalene sulfonate (SMDNS) as a cosurfactant could be achieved with chlorinated solvents. They also found that solubility enhancement in the microemulsification system was at least one to two orders of magnitude more efficient than solubilization for the same surfactant concentration.

Alkyl polypropylene oxide ether sulfate was also used to form three-phase microemulsion (Miñana-Perez *et al.*, 1995). It acts as an extended surfactant to increase the interactions on both the water and oil sides leading to an increase in solubilization. It was shown that high optimum solubilization parameters could be attained with hexadecane, ethyl oleate, C₈-C₁₀ triglyceride and soya oil. Another way to enhance the solubilization was reported by Salager *et al.*, (1998). Long-chain alcohol (above C₈) and their low ethoxylation derivatives were used as lipophilic linkers to improve oil solubilization. The best performance could be obtained when the lipophilic linker chain length is between the surfactant "tail" and the oil chain.

DOWFAX surfactant is one of the surfactant types used in enhancing subsurface remediation because it is very resistant to sorption and precipitation losses

(Deshpande *et al.*, 1999), but it is not as effective as others in enhancing contaminant solubility. Therefore, the solubility enhancement of DOWFAX components was investigated (Carter *et al.*, 1998). It was demonstrated that mixed surfactant system combined with electrolyte and isobutanol significantly increased solubility of tetrachloroethylene (PCE) by forming middle-phase microemulsion.

Arra *et al.*, (1999) discussed the effect of different electrolytes on the phase behavior of two anionic microemulsion systems as a function of temperature, salinity, and surfactant concentration. Optimal salinity was reached at lower salt concentration by using divalent cations than monovalent cations. The influence of reduced surfactant concentration on the shift in phase behavior is stronger for divalent cations than for monovalent cations.

Another approach for enhancing solubilization capacity of surfactant systems for hydrocarbon contaminants is to use “lipophilic and hydrophilic linkers” proposed by Uchiyama *et al.*, (2000). A considerable increase in the solubilization capacity of anionic surfactant system (sodium dihexyl sulfosuccinate or AMA) was observed. Using a combination of lipophilic (alcohol) and hydrophilic (SMDNS) linkers yields a strong synergism. Alcohol molecules provide strong interaction between surfactant and oil molecules, while SMDNS augments hydrophilic interaction between surfactant and water molecules.

The influence of polyols and short-chain alcohols were studied to improve oil solubilization in oil/water food grade microemulsions (Garti *et al.*, 2001). It was concluded that the oil solubilization capacity was dramatically improved by using a suitable nonionic surfactant together with polyols and short-chain alcohols.

In this research, mixed ionic-nonionic surfactant system of Dowfax 8390-AOT-sorbitan monooleate (Span 80) and sorbitan monolaurate (Span 20) was employed. Propylene glycol was also used to minimize the liquid crystal phase regions. Salinity scan was performed to drive the Type I microemulsion to Type III microemulsion.

2.2 Supersolubilization

Research on surfactant-enhanced subsurface remediation has been concentrating on minimizing surfactant losses, maximizing contaminant extraction, and implementing surfactant regeneration and reuse. It was recommended that the use of middle phase microemulsion systems should be avoided due to vertical migration concerns (Sabatini *et al.*, 2000). Therefore, the use of more efficient micellar systems well away from middle phase microemulsion system was proposed. Solubilization can be increased as high as possible (supersolubilization) without mobilizing trapped oil.

The salinity scan is commonly used to identify the supersolubilization regime for each surfactant system. It has been demonstrated that Winsor Type I solubilization is less efficient than the system exhibiting supersolubilization. Only a slight increase in removal efficiency can be achieved when the transition enters into the most efficient system which is Winsor Type III.

Wu *et al.*, (2000) used binary surfactant systems and nonalcoholic hydrotropes to formulate alcohol-free ADPODS middle-phase microemulsions for low temperature environmental applications. The mixed surfactants system consisted of mono-chain alkyl diphenyl oxide disulfonate (ADPODS) and di-tail AOT. Octanoic acid and L-tartaric acid were used as nonalcoholic hydrotrope. By using DOWFAX 8390 instead of C16MADS, middle-phase microemulsion with PCE could be produced by NaCl scan. Decane was also selected to represent a more hydrophobic oil. A higher optimal hardness, a wider three-phase region, and a smaller optimal solubilization parameter (about half of that of PCE microemulsion) were observed.

The C16MADS-AOT supersolubilization system shows an improvement of the PCE solubilization of 8.7 times greater than the original system. The C16MADS-AOT middle-phase microemulsion system enhances the PCE solubilization about 13 times the value for the untreated system.

In this study, supersolubilization system was exploited in detergency application because the low interfacial tension attained at this point is low enough to remove the oily soil from the fabric at room temperature. Another reason is the ultra-

low interfacial tension from middle-phase microemulsion might cause soil redeposition onto the fabric.

2.3 Oily-Soil Detergency

The washing efficiency of microemulsions were evaluated by Solans *et al.*, (1985). Higher washing efficiency of microemulsions was observed in comparison with 1 % aqueous solution of a commercial liquid detergent. Excellent soil removal was achieved in fabrics other than wool. Furthermore, addition of sodium tripolyphosphate or sodium citrate promotes remarkably the removal of soil.

Three principal mechanisms for removal of oily soils by surfactants are described by Rosen (1988). Removal of oily soil by aqueous baths is accomplished mainly by a “roll-up” mechanism in which the contact angle that the liquid soil makes with the substrate is increased by adsorption of surfactant from the cleaning bath. Many researchers have found that reduction of interfacial tension at the liquid soil-bath (γ_{OB}) and/or increase in θ , measured in the oily soil phase, correlates well with increase in detergency. In many cases, interfacial tension at the substrate-bath (γ_{SB}) is reduced to the point where $\gamma_{SB}-\gamma_{SO}$ is negative, with the resulting increase in θ to a value greater than 90° . Such a situation is illustrated in Figure 2.1.

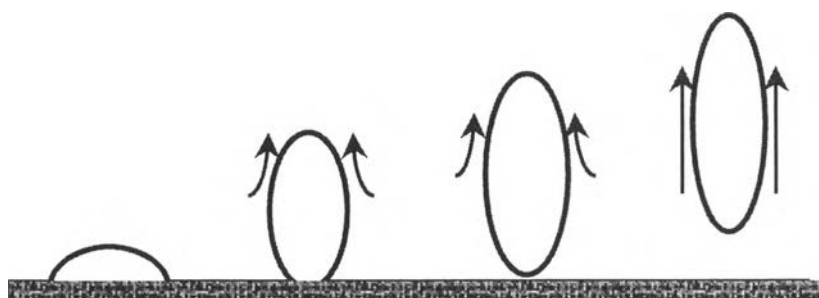


Figure 2.1 Complete removal of oil droplets from substrate by hydraulic currents when θ remains constant at $> 90^\circ$ (Rosen, 1988).

When the contact angle is less than 90° , partial drop detachment or “emulsification” occurs, even when it is subjected to the hydraulic currents of the bath

(Figure 2.2), and mechanical work or some other mechanisms are required to remove the residual soil from the substrate.

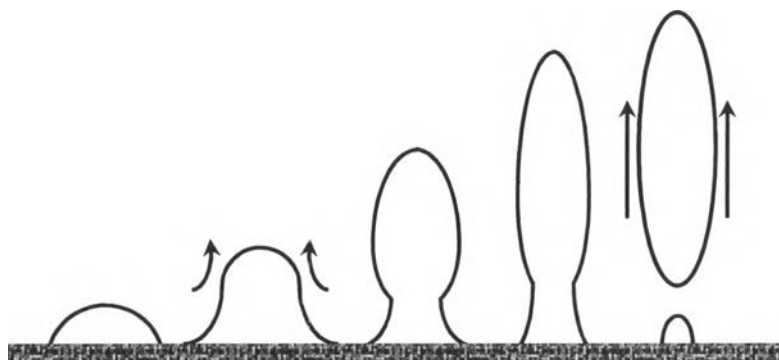


Figure 2.2 Rupture and incomplete removal of large oil droplets by hydraulic currents when θ remains constant at $< 90^\circ$. A small droplet remains attached to the substrate (Rosen, 1988).

The third mechanism is solubilization. The solubilization, or oil uptake capacity, of a surfactant system depends on the shape of the micelles. The oil uptake capacity of globular micelles is limited because the addition of oil necessarily results in an increase of the micelle surface exposed to water. Rodlike micelles are much better adapted to higher oil uptake. A surfactant forming rodlike micelles induces a lower oil-water interfacial tension and accordingly facilitates the transfer of oil from the substrate to the core of the micelles. The solubilization capacity of a given surfactant is maximum if the surfactant divides equally well between the water and the oily phase. In practice, this happens for a given surfactant system at a temperature referred to as the phase inversion temperature (PIT).

Therefore, a basic understanding of the primary mechanism of detergency at low temperature is an important aspect for the improved surfactant systems for soil removal. Raney *et al.*, (1987) found that the optimum temperatures correspond quite closely to the phase inversion temperatures of the ternary oil-water-surfactant systems. The combination of solubilization and emulsification was also proposed as the predominant mechanisms for oily soil removal rather than the roll-up mechanism.

The effect of polar soil components on the phase inversion temperature and optimum detergency conditions was also studied by Raney and Benson (1990). They proposed that the snap-off of oil drops supports the interfacial tension reduction at soil/water interface, thus influencing the removal of nonpolar/ polar soil mixtures. It was also suggested that a minimum quantity of polar material in the soil may be necessary to attain a high soil removal at the washing temperature.

Thompson (1994) reported a sharp detergency maxima which did not quite coincide with the interfacial tension minimum and therefore did not entirely confirm the correspondence of detergency maxima and interfacial tension minimum. Its failure to match the position of γ_{\min} is attributable to the low contact angle below 80° , which allows the fabric yarn containing a continuous oil phase. Double detergency maxima were also observed, one of them always corresponds to the minimum in γ_{ow} which promote the emulsification mechanism of oil removal. Whereas a second detergency maximum is attributable to the roll-up mechanism.

Relationship between interfacial tension and detergency was also studied by Dörfler *et al.*, (1996). The optimum detergency of the microemulsion systems under studied corresponds to a minimum of the interfacial tension of $\approx 10^{-3}$ mN m⁻¹ between the microemulsion and the water or oil excess phase in the heterogeneous regions of the phase diagram. From this work, comparison between the detergency of already formed microemulsions containing commercial grade components of water/n-undecane-/C_{12/14} alkylpolyglycol ether/n-pentanol and that of a standard detergent solution was evaluated. The information obtained shows that samples from microemulsion region have a bicontinuous sponge-like structure and exhibit ultralow interfacial tension with maximum solubilizing power.

Another detergency study was conducted in order to identify factors contributing to the difficult removal of used motor oil from textile materials (Chi *et al.*, (1999). It was shown that the aging process of soil does not appear to chemically affect the used motor oil. The used motor oil is not easy to remove by laundering. Radiotracer analysis shows that the color of the used motor oil-soiled fabric correlates well with the amount of oil that is present on the fabric.

To evaluate the efficiency of soil removal in this study, the incorporation of an oil-soluble dye was utilized. Moreover, the amount of the retained oil in the fabric after washing was determined by solvent extraction and quantitative analysis by UV-VIS spectrophotometer.