

CHAPTER II

LITERATURE SURVEY

2.1 Microemulsion

Microemulsions are thermodynamically stable dispersions of two immiscible liquids, i.e. water and oil. Holar and Schulman (1943) first introduced this term to describe transparent or translucent, thermodynamically stable systems obtained by titration of an ordinary water-hydrocarbon emulsion as microemulsion.

Microemulsion systems can be classified into four groups: Winsor type I, Winsor type II, Winsor type III, and Winsor type IV as shown in Figure 2.1. In Winsor type I system, an oil-in-water (O/W) microemulsion coexists with an excess oil phase and the surfactant molecules mostly present in aqueous phase whereas surfactant aggregation is in the form of normal micelle. For Winsor type II system, a water-in-oil (W/O) microemulsion is in equilibrium with an excess water phase and the surfactant molecules mostly participate in oil phase in the form of reverse micelle. The Winsor type III system consists of middle phase microemulsion, excess oil phase, and excess water phase. The middle phase microemulsion is a surfactant-enriched solution with solubilized oil and water. The orientation of surfactant molecules in Winsor type III system is in a bicontinuous form. Upon addition of an adequate amount of surfactant, microemulsion phase solubilize all the excess oil and excess water in the system and Winsor type IV or a single-phase microemulsion is found.

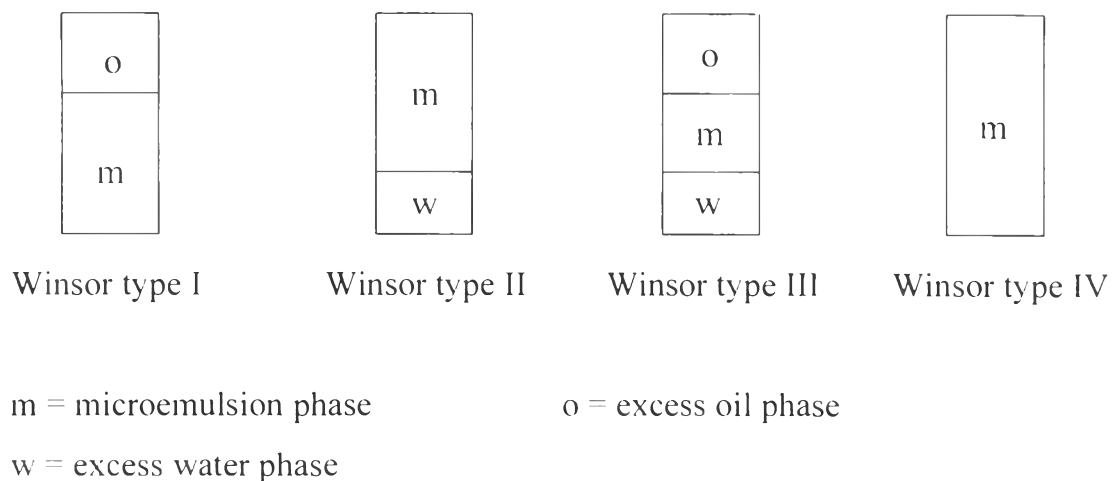


Figure 2.1 Schematic of microemulsion types.

Studies of microemulsion systems have been intensively carried out in 1970s in order to develop enhanced oil-recovery processes. Salager (1999) reported that some systems, so-called optimum for oil recovery, related to very unusual surfactant self-assembly structures, i.e. bicontinuous structure. Some of these structures have many potential applications in other fields such as detergency, polymerization, food processing, displays, cosmetics, and pharmaceuticals because they are associated with exceptional physicochemical properties such as extremely low interfacial tension and high solubilization.

Surfactant Enhanced Aquifer Remediation (SEAR) is one of the microemulsion applications for cleaning up organic contaminant. Because microemulsion formation gives two different mechanisms for removal of subsurface contaminant: surfactant-enhanced solubilization and surfactant-enhanced mobilization, utilizing surfactants in pump-and-treat or ex-situ soil washing techniques can substantially increase an efficiency of traditional processes by decreasing the time and saving the cost when properly implemented (West and Harwell, 1992).

Microemulsion formulation typically composes of surfactant, cosurfactant, water, oil, and electrolyte. Alcohols are normally used as a cosurfactant in microemulsion systems. Aboofazeli *et al.* (1995) studied microemulsion system composed of lecithin, water, and oil by using propanol and butanol as cosurfactants. Gizurarson *et al.* (1995) found that alcohols i.e. pentanol, can promote a formation of microemulsion consisted of didodecyldimethyl ammonium bromide (DDAB), dodecane, and water. Thevenin *et al.* (1997) formed a microemulsion containing sucrose ester as surfactant and alcohols with carbon atom from 3 to 8 as cosurfactant. Benito *et al.* (1997) used n-propanol and n-butanol as cosurfactant in the microemulsion formulation, which has sodium dodecylsulfate and cetyldimethylammonium bromide as surfactants in the system. Maidment *et al.* (1997) showed that adding pentanol into microemulsion can enhance the range of microemulsion stability. Miksik *et al.* (1997) reported the use of microemulsion containing sodium dodecylsulfate, n-octanol, n-butanol, and water to extract diphenylhydrazone from dicarbonyl sugar by using microemulsion electrokinetic chromatography. Shiao *et al.* (1998) showed that high alcohol content was necessary for stabilizing the microemulsion system at high ratio of oil to soap. Jimenez-Carmona and Lague de Castro (1998) found that using 1-butanol as cosurfactant in Winsor type II microemulsion can enhance the efficiency of supercritical fluid extraction.

Because microemulsions have been used in many environmental applications, therefore, recent technological studies aim to the use of environmentally friendly substances in microemulsion systems. Many research works have paid attention to the alcohol-free microemulsion systems since alcohols are volatile organics and flammable substances (Ash and Ash, 1997b). Sjoblom *et al.* (1991) studied microemulsion system composed of octanoic acid, sodium octanoate, electrolyte, water, and n-heptane. Sunwoo and Wade (1992) prepared alcohol-free microemulsion system by mixing

ethoxylated and propoxylated C₁₄ Guerbet alcohol, n-octane, n-decane, or n-dodecane and water. Lang *et al.* (1992) evaluated the droplet size of dispersed phase in microemulsion type II composing of fatty acid with alkyl chain length ranging from 3 to 9, surfactant (dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, or hexadecyltrimethylammonium bromide), chlorobenzene, and water. Kahlweit *et al.* (1995a) proposed nontoxic microemulsion formulation consisting of unsaturated fatty acid ethyl ester, long-chain soy bean lecithin, pentane-1,2-diol and sodium chloride. Kahlweit *et al.* (1997) presented nontoxic microemulsion formulation, which have isopropyl myristate, epikuron, C₅-diol, and water. Meziani *et al.* (1997) used aldehyde instead of alcohol as a cosurfactant and studied the ternary phase diagrams of water/SDS/aldehyde and compared to the corresponding alcohol systems. The results showed that the ternary phase diagrams of aldehyde was similar to that of alcohol. Solans and Kunieda (1997) used polyglycerol and ether phosphate as cosurfactant in place of alcohol in fragrance product, which has polyethylene glycol derivatives as surfactant because alcohol is harmful to the skin. Osborne *et al.* (1998) proposed alcohol-free microemulsion composed of water, hexadecane, dioctyl sodium sulfosuccinate and sorbitan laurate to use in pharmaceutical application. Aowiriyakul (1998) studied the use of octanoic acid as cosurfactant in microemulsion consisted of DOWFAX 8390, perchloroethylene, sodium chloride or calcium chloride, and water.

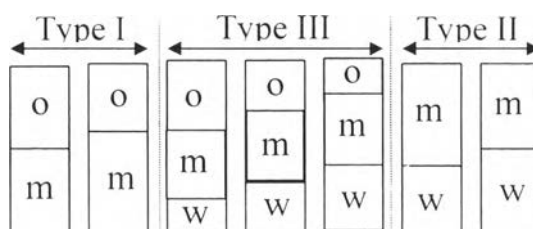
2.2 Phase Diagram

Phase diagrams provide a simple perspective of phase behavior or Winsor phase boundaries for microemulsion systems as a function of composition and temperature. It is necessary to study a phase diagram for evaluating the application of microemulsion. There are many ways to

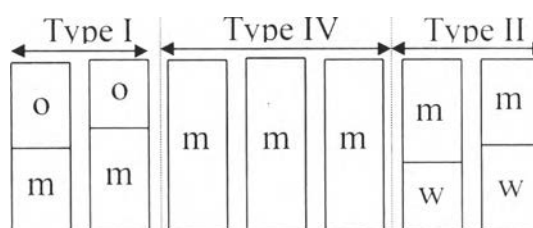
illustrate the phase diagram, i.e. two-dimensional, three-dimensional, and multidimensional phase diagrams. The two-dimensional phase diagram is the easiest one to draw and interpret.

Surfactant concentration has an effect on the phase behavior of microemulsion, which reflects in the salinity requirement diagram. For microemulsion systems containing ionic surfactant, increasing the electrolyte concentration in the system results in the phase transition of microemulsion from Winsor type I to III to II at low surfactant concentration and I to IV to II at high surfactant concentration as shown in Figure 2.2.

a. LOW SURFACTANT CONCENTRATION



b. HIGH SURFACTANT CONCENTRATION



m = microemulsion phase o = excess oil phase

w = excess water phase

Figure 2.2 Schematic illustration of phase transition for microemulsion containing equal volume of aqueous phase and oil phase.

2.3 Solubilization

The enhanced solubility of a compound associated with the micelle or inverted micelle formation has been termed “solubilization”. Because the solubilization of either oil or water into the microemulsion phase is the main purpose in preparing microemulsions, their ability to solubilize is an important property. Moreover, the solubilization capacity is another critical factor in selecting the preferred microemulsion system. Healy and Reed (1976) defined the solubilization parameter as:

$$SP_o = V_o/V_s \quad (2.1)$$

and
$$SP_w = V_w/V_s \quad (2.2)$$

where SP_o and SP_w are solubilization parameters for oil and water, respectively; V_o and V_w are solubilized volumes of oil and water, respectively; and V_s is the volume of surfactant in the microemulsion phase excluding the cosurfactant volume (if present).

Wu (1997) presented a modified oil solubilization parameter as solubilized oil volume per unit mass of surfactant as follows:

$$SP_o = V_o/M_s \quad (2.3)$$

where M_s is the total mass of surfactant(s) present excluding the mass of cosurfactant. Figure 2.3 shows a typical variation of the solubilization parameter of oil and water for microemulsion prepared from ionic surfactant as a function of electrolyte concentration, which promotes the I-III-II phase transition. The volume of dissolved oil in the aqueous continuous phase is very small at low electrolyte concentration. An increase in the salinity results in an increase in the solubilization of oil in Winsor type I system while the

solubilization of water is essentially constant because virtually all the water is contained in the microemulsion phase. In Winsor type III regime, water is expelled from the microemulsion phase and SP_w begins to decrease. At the same time, the oil uptake in microemulsion phase continues to increase up to the point where Winsor type II is obtained and all the oil present in the system is solubilized. At this point, SP_w is seen to decrease and SP_o is constant, regularly.

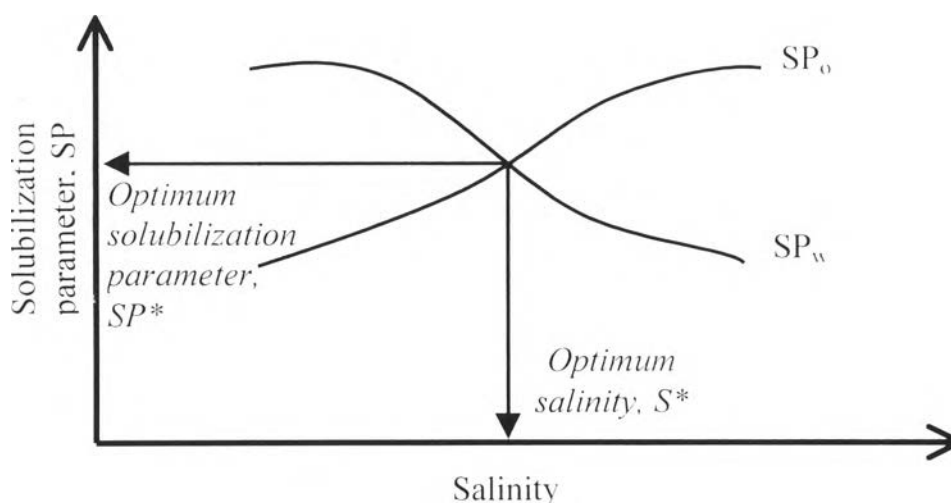


Figure 2.3 Solubilization parameter as a function of salinity.

The SP_o and SP_w curves intersect inside the three-phase region. At the intersection point, the microemulsion contains equal amounts of water and oil and the corresponding condition is noted as optimum condition. The corresponding solubilization parameter and electrolyte concentration are referred as optimum solubilization parameter (SP^*) and optimum salinity (S^*), respectively.

2.4 Electrical Conductivity of Microemulsion

In general, electrical conductivity is used to determine which phase (water or oil) is the continuous phase because this measurement is often

decisive. Oil-in-water emulsion yield water-like solution electrical conductivity, and vice versa. Micellar solution exhibits intermediate conductivities and the electrical conductivities attending the phase transition of microemulsion have been reported in three features. Bourrel and Schechter (1988a) found that when the phase transition occurred by increasing salinity, the conductivity of microemulsion continuously decreased due to the gradual change in the proportions of oil relative to water in microemulsion phase. In addition, if liquid crystals, gels, or even high-viscosity Newtonian fluids exist along any one of the scans, the electrical conductivity may exhibit both maxima and/or minima, reflecting the changes in the ion mobility caused by variations in viscosity. They also concluded that the conductivity of microemulsion might change trivially if the micellar phase structure does not change markedly.

2.5 Interfacial Tension of Microemulsion

Interfacial tension is the minimum amount of work required to create unit area of the interface or to expand it by unit area. It is a very important property of microemulsion systems because low interfacial tension between oil and water phases are required in a number of applications and microemulsion systems always give the desired state. When microemulsion is formed, one phase in the system breaks up into very small droplets reflecting the low interfacial tension in the system and resulting in the large amount of interfacial area between two immiscible phases. The low interfacial tension has the origin in two different mechanisms. First, interfacial surfactant orients itself with the hydrophilic group toward the water and the hydrophobic group toward the oil causing the interfacial tension between oil and water phases to decrease. This mechanism is the prominent one as the concentration of the surfactant is increased until micelles form. At this point, further increase in

the surfactant concentration will not lower the interfacial tension because the chemical potential of surfactant is essentially constant almost independent of concentration. Another mechanism helps the system to create the low interfacial tension. Certainly, as two phases approach a critical endpoint, the interfacial tension between them vanishes. Ultralow interfacial tensions may be thought to originate at critical points.

Measurement of the interfacial tension is accomplished readily by a number of methods, for example, drop-weight method, Wilhelmy plate method and spinning drop method. A typical result related to the microemulsion phase transition by salinity scan is shown in Figure 2.4. The interfacial tension between microemulsion and oil phases (γ_{mo}) is seen to decrease when the electrolyte concentration is raised, while the interfacial tension between microemulsion and water phases (γ_{mw}) increases. The two curves intersect inside the Winsor type III region and the corresponding system has been designated as optimum condition. The value of interfacial tension at the intersection point is denoted as optimum interfacial tension (γ^*) where $\gamma_{mo} = \gamma_{mw} = \gamma^*$ and the value of electrolyte concentration is noted as optimum salinity (S^*).

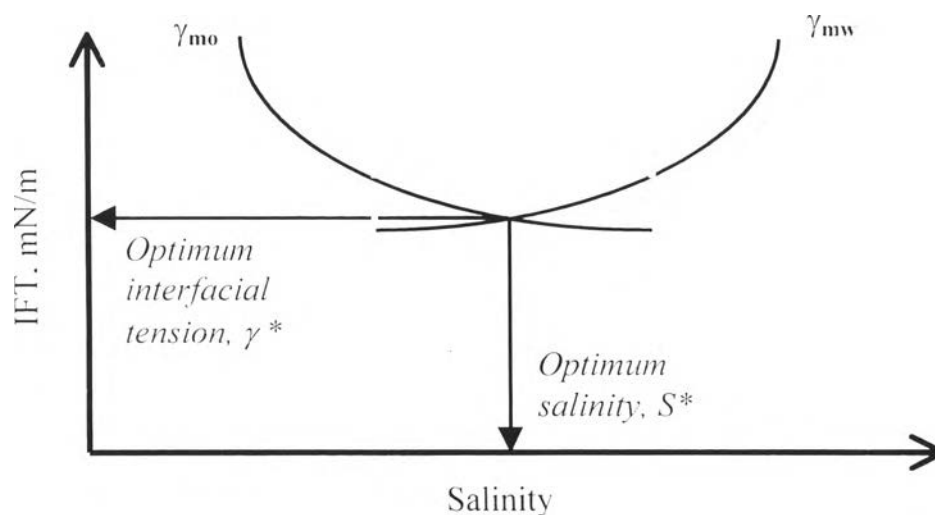


Figure 2.4 Interfacial tension as a function of salinity.