

CHAPTER II

LITERATURE SURVEY

2.1 Surfactant

Surfactant is an abbreviation of "surface active agent". Surfactant is a molecule having two distinct groups which differ greatly in their solubility relationship. They consist of a hydrophilic, or water soluble, moiety (head group) and a hydrophobic, or water insoluble, moiety (tail group), as shown in Fig 2.1. This structure is known as amphiphilic and surfactants are considered to be amphiphiles. Depending on the charge associated with the hydrophilic head group, the surfactants can be classified into four main classes: anionic (negative), cationic (positive), nonionic (no charge), and zwitterionic (both positive and negative) (Rosen, 1989).

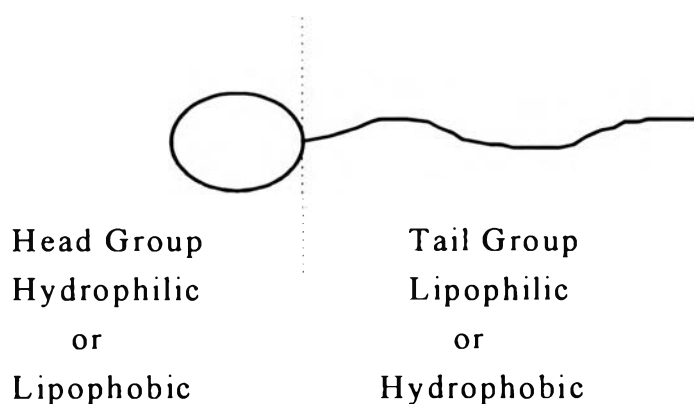


Figure 2.1 Schematic of surfactant monomer.

Surfactant behavior depends on its aqueous concentration. At low concentrations, surfactants are present in a solution as monomers. Surfactants do exactly what their name implies; they accumulate at the surface, thereby altering the interfaces which they contact. Surfactants are thereby able to decrease interfacial tension, thus mobilization occurs. As the surfactant concentration increases above a certain concentration, the surfactant monomers aggregate to form aggregates known as micelles. This concentration is known as the critical micelle concentration (CMC). (Figure 2.2 and Figure 2.3) The hydrophobic portion of the surfactant is repelled by water, whereas the hydrophilic portion exposes to water. From this nature of surfactant structure, surfactants quite often form spherical micelles with the hydrophobic portion on the interior, organic or oil-like environment, and the hydrophilic portion on the exterior. The center core of micelle has properties of a oil pseudo-phase, so organic contaminants can partition into the core of micelles. As the number of micelles in the solution increases, solubilization increases. Surfactant concentrations above the CMC can dramatically enhance the aqueous solubility of hydrophobic organic compounds (Kile and Chiou, 1989; Edwards et al., 1991; West et al., 1992).

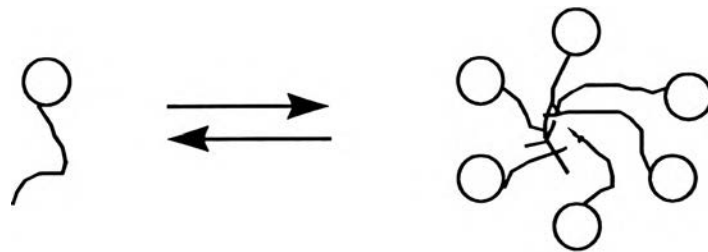


Figure 2.2 Schematic of monomer and micelle equilibria.

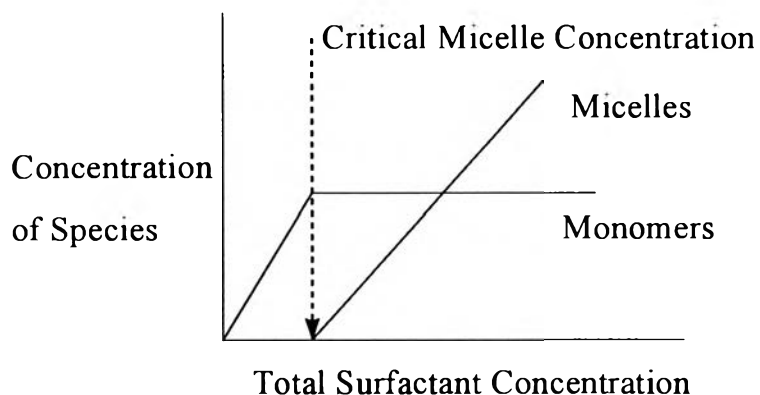


Figure 2.3 Surfactant monomer and micelle concentration as a function of total surfactant concentration.

Gemini surfactants are surfactants that have two hydrophilic groups and two hydrophobic groups per molecule, which differs from conventional surfactants (a single hydrophilic and single hydrophobic groups) (Figure 2.4). The unexpected properties of geminis include the unusually low CMC (Rosen, 1993). The lower the CMC, the easier is micelle formation and the higher the solubilization capacity on a unit mass basis.

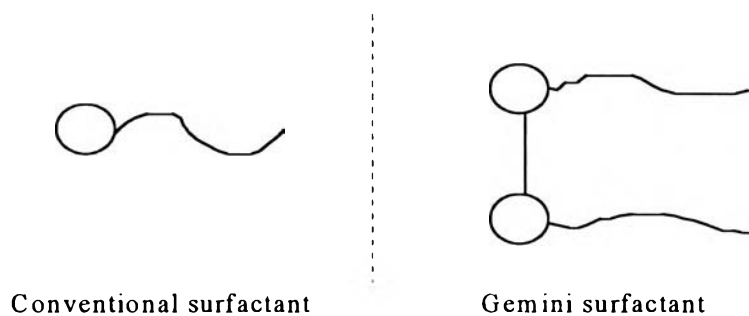


Figure 2.4 Simplified representation of surfactant structure.

2.2 Microemulsion

The term microemulsion was first introduced to describe transparent or translucent, thermodynamically stable systems obtained by titration of an ordinary water-hydrocarbon emulsion (Hoar and Schulman, 1943). Alcohols and electrolytes (e.g., sodium and calcium salts) can be added to form a middle phase microemulsion, and these titrations are known as salinity or hardness scans.

With addition of a suitable composition, containing a surfactant concentration above the CMC, at appropriate electrolyte and co-surfactant concentrations, oil and water can be emulsified to four types of microemulsion. The number of phases that appear can determine the system type. Type I and II systems exhibit two phases, Type III system exhibits three phases, and Type IV systems exhibit a single phase (Figure 2.5). The classification of a microemulsion system will depend on the surfactant concentration, whether it is mostly present in which phase. In a Type I system, an oil in water (O/W) microemulsion micellar solution coexists with an excess oil phase and the surfactant is mostly present in the aqueous phase. In a Type II system, a water in oil (W/O) microemulsion reverse micellar solution coexists with an excess aqueous phase and the surfactant is mostly present in the oil phase. In a Type III system, a middle phase microemulsion which contains surfactant enriched with solubilized water and oil, coexists with both excess phases. Upon addition of a sufficient quantity of surfactant, a single-phase (Type IV) system is found. There is no appearance of a phase boundary, and all compositions are soluble (Winsor, 1954; 1984).

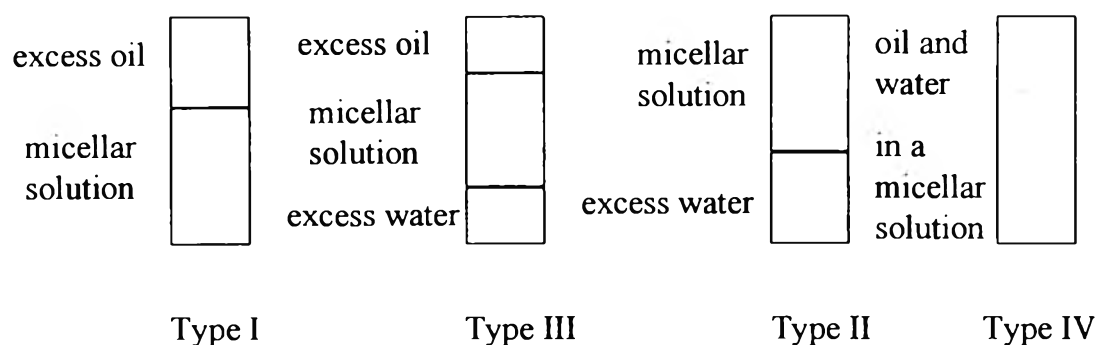


Figure 2.5 Schematic of microemulsion types.

The solubilization capacity of a middle phase microemulsion is another critical factor in selecting the preferred surfactant system. Reed and Healy (1997) define the solubilization parameters as:

$$SP_O = V_O/V_S \quad (1a)$$

and

$$SP_W = V_W/V_S \quad (1b)$$

where SP_O and SP_W are solubilization parameters for oil and water, respectively; V_O and V_W are volumes of oil and water solubilized in the micellar solution, respectively; and V_S is the volume of surfactant in the micellar solution, excluding the alcohol volume (if used).

A modified oil solubilization parameter was used in this study. The solubilization power is defined per surfactant unit mass rather than per unit volume, as follows:

$$SP_o = V_O/M_S \quad (2)$$

where M_S is the total mass (moles) of surfactant(s) present. In this definition alcohol mass is also excluded in calculation of M_S . However, when other surfactants are used as cosurfactants, they are included in calculating (Wu et al., 1997).

The solubilization parameters, SP_o and SP_w , curves, intersect inside the three-phase domain. At this point the micellar phase contains equal amounts of water and oil and the corresponding solubilization parameter is noted as an

optimum solubilization parameter for both oil and water, SP^* , an optimum salinity (s^*) for the concentration of salt. According to the definition at optimum salinity (s^*):

$$SP_o = SP_w = SP^* \quad (3)$$

The optimum system is a system which the minimum quantity of amphiphile and salinity can solubilize all volumes of oil and water to achieve a single phase. Certain applications may require system other than type III. The performance at optimum can be used as a guide to select an appropriate surfactant for contaminant mobilization.

2.3 Microemulsion Formation

Forming a middle phase microemulsion requires a delicate balance among surfactant type and concentration, co-surfactant, oil, electrolyte, and temperature. When applying microemulsions in industry or research, in general, the temperature of application, T_{exp} , the composition of the oil, and that of brine are prescribed. Wanted is an efficient amphiphile for preparing the desired type of emulsion at these particular conditions. The separation into three liquid phases is a consequence of a rapid inversion of the distribution of the amphiphile (C) between oil (B) and water (A) (Kahlweit and Strey, 1985). Defining the distribution coefficient (at mean composition above the CMC) by

$$K_C \equiv c_B/c_A \quad (4)$$

at ambient temperature both nonionic and ionic amphiphiles are much more soluble in water than in oil, i.e., $K_C \ll 1$. Where $c_B \equiv$ concentration of amphiphile in the oil and $c_A \equiv$ concentration of amphiphile in the water. With ionic amphiphiles, K_C decrease with increasing temperature so that $K_C \ll 1$ at all temperatures (Figure 2.6). For overcoming the counteracting effect of

thermal energy, the distribution inversion of ionic amphiphiles must, therefore, be enforced by salting out the amphiphile from the water into the oil. The addition of salt is considered indispensable (Kahlweit, 1995). Recent study has shown that to form microemulsions of ionic surfactant which contains a single hydrocarbon chain (e.g. sodium dodecylsulphate, SDS), the addition of a co-surfactant (e.g. a medium size aliphatic alcohol) and electrolyte is considered to be indispensable. With a double chain ionic surfactants (e.g. Aerosol OT, AOT), the presence of a co-surfactant may not be necessary (Lekkerkerker et al., 1996).

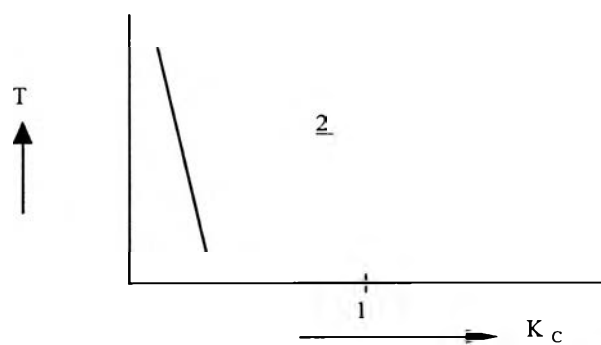


Figure 2.6 Schematic of temperature dependence of the distribution of ionic amphiphiles between oil and water in salt-free mixture (Kahlweit, 1995).

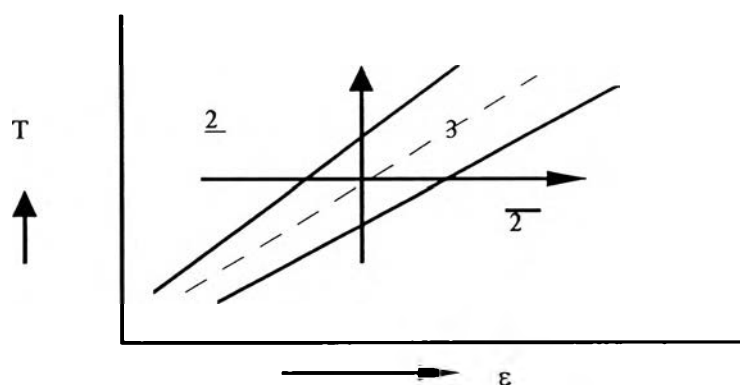


Figure 2.7 Schematic of salting out of amphiphiles: T - ϵ cusp for ionic amphiphile.

Kahlweit (1995) summarized recipes for how to systematically search for appropriate amphiphiles. At fixed oil and amphiphile, the amount of salt required for traversing the three-phase salt interval ($\Delta\varepsilon$) increases with decreasing K_C . Hence, on a T - ε plot –with ε denoting the salt concentration in brine– $\Delta\varepsilon$ shapes a cusp that ascends and widens with ionic amphiphiles (Figure 2.7). For fixed temperature and oil, the amount of salt required decreases with increasing lipophilicity of the amphiphile, which makes the cusp in figure 2.7 move to the left. In this work, preparation of ionic microemulsion formation at prescribed T_{exp} , oil, and ε by using a sufficiently lipophilic double-tailed ionic amphiphile, and varying its effective lipophilicity by mixing it with either a less lipophilic or a more lipophilic ionic amphiphile has been demonstrated by using Kahlweit recipes.