CHAPTER II

BACKGROUND & LITERATURE SURVEY

2.1 Surfactants

Surface active agents or surfactants are amphiphilic molecules. They have both polar and non-polar characteristics in the same molecule. Therefore, a surfactant molecule has both hydrophilic (water-loving) and hydrophobic (water-hating) characteristics. Symbolically, a surfactant molecule can be represented as having a polar "head" and a non- polar "tail" as shown in Figure 2.1.

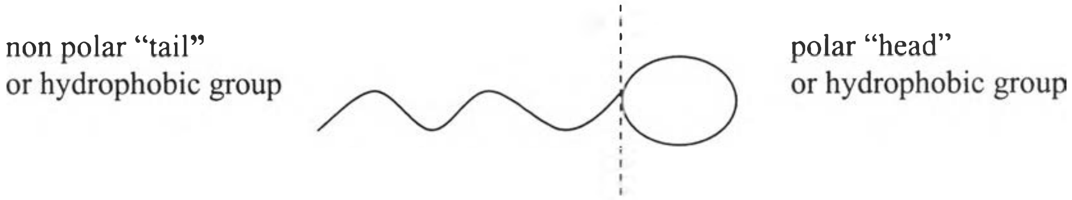

Figure 2.1 Structure of surfactant molecule

Surfactants fall to the following classifications according to the nature of the hydrophilic group:

- Anionic: hydrophilic head is negatively charged.
- Cationic: hydrophilic head is positively charged.
- Nonionic: hydrophilic head is polar but not charged.
- Zwitterionic: molecule has both potential positive and negative groups; charge depends on pH of the medium.

The amphiphilic nature of surfactant molecules causes them to accumulate at interface. Furthermore, surfactant molecules can self-assemble into dynamic aggregates known as micelles. The surfactant concentration at which the first micelle is formed is known as the critical micelle concentration (CMC). Beyond the CMC, any surfactant added to aqueous solution does not increase the number of surfactant monomers in aqueous solution, but rather will contribute to the formation of additional micelles.

2.2 Anionic and Cationic Surfactant Mixtures

At low aqueous concentration of anionic and cationic surfactants, each surfactant completely dissociates and exists only as ionic monomers. As the surfactant concentration increases, micelles begin to form when the CMC is reached. Liquid crystal or precipitate phases will occur whenever the monomer concentration of anionic and cationic surfactants exceed the solubility product. There are two basic equilibria in solutions of anionic-cationic surfactant mixtures: monomer-micelle equilibrium and monomer-precipitate equilibrium (Stellner *et al.*, 1988; Amante *et al.*, 1991; Scamehorn and Harwell, 1993). The schematic diagram in Figure 2.3 demonstrates this point.

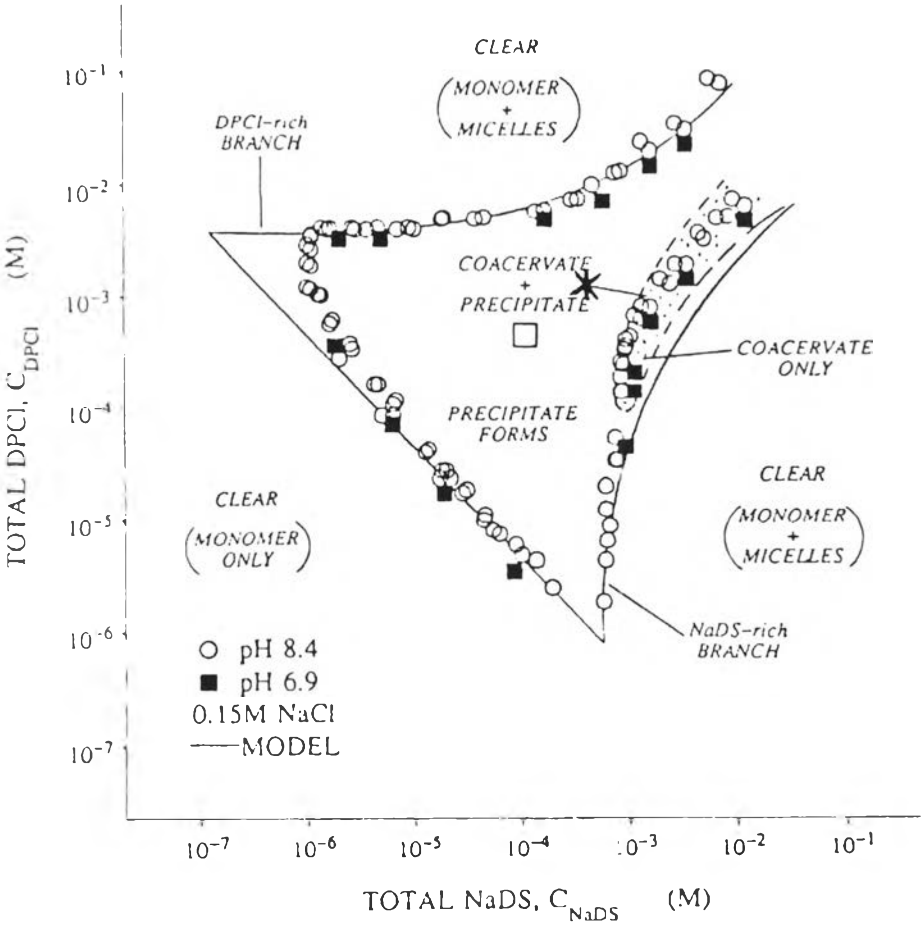

Figure 2.2 Schematic of the precipitation phase diagram in a mixture of an anionic and a cationic surfactant (Stellner *et al.*, 1988).

From Figure 2.2, a monomer-precipitate equilibrium curve indicates where no micelles exist in solution, and two branches (one anionic-rich and one cationic-rich) are where monomer, micelles, and precipitate occur in equilibrium. The negative slope represents the monomer-precipitate equilibrium or solubility product of the solution. These sharp breaks along the phase boundary correspond to the points where micelles begin to form in the solution.

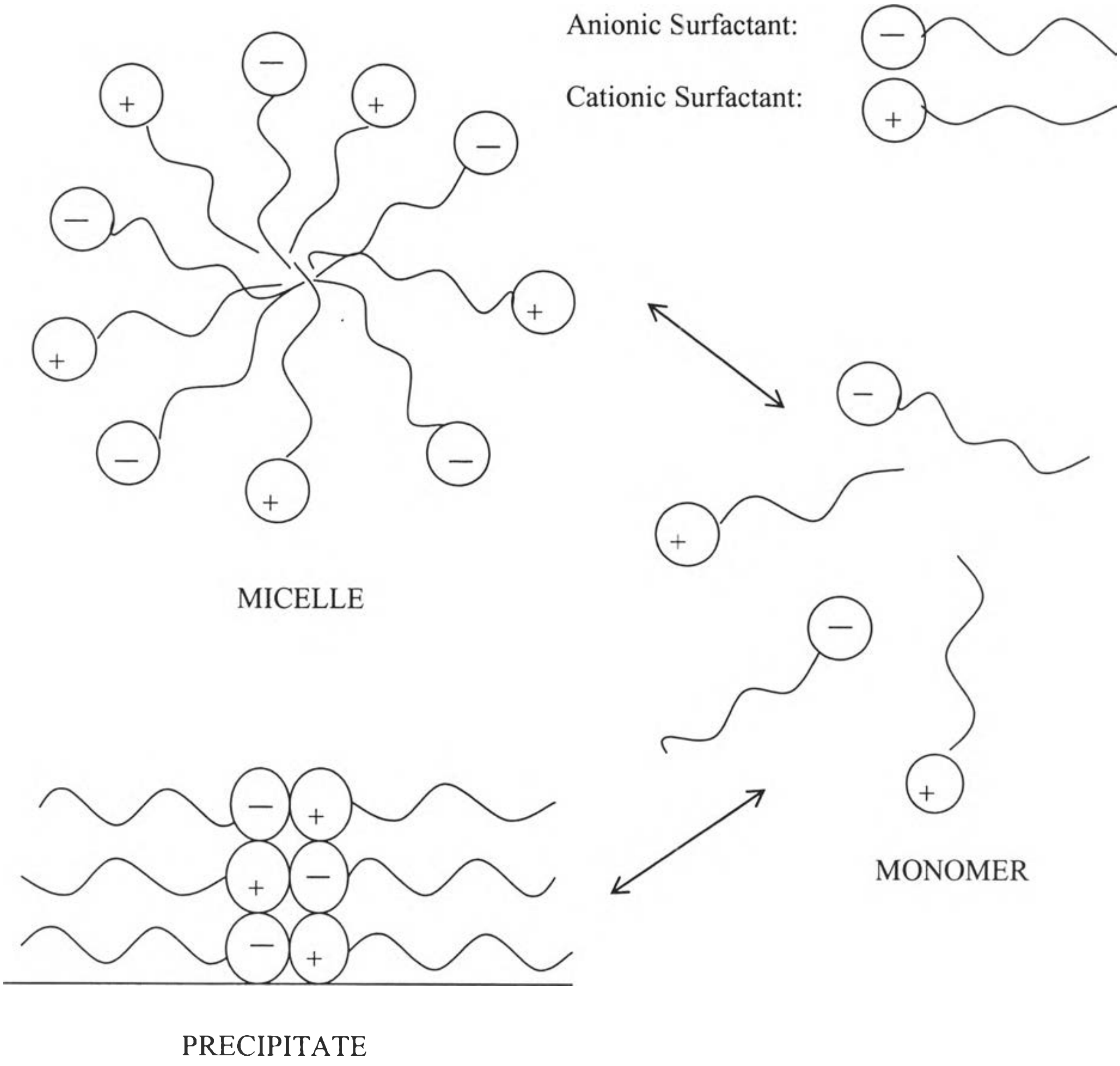

Figure 2.3 Schematic of the equilibrium in a micellar system containing anionic surfactant and cationic surfactant which precipitate forms (adapted from Stellner *et al.*, 1988).

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As shown in Figure 2.3, the anionic and cationic surfactants can be present in three environments: as a monomer, in mixed anionic-cationic micelles; and as precipitate. The counter ions (Na^+ and Cl^-), which have been excluded from Figure 2.3 for clarity, can be bound onto the micelle surface or present as unassociated ions in solution (Stellner *et al.*, 1988).

The mixtures of anionic and cationic surfactants can also be expressed in the association reaction as the equilibrium:

$$A^- + C^+ \rightleftharpoons AC \qquad (2.1)$$

where A^- is an anionic amphiphile and C^+ is a cationic amphiphile, while the counterions are not mentioned. If the anionic surfactant is some sodium sulfonate $R'\text{-}SO_3^-Na^+$, and the cationic one is an alkyltrimethylammonium chloride $R''(CH3)_3\ N^+Cl^-$, then A^- stands for $R'\text{-}SO_3^-$while C^+ indicates $R''(CH3)_3\ N^+$. The AC association compound, has been referred to as a catanionic structure (Kumar and Mittal, 1999; Marques *et al.*, 1993).

The strong electrostatic interaction between the oppositely charged head groups may lead to significant changes in the behavior of the overall surfactant solution and evidence the non-ideal effects in the aggregate. Physical properties, such as the CMC and interfacial tension, are lowered substantially in mixed anionic-cationic surfactant versus either individual surfactant (Holland and Rubingh, 1990; Tomastić *et al.* 1991; Herrington *et al.* (1993); Li *et al.*,1999; Li and Kunieda, 2000; Bergstrom, 2001; Kang *et al.*, 2001; Doan, 2002; Raghavan *et al.*, 2002). Mixed micelles in anionic-cationic surfactant systems are different from their ionic surfactant component and behave like those of nonionic surfactants, which exhibit a lower boundary and hence have been called “pseudo nonionic”. In an ideal system, the mixed CMC is always intermediate in value between the CMCs of the two pure surfactants. In the anionic-cationic surfactant system, the mixed CMC is much lower than that of the ideal mixture (Scamehorn and Harwell, 1993; Doan, 2002).

Among the large body of work concerned with the mixtures of various surfactants, the investigation of blends of cationic and anionic surfactant has only recently been developed, even though the existence of anionic-cationic mixed micelle has been known for a long time. From the standpoint of industrial applications, formulations involving mixtures of anionic and cationic surfactants have been claimed in a number of recent patents (Bourrel and Schechter, 1988) e.g., in pharmacy, analytical chemistry, waste water treatment, and detergency (Stellner *et al.*, 1988).

Stellner *et al.* (1988) evaluated precipitation phase boundaries of anionic and cationic surfactants over a wide range of surfactant concentrations for a sodium dodecyl sulfate (SDS)-dodecyl pyridinium chloride (DPCl) mixture. This system showed a pronounced increase of solubility due to the formation of DP/DS mixed micelles characterized by the interaction energy parameter W= -8.6RT. As expected, this value is higher than one obtained for the interaction of nonionic/anionic surfactants; W= -6RT (Tomastić *et al.* 1991). The effects of pH, temperature and surfactant alkyl chain length in the mixture of SDS-DPCl were considered by Amante *et al.* (1991). Increasing temperature from 30 to 40°C tended to decrease the precipitate is potential. The other anionic surfactants used for investigating the effect of surfactant alkyl chain length were sodium decyl sulfate (SDeS) and sodium octyl sulfate (SOS). As the alkyl chain length decreases, precipitation required a higher anionic surfactant concentrations were required for precipitation. However, pH was not observed to impact the precipitation for two pH levels of 6.6 and 8.4.

The aqueous phase behaviour and properties of cetyltrimethyl ammonium tosylate (CTAT) and sodium dodecylbenzene sulfonate (SDBS) were investigated by Kaler *et al.* (1992). In these mixtures, vesicles were quite stable with large vesicle phases presented in the pseudo ternary phase diagram for both cationic and anionic rich mixtures. A crystalline precipitate, presumably the 1:1 salt of amphiphilic ions, was present only in equimolar mixtures. Herrington *et al.* (1993) evaluated the effect of surfactant structure by considering the pair SDS and DTAB (dodecyl trimethyl ammonium bromide), surfactants with linear tail groups of equal length. It was found that micelles of anionic surfactants grew upon addition of cationic surfactant and the microstructure of mixed surfactants was strongly affected by the surfactant geometry. A crystalline precipitate dominated behavior when two surfactants are linear and symmetric in chain length. Micelles and vesicles were observed only at high concentration when the surfactants are branched and/or contain a bulky substituent (e.g. a benzene group) in the tail group, the precipitate phase stability was reduced relative to that of micellar and vesicular phases.

Filipović-Vioekivić *et al.* (1995) found that the phase behavior of anionic/cationic surfactant mixtures of the same chain length (n = 10, 12 or 14) strongly depended on the molar ratio and the concentration of surfactants. Increasing in the alkyl chain length increased the tendency for both precipitation and micellization to occur. Furthermore, the addition of oppositely charged surfactant can diminish the surfactant charge density at the mixed micelle/solution interface and enhance the apparent degree of dissociation from mixed micelles. The phase transition from a solid crystalline catanionic to mixed micelle anionic/cationic surfactant mixture having the same alkyl group (n=14) was evaluated by Bujan *et al.* (1996). It was observed that a transition from solid crystalline catanioic phase through mixed liquid crystalline phase to mixed micelles took place as the concentration of one of the surfactants increased.

Patist *et al.* (1997) investigated the effect of chain length compatibility on the micellar stability for mixtures of SDS and alkyltrimethyl ammonium bromides (C_nTAB, *n*=8, 10, 12, 14, 16) at a 20/1 molar ratio. It was observed that the surface tension was lowest when the chain length of both surfactants was the same ($SDS/C_{12}TAB$). Mixtures of anionic and cationic surfactants showed a lower surface tension than pure anionic or cationic surfactant solutions because of the Colombic interaction between the ionic head groups. However, the lowest surface tension as observed for $SDS/C_{12}TAB$ can be explained on the basis of chain length compatibility of both surfactants molecule. The hydrophobic interaction between the alkyl chains causes the molecule to pack closer in both micelles and at the air/water interface.

Talhout and Engberts (1997) characterized two aqueous mixtures of anionic and cationic surfactants: SDS/DTAB and sodium heptyl sulfate (SHS)/ hexadecyltrimethyl ammonium bromide (CTAB). These mixtures differed in the hydrophobic match of their tails. Both mixtures showed high synergism in critical aggregation concentration. The SDS/DTAB mixture had more this synergism due to the higher hydrophobic match compared to that of the SHS/CTAB mixture. Moreover, the hydrophobic match profoundly influenced the phase behavior of the mixtures. SHS and CTAB can be mixed in a 1:1 ratio without precipitation, forming both small, unilamellar and large, multilamellar vesicles. In SDS/DTAB mixtures, however, the catanionic surfactants occurred for a mole fraction of DTAB (X) between 0.3 and 0.7, while both vesicles and large bilayer fragments were formed for X = 0.8.

Kang *et al.* (2001) examined the mixed micellization of ammonium dodecyl sulfate (ADS) and octadecyltrimethylammonium chloride (OTAC) solutions. It was observed that mixed micelles were formed at low (< 0.2 wt %) total surfactant concentration. Although not substantially, the mixed CMCs and surface tension were observed and therefore ADS and OTAC exhibited synergistic behavior in the mixed micelles.

Raghavan *et al.* (2002) studied mixtures of the C_{18}-tailed anionic surfactant, sodium oleate (NaOA), and cationic surfactants from the trimethyl ammonium bromide family (C_nTAB). It was determined that attractive interactions in mixture of cationic and anionic surfactants are governed chiefly by the surfactant tail lengths. First, if there is one long and one very short tail (e.g., NaOA-C_6TAB), weak interactions ensue between the surfactants, leading to weak micellar growth. Second, if both tails are long (e.g., NaOA-$C_{12}TAB$), strong attractive interactions occur, leading to precipitation of catanionic salt at the equimolar composition and the formation of bilayer structures over a wide range of compositions. Last, if one tail is long and the other is moderate length (e.g., NaOA-C_8TAB), in this case, the attractive interactions are strong enough to cause dramatic micellar growth, but not strong enough to induce bilayer structures or phase separation.

As mixed anionic cationic surfactant systems form precipitate easily, reserach on these mixtures has been largely limited to regions far from equimolar composition or having very low concentration. Among the anionic cationic surfactant mixtures, alkyltrimethyl ammonium and alkyl sulfate are most common in studied and deeply studied. Chen *et al.* (2002) investigated aqueous mixtures of alkyl triethyl ammonium bromide and sodium alkyl sulfonate and found that these mixtures could form homogeneous solutions even at high concentration. It was shown that the solubility of mixtures is greatly improved when alkyl sulfonate instead of alkyl sulfate and alkyltriethyl ammonium bromide instead of alkyltrimethyl ammonium were used. This may be due to the fact that the bigger head group decreases electrostatic repulsion between opposite headgroups.

2.3 Microemulsion Systems

A microemulsion is a thermodynamically stable mixture of one liquid phase into another, stabilized spontaneously by an interfacial film of surfactant. A Winsor Type I microemulsion is an oil-in-water (O/W) microemulsion in equilibrium with an excess oil phase with the surfactant molecules mainly existing in the aqueous phase in the form of normal micelles. For a Winsor Type II microemulsion, a water-in-oil (W/O) microemulsion coexists with an excss water phase and the surfactant molecules mostly aggregate in the oil phase in the form of reverse micelle. A Winsor Type III system consists of middle phase microemulsion in equilibrium with both excess oil and water phases. The middle phase microemulsion has surfactant molecules, which orientate with solubilized water and oil in a bicontinuous form. Ultra-low interfacial tensions (IFT) and maximum solubilization of both the middle-phase microemulsion/water and the middle-phase microemulsion/oil occur when an amount of excess oil phase equals to an excess water phase.

Varying a selected parameter (e.g., temperature, electrolytes, surfactant, cosurfactant, and oil) can transform the phase of surfactants from Winsor Type I to Winsor Type III to Winsor Type II microemulsion as shown in Figure 2.4.

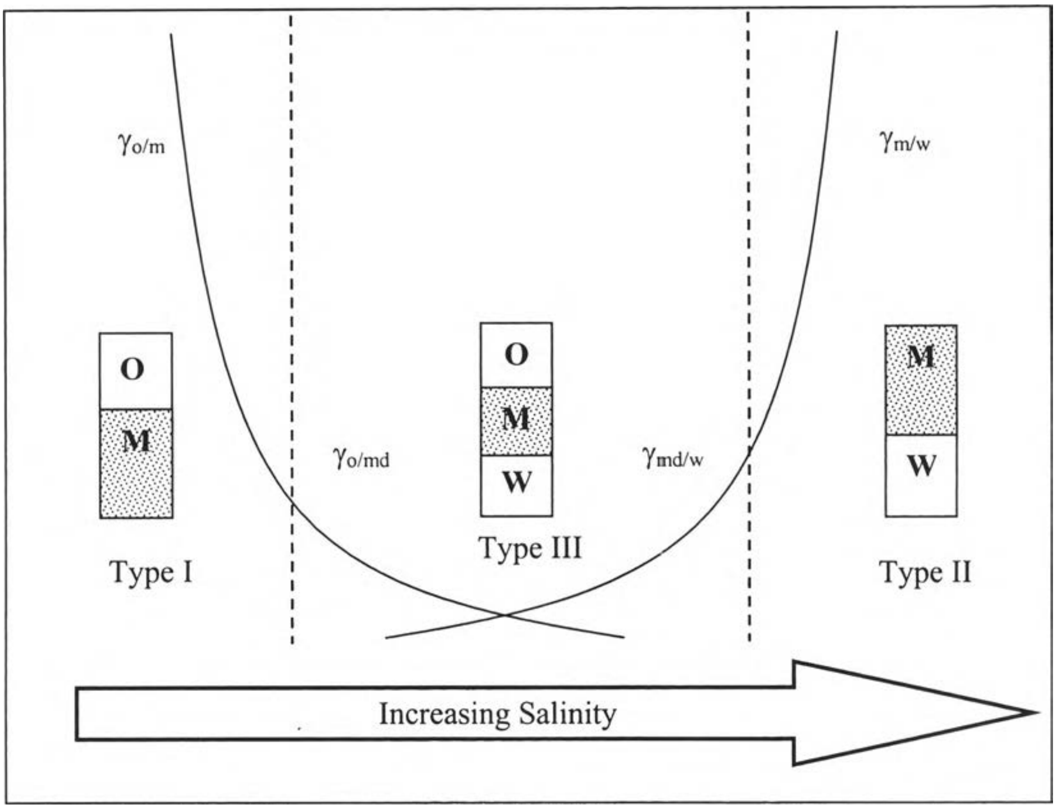


Figure 2.4 Schematic illustration of the progression of microemulsion phase equilibrium and interfacial tension for an ionic surfactant system as a function of salinity (note: equal volume of an aqueous phase and an oil phase).

In addition, the changing of microstructure in the phase transition from Winsor Type I to III to II plays an important role in the two attractive properties of microemulsion, which are ultra low interfacial tension and ultra high solubilization.

2.4 Interfacial Tension

Since a number of applications require low interfacial tensions between oil and water to achieve the desired state, interfacial tension is one of the most commonly measured properties of microemulsions. The interfacial tension or surface free energy per unit area is the minimum amount of worked required to bring sufficient molecules from the interior to the surface to expand the surface by unit area.

At the interface between two condensed phases, the dissimilar molecules in the adjacent layers facing each other across the interface also have potential energies different from those in their respective phases. If surfactant is added to a system of two immiscible phases (e.g., hexane and water) and then adsorbed at the interface between them, it will be oriented with the hydrophilic group toward the water and the hydrophobic group toward to hexane. The tension across the interface is significantly reduced by the presence of the surfactant at the interface.

Recall from Figure 2.4 that the interfacial tension between a microemulsion and oil phase ($\gamma_{m/o}$) (left side of figure) decreases as the salinity increases, while the interfacial tension between water phase and microemulsion ($\gamma_{w/m}$) increases (right side of figure). The two curves intersect inside the Winsor Type III region and the corresponding system has been designated as optimum condition (equal volumes of oil and water). The value of interfacial tension at this intersection point is denoted as optimum interfacial tension (γ^*) where $\gamma_{m/o} = \gamma_{w/m} = \gamma^*$ (Lohateeraparp, 2001).

2.5 Solublization Parameter

Surfactants are often added to water to help blend of oil and water to form microemulsion is often the purpose of surfactants. The solubilized volumes of oil and water dissolved within the micellar solutions are considered in term of the "solubilization parameter".

Wu *et al.* (1997) defined a modified oil solubilization parameter as solubilized oil volume per unit mass of surfactants as follows:

$$SP_o = \frac{Vo}{Ms} \tag{2.2}$$

where SP_o is solubilization parameter for oil, V_o is solubilized volume of oil, and Ms is the total mass of surfactant(s) present excluding the mass of alcohol (if used). If other surfactants are used as a cosurfactant, they are included in calculation. The solubilized volume of oil is replaced by solubilized volume of water for water solubilized parameter (SP_w) calculation.

The optimum condition of microemulsion systems occurs when an amount of excess oil phase equals to an amount of excess water phase. It can be implied that the solubilization parameter of oil will be equal to the solubilization parameter of water at this point. The solubilization parameter at the optimal formulation (SP*) can be defined as (Acosta *et al.*, 2001):

$$SP^{*} = SP_O = SP_W \tag{2.3}$$

$$SP^{*} = \frac{V_O}{M_S} \tag{2.4}$$

Figure 2.5 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 microemulsion transition from Winsor Type I-III-II. The volume of dissolved oil in the aqueous continuous phase is very small at low electrolyte concentration. An increase in the salinity reproduces 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 the Winsor Type III region, 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 usually constant.

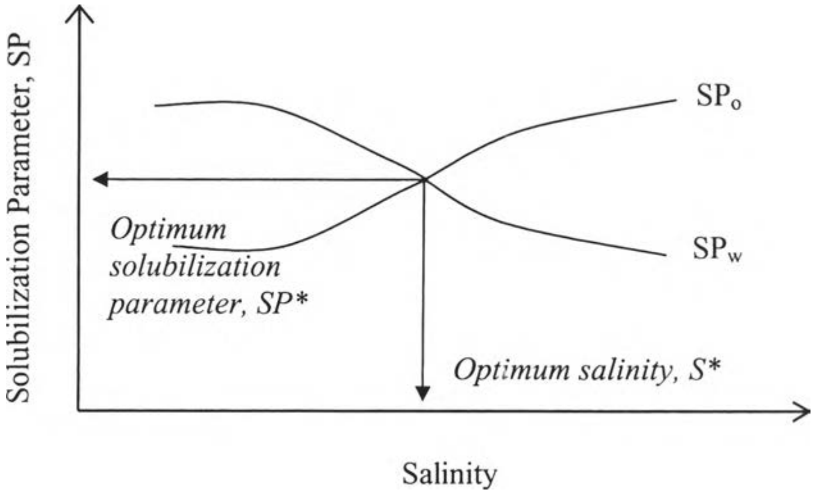


Figure 2.5 Solubilization parameter as a function of salinity (Lohateeraparp, 2001).

The correlation between the interfacial tension and solubilization can be considered by Chun-Huh relationship, as shown in equation 2.5:

$$S = \sqrt{\frac{C}{IFT}} \qquad (2.5)$$

where, S is solubilization parameter, defined as volume of oil / volume of surfactant, C is constant, and IFT is interfacial tension.

The Chun-Huh relationship indicates that the solubilization potential is inversely proportional to the square root of the interfacial tension. Since interfacial tension decreases continuously as we move towards a middle phase microemulsion system, from the Chun-Huh relationship the solubilization potential also increases continuously, both within the Winsor Type I region and inside the Type III region up to the optimum (Sabatini *et al.*, 2000).

Since microemulsions posses special characteristics of relatively ultra-low interfacial tension and large solubilization capacity as compared with many other colloidal systems, these special features offer great potential for a wide range of industrial and technological applications (e.g., tertiary oil recovery, detergency, catalysis, drug delivery, etc.).

2.6 Microemulsion with Anionic and Cationic Surfactant Mixtures

It is well-known that surfactant mixtures can improve the surface activity of a microemulsion system. Although mixtures of an anionic and a cationic surfactant can exhibit many synergisms, microemulsion formulations with mixed anionic-cationic surfactant systems were not reported until last few decades, due in large part to the limitations of precipitation and liquid crystal formation. Many researchers used alcohol as a cosurfactant to eliminate the precipitation and liquid crystal formation problem and also promote the microemulsion formation.

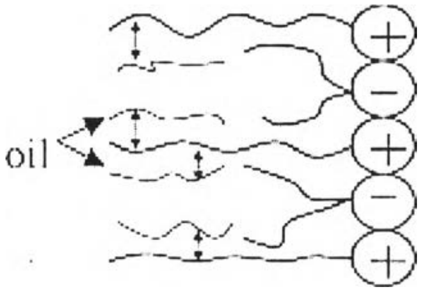
Li *et al.* (1996) studied the phase behaviour and microemulsion formation of anionic and cationic surfactants (SDS and CTAB) with alcohols in equal volumes of water and heptane. The surfactant ratio and the cationic weight fraction necessary to form microemulsions versus liquid crystals were investigated. This experimental work showed that the structure and phase inversion phenomena in microemulsions were obtained by measuring the conductivity. It was found that increasing alcohol and/or cationic weight fraction shrinks the liquid crystal region rapidly.

Li *et al.* (1999) investigated the minimum amount of surfactant necessary to solubilize equal amounts of water and oil in a single microemulsion phase, using NaBr/SDS/CTAB/hexanol/dodecane systems. The interaction is too strong to form a flexible surfactant layer around the equal molar mixture of cationic and anionic surfactants. Liquid crystals were formed instead of an isotropic microemulsion and consequently, the solubilzation capacity decreases accordingly. However, it was found that the microemulsions were formed with high alcohol content.

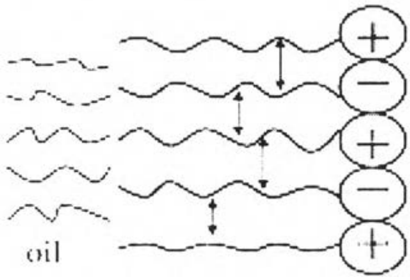
Microemulsions have been employed in many environmental applications and consumer products; therefore, recent studies aimed to form alcohol-free anionic-cationic microemulsions by investigation optimal surfactant structures. Doan (2002) exploited the mixtures of anionic-cationic surfactant to form alcohol-free middle phase microemulsion. Microemulsion phase behavior was studied for three anionic-cationic surfactant systems and three oils of widely varying hydrophobicity (trichloroethylene, hexane, and hexadecane). It was observed that in the system of SDS and Dodecylpyridinium Chloride (DPCl) which have the same tail length, middle phase microemulsion were not formed. Moreover, using a branched surfactant with varying tail length successfully avoided liquid crystal formation and formed alcohol-free middle phase microemulsion. As the oil hydrophobicity increased (i.e., TCE to hexane to hexadecane), the anionic to cationic molar ratio required to form microemulsions approached to equimolar without liquid crystals formation. The precipitation phase boundaries were also investigated in the absence of oil phase.

The main purposes of this work were to further evaluated alcohol-free anionic-cationic middle phase microemulsions, and the evaluation of relative efficiency of these mixed anionic-cationic systems compared with single surfactant. The first hypothesis of this work is that the use of mixtures of an anionic and a cationic surfactant with asymmetric tails-- different tail length or branched tail-- can inhibit the surfactant precipitation. According to enhancement the space between the hydrophobic parts, the surfactant tail- oil phase interaction will be increased (Figure 2.6a). Consequently, the middle phase microemulsion can be formed without adding alcohol. Whereas a mixture of an anionic and a cationic surfactant with similar structure and without branching tail as shown in Figure 2.6b, the hydrophobic groups of surfactants have a strong affinity to interact with one another. The interaction between the hydrophobic groups and the oil phase will be reduced.

The second hypothesis is, as the oil becomes more hydrophobic (the equivalent alkane carbon number (EACN) of the oil increases), the mixed ratio of anionic-cationic surfactant mixture for the middle phase microemulsion formation will approach 1:1 for univalent cationic/ anionic surfactants, and 2:1 for monovalent cationic and divalent anionic surfactants.



(a) Varying tail length and with branching



(b) Similar tail length and without branching

Figure 2.6 Schematic illustrating the conceptual of anionic and cationic surfactants interactions.