CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Organometallic Compounds

2.1.1 Tetraethyl Lead

Tetraethyl lead (TEL) is a neutral organometallic compound which was discovered by Charles Kettering in 1921, a general motor (GM) corporation researcher. It was used extensively as an additive to prevent knocking in fuel engine (gasoline) and increase the fuel's octane number. The used of TEL in gasoline was initiated in the United Stated (U.S.) and only few years led the universality switch to the leaded gasoline (Rhue et al., 1992; Wikipedia, 2008). Until 1973, United States Environmental Protection Agency (USEPA) was initiated to phase out this poisonous substance due to its extremely toxicity to human and environment (Detwyler, 1998). Another accomplished way to reduce the consumption of leaded gasoline, new alternative antiknock agents such as methyl cyclopentadienyl manganese tricarbonyl (MMT), methyl tertiary butyl ether (MTBE), and ethyl tertiary butyl ether (ETBE) were introduced in the gasoline world market (Wikipedia, 2008). However, TEL is still used in aviation fuel and racing cars (Ouyang et al., 1996; Unob et al., 2003) and a number of developing countries (ATSDR, 2007).

TEL is on the right to know hazardous substance list because it is regulated by Occupational Safety and Health (OSHA) and cited by American Conference of Govermental Industrial Hygienists (ACGIH), Department of Transportation (DOT), National Institute for Occupational Safety and Health (NIOSH), National Toxicology Program (NTP), New Jersey Department of Environmental Protection (DEP), International Agency for Research on Cancer (IARC), Integrated Risk Information System (IRIS), and Environment Protection Agency (EPA). Additionally, this substance is on the Special Health Hazard Substance list because it is reactive (Hazardous substance fact sheet). TEL is said to account for 80-90% of all environmental lead contamination and is known to damage

the kidney, central nervous system, cardiovascular system, and human reproduction. Moreover, death of fetuses and young children were found as severe case. The evidence in U.S. showed that 80% of TEL plant workers has been killed or were severely poisoned from this organolead. Since 1920s to 1986, total lead (Pb) used in U.S. gasoline were found equal to 7 million metric tons (15.4 billion pounds) totally (Detwyler, 1998).

Thailand in the late 1980s, a number of communities was excessive exposure to lead from the consumption of leaded gasoline. There are 200,000 to 500,000 cases of hypertension, resulting in roughly 400 deaths per year was found in Bangkok (Njora, 2003).
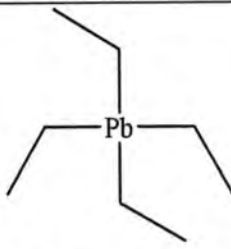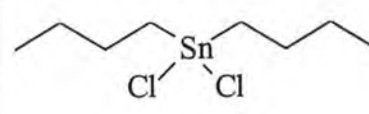
Even though the TEL added in automobile fuel is gone out for a long time, the abundant legacy lead still remains in soil and dust that are major contributor of the environmental pollution and high level of lead are found near roadways, abandon gas stations, and manufacturing sites (Detwyler, 1998). More evidences of area contamination were found in U.S.: Oakley, California where is the TEL manufacturing site in 1956-1997 (DTSC, 2006), Fort Richardson, Alaska where is the U.S. Army in 1988 (DEC contaminated sites database, 2008), and Yuma, Arizona where is the air station in 1996 (JEG, 1996).

According to their contaminations are shown in many areas, an effective remediation technique should be applied to remedy the areas. TEL is very unstable in soil as it can be degraded to triethyl lead (TREL), diethyl lead (DEL) and finally to Pb^{+2}. Even degradation of these organoleads, the toxicity are decrease as well as organolead is much more toxic than inorganic lead (Gallert and Winter, 2004).

There are several methods designed to solve the TEL contamination problem such as degradation of alkyllead compounds (TEL) to inorganic lead by bacteria, fungi or microorganism (Macaskie and Dean, 1990; Gallert and Winter, 2002; DuPont, 1994) and phytoremediation (Bernstein, 1992). The limitation of biological techniques was observed when dealing with high concentration of contaminant. Furthermore, the conversion of organolead to inorganic lead by microorganism is taking more times to remediate and ultimately the site still contaminated by lead (Pb). The more challenge is to implement the engineering method namely pump-and-treat technique. Although, pump-and-treat is well known and widely used, it is solely water flushing which is quite ineffective if applied to

contaminants that are water-immiscible or having high hydrophobicity such as TEL. The physical and chemical properties of TEL are shown in Table 2.1. Furthermore, TEL is defined as a dense nonaqueous phase liquid (DNAPL) thus, required the robust remediation technology to prevent a vertical migration. The surfactant-based remediation technology is an innovative technique gaining more attractions for NAPLs contaminated sites remediation (Sabatini et al., 2000).

Table 2.1 Organometallic compound properties

Properties	Tetraethyl lead	Dibutyltin dichloride
Physical form	Colorless oily liquid	Colorless solid
Formula	$Pb(C_2H_5)_4$	$Cl_2Sn(C_4H_9)_2$
Molecular weight (g/mole)	323.44	303.83
Structure		
Boiling point (°C)	84-85 @ 15mmHg	135 @ 10 mmHg
Melting point (°C)	-136	37
Density (g/mL at 25°C)	1.653	1.36
Water solubility (ppm)	0.29	36
Vapor pressure (mmHg at 25°C)	0.26	0.012
LogKow	4.15	1.56
Toxicity LD_{50} (oral rat, mg.kg^{-1})	12.3	50

Source: Physical properties obtained from Sigma-Aldrich material safety data sheet

According to its extreme toxicity (shown in Table 2.1), conducting the experiment directly on TEL is much more difficult to handle. Thus, the better way is to find another substance to be used as TEL surrogate. The most excellent candidate in a number of oils is dibutyltin dichloride (DBTDC) due to they are DNAPL and are considered as organometallic compounds. Their properties are described in the following section.

2.1.2 Dibutyltin dichloride

Dibutyltin dichloride (DBTDC) is categorized as organometallic compound same as TEL. It is commonly known to use as stabilizers for polyvinyl chloride (PVC) resins process and catalyst for many applications, for example; in electrodeposition coatings applied for corrosion protection on motor vehicles; in silicones process such as sealants; esterification reactions such as phthalates, polyesters, and alkyd resins; and in polyurethanes process such as printing and adhesives (Risk & Policy Analysts Limited, 2002). The widely use of organotin compounds resulting in more challenge clean-up technique requirement. Study on using DBTDC as TEL surrogate, not only give us a benefit for achieve goal of remediation itself, but also provides a tendency success for TEL remediation too. Even though DBTDC is dissimilar form compare with TEL, solid form, it still has attractive properties overcome other substances. The dominant properties are similar type of compound, structure, molecular weight, and density, while causing lower toxicity than TEL as shown in Table 2.1.

2.2 Innovative Surfactant Based Remediation Technologies

Because of the limitations of pump-and-treat technology, attention is now drawing on the feasibility of surfactant to enhance the remedial efficiency. Two different mechanisms are involved namely "solubilization" and "mobilization" (Wu et al., 2000). Surfactant can enhance oil solubilization because oil contaminants will partition into the hydrophobic (interior) core of surfactant micelles. In addition, surfactant can enhance oil mobilization resulting in a bulk-oil displacement because

surfactant can form a Winsor type III microemulsions that reduces the interfacial tensions (IFTs) to ultralow region that overcome the capillary forces between trapped oil and water in the porous material. Whereas surfactant enhanced solubilization can increase remedial efficiency by one to two orders of magnitude, surfactant enhanced mobilization achieves even greater efficiencies. In an economic viewpoint, the mobilization is more preferable but not for the DNAPLs treatment due to the occurrence of vertical migration resulting in much more complicated remediation than solubilization (Rouse et al., 1993).

2.2.1 Surfactant

Surface active agent or surfactant is an amphipatic molecule consisting of two dissimilar groups, a hydrophilic head group (water-soluble) and hydrophobic carbon tail group (water-insoluble) moiety. The hydrophilic group that has a strong attraction with water can be nonionic, ionic or zwitterionic (combination of cationic and anionic groups). Up to the type of surfactant head groups, they are classified as cationic, anionic, nonionic and zwitterionic. The hydrocarbon chain tail interacts weakly with water molecules in an aqueous environment whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion–dipole interactions. This strong interaction with the water molecules renders the surfactant to be soluble in water. When a surfactant is dissolved in a solvent, the presence of the hydrophilic group in the solvent may distort the solvent liquid structure caused an increasing of the free energy in the system. In an aqueous solution, the distortion of water molecules by the hydrophobic group of the surfactant occurs when it is dissolved resulting in an increase in the free energy of the system. Less work is needed to bring a surfactant molecule to the surface than that of needed for a water molecule (Rosen, 1989). The balance between hydrophobic and hydrophilic parts of the surfactant molecule gives these systems some special properties e.g. accumulation at various interfaces and association in solution to form micelles. In other word, when the aqueous surfactant concentration exceeds a certain level, the surfactant molecules (monomers) self-aggregate into spherical aggregates known as "micelles". The concentration at which micelles first begin to form is known as the critical micelle

concentration (CMC) which is different for each surfactant. As a number of micelles in solution increases, solubilization increases too. Thus, the concentration well above the CMC is necessary for the solubilization enhancement. Solubilization occurs in such a way that contaminant droplets tend to be encased in surfactant micelles as shown in Figure 2.1 (Ouyang et al., 1996).
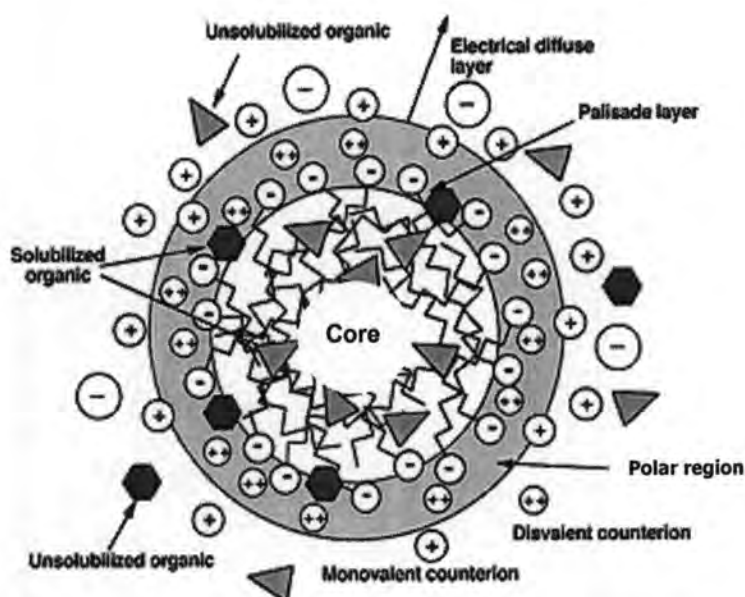

Figure 2.1 Schematic of oil solubilized in anionic surfactant micelle (adapted from Lemordant, 2006)

According to the oils solubilization, it is well known that oils are normally solubilized in their preferably regions, depending on their polarity and molecular structure. Figure 2.1 is the schematic of surfactant micelle shows three main locations of oils solubilized inside the surfactant micelle: 1.) polar surface region (surfactant head groups) 2.) palisade layer (between surfactant tails) and 3.) hydrophobic core. Upon these regions, non-polar oils are solubilized in the micelle core region whereas semi-polar and polar oils preferably solubilized at the palisade and surface regions, respectively (Szekeres et al., 2005).

The use of surfactants to clean up NAPLs from contaminated soils has shown significant potential for real site applications; however, one of the major obstacles is the potential of unstable macroemulsions to form with unfavorable phase conditions such as gels. Macroemulsions are defined as thermodynamically unstable and have diameter droplet sizes ranging from 0.1 to 10 μm. There are several

evidences reported that the flow of macroemulsions inhibits the transportation of NAPLs throughout the soil. This inhibition occurs because macroemulsions are unstable and can be broken up into two immiscible phases such as NAPL and water. In addition, the relatively large size of droplets in the macroemulsion system has a tendency to clog micropores during transportation in soils (Ouyang et al., 1996).

2.2.2 Microemulsion

Microemulsions are different from macroemulsions as their transparent and thermodynamically stable although the system contains the same 3 main components as water, oil and surfactant. Diameter of droplet in microemulsions ranges from 0.1 to 0.01 μm (Wu et al., 2001). Microemulsions can be classified into three types: oil in water microemulsion (O/W$_m$, Winsor type I), middle phase microemulsion (Winsor type III) and water in oil microemulsion (W/O$_m$, Winsor type II) as shown by the Winsor phase diagram in Figure 2.2.

Middle phase microemulsions are surfactant oil-rich systems that exist in equilibrium with excess water and oil phases. Equal volume of oil and water are solubilized whereas most of surfactant accumulates in this oil-water interface (as shown at intermediate salt concentrations in Fig. 2.2). Winsor refers to this new phase as Type III microemulsion, as opposed to Type I (micelles) and Type II (reverse micelles) microemulsions (Rosen, 1989). The special attraction of microemulsion systems is their ability to produce an ultralow IFT between oil-water interface and ultrahigh contaminant solubilization.

The solubilization capacity of middle phase microemulsion is defined by the solubilization parameters as (Healy and Reed, 1977):

$$SP_o = V_o / V_s \tag{1}$$

and

$$SP_w = V_w / V_s \tag{2}$$

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 surfactant solution, respectively; and V_s is the volume of surfactant contained in solution, excluding the alcohol volume (if used).

According to the Chun-Huh relationship, the oil-water solubilization capacity increases as the interfacial tension (IFT) of the microemulsion systems decreases, as shown in the following equation (Pope and Wade, 1995; Huh 1979):

$$SP^2 = \frac{C}{IFT} \qquad (3)$$

where SP is known as the solubilization parameter (mL of oil/ g of surfactant) of the microemulsion system as obtained from equation (1) and (2), C is the Chun-Huh constant which is dependent to type of the surfactant and IFT is the interfacial tension between excess oil and water phases (mN/m).

From Chun-Huh relationship, the solubilization potential also increases continuously due to a reduction of IFT, both within the Winsor Type I and Type III region up to the optimum as shown in Figure 2.2. We refer to this increased solubilization within the Type I region as the supersolubilization as mentioned above.
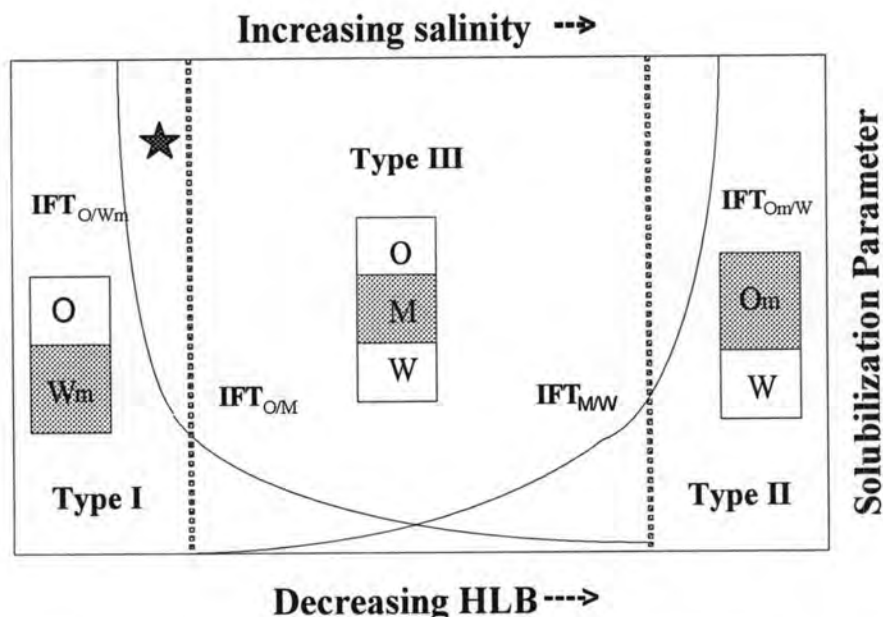

Figure 2.2 Winsor phase diagram (Tongcumpou et al., 2003)

Supersolubilization is the region shown as ★ in Figure 2.2. The supersolubilization condition is located in Winsor type I but provides the highest solubilization although the IFT is not minimal as an optimum condition in Winsor type III systems. This condition poses a special characteristic that provides the maximum solubilization while minimizing a vertical migration, which is a major concern when dealing with DNAPLs remediation.

Consequently, surfactant enhanced soil remediation using microemulsion systems has been reported (Ouyang et al., 1996). Thanks to the stability and complimentary phase behavior of microemulsions, also the harmonization between the small droplets size dispersed in aqueous phase and soil pores size, the displacement of microemulsions through aquifer or soil can minimize the clogging in remediation process.

Unfortunately, laboratory experiments have not been reported on the removal of TEL as much, therefore this research will demonstrate the potential of microemulsion for TEL clean-up.

2.3 Surfactants Selection

Perceptive the right way to select surfactant systems can be helpful and reduce in time consumption. Rosen, 1989 had presented the general guidelines of surfactants selection as described below:

2.3.1 The HLB Method

The hydrophile-lipophile balance (HLB) is one parameter that can characterize surfactants in term of their abilities to produce optimum emulsion with oils developed by Griffin, 1949 (Tadros, 2005). Griffin developed the simple equations to calculate the HLB number for simple nonionic surfactants ranging from 0-40 while cannot be used for anionic surfactants. Thus, Davies (1959) established a method for calculating the HLB number of anionic surfactants from their chemical structure listed in Table 2.2. The HLB is given by the following empirical equation:

$$\text{HLB} = 7 + \Sigma(\text{hydrophilic groups number}) - \Sigma(\text{lipophilic groups number}) \qquad (4)$$

Surfactants with relatively high HLB numbers (left-hand side of Winsor phase diagram, type I) are water soluble while relatively low HLB numbers (right-hand side of Winsor phase diagram, type II) indicate oil soluble surfactants. Along with these, a balanced surfactant system produces middle phase microemulsion (center of Winsor phase diagram, type III). The HLB of a surfactant or surfactant mixtures varying HLB between 20 to 5, it transitions from water-soluble surfactants (micelles, type I) to oil-soluble surfactants (reverse micelles, type II). This transition occurs at HLB values of approximately 10–12, depending on the oil. By altering the salt concentration, the water-soluble surfactants (high HLB number) will partition into the oil phase resulting in HLB change. Consequently, increasing of the salt concentration in an ionic surfactant solution will eventually cause the surfactant to partition into the oil phase called reverse micelles. This is illustrated in Figure 2.2, which shows aqueous micelles at lower salt concentrations and reverse micelles at higher salt concentrations. Likewise, adjusting the system temperature will affect to system HLB for nonionic surfactant systems (Sabatini et al., 2000).

Table 2.2 HLB group numbers

Group	HLB number
Hydrophilic	
$-SO_4Na^+$	38.7
$-COO^-$	21.2
-COONa	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
-O-	1.3
CH- (sorbitan ring)	0.5
Lipophilic	
$(-CH-)$, $(-CH_2-)$, CH_3	0.475
Derived	
$-CH_2-CH_2-O-$	0.33
$-CH_2-CH_2-CH_2-O-$	-0.15

Source: Tadros, 2005.

When using mixtures of surfactants, the HLB number is adjusted depended on the proportions of mixed surfactants. The average HLB numbers can be calculated by Equation (5):

$$HLB = x_1HLB_1 + x_2HLB_2 \tag{5}$$

where x_1 and x_2 are the weight fractions of the two surfactants with HLB_1 and HLB_2, respectively.

2.3.2 The maximum solubilization method

The method to specify the oil solubilization, the partitioning of the various contaminants into the micelle, can be described by the micellar partition coefficient (K_{mic}) as shown in Equation (6), the higher K_{mic} designates in the higher solubilization.

$$K_{mic} = \frac{X_{mic}}{X_{aq}} \tag{6}$$

where X_{mic} is the mole fraction of the contaminant in the micelle pseudophase and X_{aq} is the mole fraction of contaminant in the aqueous phase. X_{mic} and X_{aq} are calculated by using the following equations:

$$X_{mic} = \frac{MSR}{1 + MSR} \tag{7}$$

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \tag{8}$$

where the molar solubilization ratio (MSR) refers to the moles of the contaminant solubilized per mole of surfactant in the micelles and is determined by the slope of the graph that correlates between surfactant concentration and oil solubilization in molar unit. C_{eq} is an equilibrium concentration of contaminant in water alone (as defined by water solubility of oil contaminant) and 55.55 is the inverse molar volume of water.

2.4 EACN determination of TEL

Due to TEL is on the Hazardous Substance List (TEL fact sheet), the research dealt with this substance is not preferable. The use of oil surrogate similarly in physical and chemical properties with TEL would be the greatest way to avoid the direct contact with TEL. However, the challenging problem is what kind of properties that should be used as criteria to select the oil surrogate. Recent year, many researchers use the oil hydrophobicity to determine the surfactant system used (Baran et al., 1994; Wu et al., 2001; Witthayapanyanon et al., 2006). The hydrophobicity can be addressed in terms of the equivalent alkane carbon number (EACN) as defined by Salager et al., 1979 that oil with higher EACN is more hydrophobic. The EACN assigns a single "alkane analog" to represent the behavior of a mixed hydrocarbon system.

2.4.1 Empirical Relationship for Formulating Microemulsions

Microemulsion formulation is largely a trial-and-error process. Empirical models can help to expedite this trial-and-error process. For systems containing hydrocarbon, anionic surfactant, alcohol, and salinity, the following relationship has proven to be valid (Salager et al., 1979):

$$\ln S^* = K(\text{EACN}) + f(A) - \sigma \qquad (9)$$

where S^* is an optimum salinity, K is a constant (a function of the hydrophilic group of the surfactant), $f(A)$ is a value specific to the alcohol utilized and σ is a characteristic surfactant parameters (or surfactant mixture).

For mixtures having multiple components, researchers have found that:

$$(\text{EACN})_M = \Sigma X_i(\text{EACN})_i \qquad (10)$$

where $(EACN)_M$ and $(EACN)_i$ are the equivalent alkyl carbon number for the oil mixture and component i, respectively. X_i is the mole fraction of the component i in the mixed oil phases that is $\Sigma X_i = 1$. Thus, $(EACN)_M$ can be substituted into Equation 9, resulting in:

$$\ln S^*_M = K(EACN)_M + f(A) - \sigma \qquad (11)$$

2.5 Literature Reviews:

Ouyang et al. (1996) have done the experiment on removing organolead from contaminated soil by applying the microemulsion systems. The result showed that sodium lauryl sulfate (SLS) cooperated with co-surfactant (n-pentanol) was able to remove TEL up to 90%. The SLS might not be a good choice for soil remediation because it tends to precipitate by hardness ions in subsurface.

Rouse et al. (1993) reported the way to minimize surfactant losses by using twin-head anionic surfactants (Dowfax series) in subsurface remediation. They showed that disulfonated surfactants minimize losses while maintaining good solubilization capacity as compare to monosulfonated surfactants. Thus, by the advantages of Dowfax, less susceptible to precipitation and sorption on media than nonionic surfactants has been demonstrated that it is a promising surfactant to use in the subsurface remediation. Additionally, other research works done by Deshpande et al. in 1998 and 2000 showed the similar result as to its robustness and conservative nature.

Deshpande et al. (1998) presented the guidelines for surfactant selection for enhancing EX- SITU soil washing. They studied on both soil rollup and solubilization mechanisms during soil washing. If the soil rollup mechanism is significant, the lower CMC of nonionic surfactants may cause them economically preferred. Also for the anionic surfactants, the ones owing less sorption and high solubilization potential are capable.

Sabatini et al. (2000) have illustrated the importance of system solubility enhancement, IFT, viscosity and density to be used as a guideline for surfactant selection system. In addition, the supersolubilization and gradient approaches have been introduced to maximize the contaminant solubilization while minimizing the vertical migration, when DNAPLs are addressed. In summary, they showed the potential of surfactant gradient system to gradually increase the surpersolubilization potential without inducing mobilizing of free oil phase.

Wu et al. (2001) have demonstrated that the oil hydrophobicity can be characterized by its EACN and also proposed the way to estimate the EACN of oil mixtures. They reported that the more hydrophobic oil (high EACN, e.g. hexadecane), the more hydrophobic the surfactant (low HLB, e.g. Tween80) system must be used to achieve the desirable phase behavior. However, solely use of high HLB Dowfax8390 will not be effective for high EACN diesel and other oils, thus mixed surfactant is an alternative to form microemulsion systems with high hydrophobic oil. The result showed that the system containing of 2%AOT , 2%Tween80 and NaCl can form microemulsion type I-III-II with hexadecane (EACN = 16) while AMA, isopropyl alcohol (IPA) and $CaCl_2$ cannot be achieved.

Childs et al. (2004) applied the gradient concept for tetrachloroethylene (PCE) removal in column study. Moreover, they introduced the capillary or trapping curve that can help to predict and design the appropriate gradient approach. In the phase behavior study, they also provided the criteria for surfactant selection which are 1.) low microemulsion density to prevent vertical migration 2.) fast coalescence to avoid the metastable macroemulsions occurrence 3.) low microemulsion viscosity to prevent PCE displacement and high head loss 4.) high solubilization capacity to decrease the pore volume flushing 5.) high enough microemulsion IFT to eliminate the vertical migration 6.) temperature independent phase behavior and 7.) low surfactant sorption. The result showed that the system containing alcohol such as IPA gives the faster coalescence times, provides the appropriate viscosities of surfactant formulations that should be larger than 2 cP, and IFT range is between 1-5 mN/m (especially for this case). Ultimately, they can overcome the mobilization concern by using mixtures of Dowfax/AMA with gradient concept.