CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1   Nonaqueous Phase Liquids (NAPLs)

Nonaqueous phase liquids (NAPLs) are immiscible (undissolved) hydrocarbons in the subsurface due to the physical and chemical property differences between water and liquid hydrocarbons. Because of their density, the behavior of NAPLs can be divided to two classes: light nonaqueous phase liquids (LNAPLs) and dense nonaqueous phase liquids (DNAPLs).

2.1.1   Light nonaqueous phase liquids (LNAPLs)

LNAPLs are organic immiscible liquids with a specific gravity (density relative to water) less than water, and therefore will float on the water table. LNAPLs are primarily associated with petroleum production, refining, and wholesale distribution and retail distribution (service station) of petroleum products (Newell et al. 1995).

2.1.1.1 Sources

Spills and accidental releases of petroleum hydrocarbons in the subsurface such as gasoline, kerosene, diesel and motor oil are common oil of LNAPLs. There are five main sources of petroleum hydrocarbons contamination: underground or above-ground storage tanks, tanker tricks, transfer terminal pipelines, and refineries. Significant amounts of LNAPLs in the subsurface media occur at locations with leaking underground storage tanks and around some petroleum refineries (National Research Council, 1997).

2.1.1.2 Transport

The transport of contaminants through an aquifer depends on the presence of contaminants as nonaqueous phase liquid or solution. When LNAPLs are released at the surface, they first migrate downward through the unsaturated zone under the force of gravity. After that, they accumulate in a soil layer above the water table. If the leaked hydrocarbons saturate the soil, free phase liquids are allowed to migrate and float on the top of the water table (National Research Council, 1997). A cross-section schematic of subsurface contamination by LNAPLs is shown as Figure 2.1.
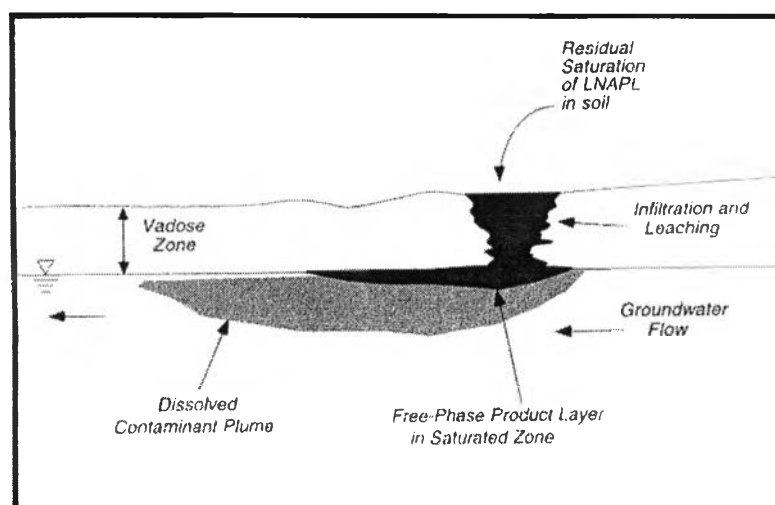
Figure 2.1 Subsurface contaminations by Light Nonaqueous Phase Liquids (Bedient et al, 1999).

2.1.2 Dense nonaqueous phase liquids (DNAPLs)

The term of DNAPLs is used to describe the nonaqueous phase liquids with a density greater than water (e.g. chlorinated hydrocarbon).

2.1.2.1 Sources

DNAPLs are related to a wide variety of industrial activities including metal stripping, chemical manufacturing, pesticide production, and creosote operations, or other activities involving chlorinated solvent such as trichloroethylene (TCE) and tetrachloroethylene (PCE). They include a wide range of chlorinated hydrocarbons, and pentachlorobiphenyls (PCBs). Chlorinated solvents are commonly used in industry as chemical carriers, solvents, paint removers, and cleaning solvents. Due to their widespread use in industry, commercial establishment, agriculture, and homes, chlorinated solvents are the most common groundwater contaminant (Bedient et al., 1999, and National Research Council, 1997).

2.1.2.2 Transport

The movement and dispersion of chlorinated solvents in the subsurface are very dependent on whether the solvents were released as a neat liquid or in dissolved form. If they are released in dissolved form, hydrogeological processes will

govern the chlorinated solvent's migration. In contrast, the chlorinated solvent will migrate downward through the soil column under the forces of gravity. When DNAPLs encounters the water table, they spread out along the water table and then move across the water table and further into the saturated zone of the groundwater aquifer due to the much greater density of DNAPLs relative to water. DNAPLs are the most difficult to treat because they are difficult to locate. In addition, when DNAPL sources are located, they are often difficult to access because they are usually at the bottom of the aquifer (Bedient et al., 1999, and National Research Council, 1997). A cross-section schematic of subsurface contamination by DNAPLs is shown as Figure 2.2.
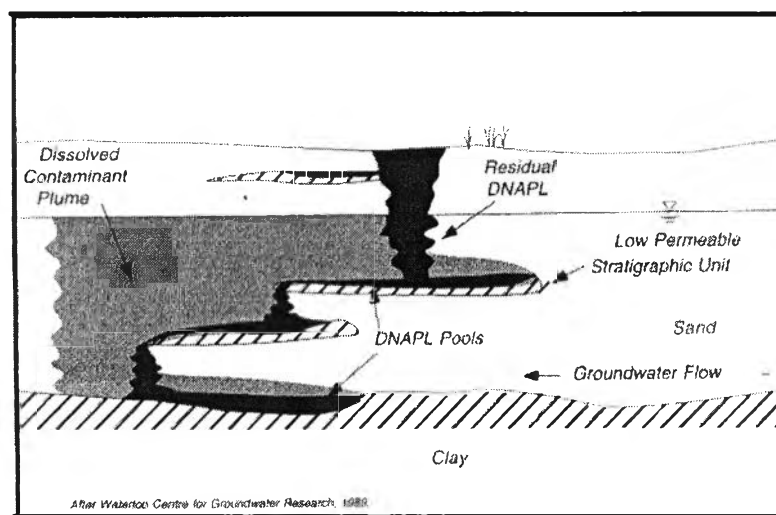

Figure 2.2 Subsurface contaminations by Dense Nonaqueous Phase Liquids (Bedient et al, 1999).

The release of nonaqueous phase liquids (NAPLs) to the subsurface has resulted in numerous problems of groundwater contamination in fractured rock and the potential for groundwater contamination by NAPLs is high due to their widespread use and physicochemical properties as contaminants. Currently, it is very difficult or impossible to remove all the NAPLs that have been released to the subsurface due to their capillary forces (Bedient et al., 1999).

2.2 Diesel

Diesel fuel is a complex combination of hydrocarbons produced by the distillation of crude oil. Crude oil is a mixture of hydrocarbon molecules-from small, lighter molecules to large, heavy molecules. By boiling or distilling the crude oil, it can be separated into fraction or cut based on the boiling point temperature of each fraction. Smaller hydrocarbon molecules have a lower boiling point and larger molecules have a higher boiling point.

2.3 Motor oil

Motor oil is complex in its composition and is highly hydrophobic. The major fraction of the majority of motor oil is derived from crude oil. It generally consists of at least five main components: n-parafin, isoparafin, cycloparafin, aromatic hydrocarbon, and mixed aliphatic and aromatic ring compounds. In addition to these five components, several additives are commonly added to the oil to act as a rust inhibitor, oxidation inhibitor, detergent-dispersant, viscosity-index improver, poor-point dispersant, and antifoam (Marmur, 1992). The EACN (equivalent alkane carbon number) is a parameter used to characterize the hydrophobicity of the oil. It has an equivalent number of carbons in the complex mixed oil as compared to a single component alkane oil. The higher EACN, the higher the hydrophobicity of the mixed oil is. Wu et al. (2000) studied and reported the EACN value of motor oil to be 23.5.

2.4 Surfactants

Surfactants or surface-active agents are commonly known as amphiphilic molecules; they combine a hydrophobic tail group (oil-like) and hydrophilic head group (water-like) (see Figure 2.3). With this structure, surfactants can be facilitate oil and water in the same solution (Rosen, 2004).
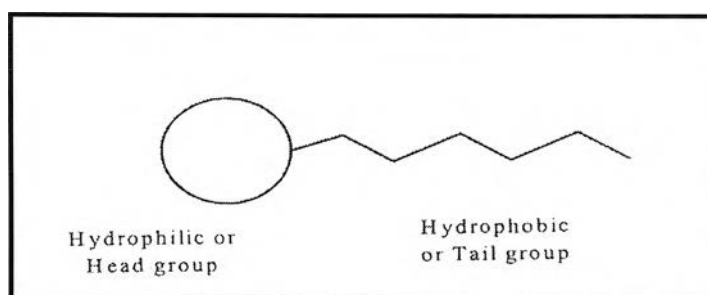
Figure 2.3 Structure of a surfactant molecule.

Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, zwitterionic and nonionic surfactants.

1) Anionic surfactants will adsorb onto the positively hydrophilic surface because the surface-active portion of anionic surfactants has a negative charge.

2) Cationic surfactants will adsorb onto the negatively hydrophilic surface because the surface-active portion has a positive charge.

3) Zwitterionic surfactants carry both positive and negative changes, and therefore can adsorb into both negatively and positively charged surfaces without changing the charge of the surface significantly.

4) Nonionic surfactants adsorb onto the surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of surface.

The surfactant molecules or surfactant monomers have an ability to self-assemble into dynamic aggregates known as micelles (Figure 2.4). Micelle formation occurs when the surfactant concentration is increased until the critical micelle concentration (CMC) is reached. Micelles are highly soluble in water because of their polar exterior. At the same time, their non-polar interior provides a hydrophobic sink for organic compounds, thus increasing their organic compound solubility. Contaminant solubility and extraction efficiency is maximized when the surfactant concentration is above the CMC. On the other hand, a minimal effect on enhanced contaminant solubility is produced when adding surfactant concentrations near or only slightly above the CMC (Sabatini et al.,

2000). Surfactants are used to reduce interfacial tension (IFT) between the oil and water phases and to increase oil solubilization within the surfactant micelles as an emulsion (Rosen, 2004).
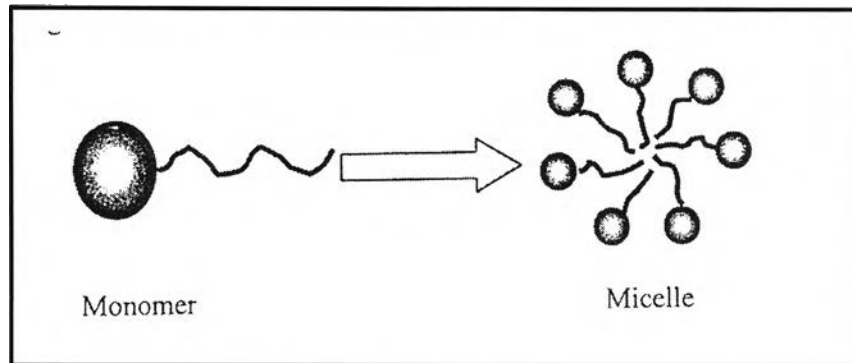

Figure 2.4 Formation of a micelle.

There are two types of micelles, which are normal and inverse (or reverse) micelles. In an aqueous solution, normal micelles are formed with their hydrophobic parts in the interior and hydrophilic parts in the exterior. In contrast, inverse micelles are formed in a non-polar solvent with the hydrophilic part in the interior and hydrophobic part in the exterior. The pictures of normal and inverse micelles are show in Figure 2.5.
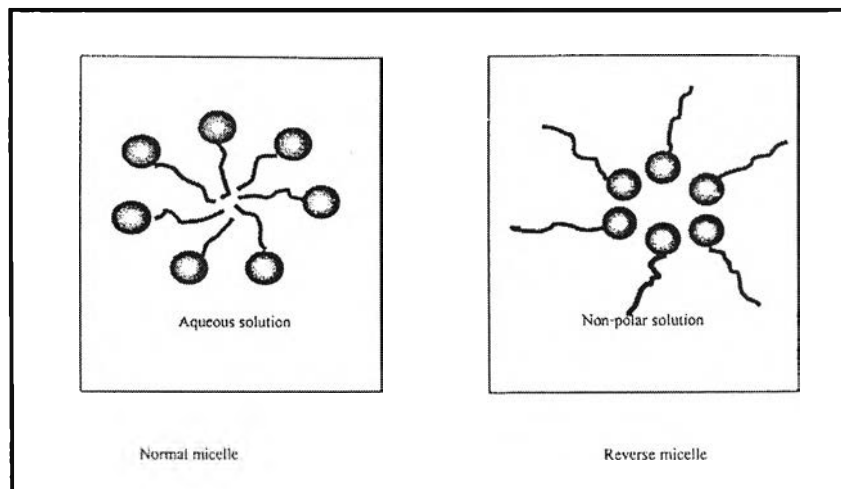

Figure 2.5 Normal micelles and inverse micelles.

2.5 Solubilization

Solubilization is one of the most important phenomena for surfactant solutions, which is generally used to describe the ability of the surfactant to enhance the aqueous solubility of sparingly soluble organic substances. One of the important properties of surfactants that is directly related to micelle formation is solubilization. Solubilization can be defined as the spontaneous dissolution of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen, 2004). Solubilization produces the ultra-low interfacial tension required for oil mobilization in enhanced oil recovery. The location that solubilization occurs depends on the nature of the solubilizate and the type of interaction between the solubilizate and surfactant. Solubilization can occur at different sites in the micelle:

a. On the surface of the micelle or at the micelle-solvent interface

b. Between the hydrophilic head group

c. In the palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups

d. More deeply in the palisade layer

e. In the inner core of the micelle

Solubilization is distinguished from emulsification (the dispersion of one liquid phase in another) by the fact that in solubilization, the solubilized material (the solubilizate) is in the same phase as the solubilizing solution and the system is consequently thermodynamically stable. There are many factors to determine the extent of solubilization such as the structures of the surfactants, solubilizate, electrolytes, and temperature.

2.6 Microemulsions

Microemulsions are defined to be clearly thermodynamically stable with homogeneous mixtures of oil, water and surfactant. Microemulsions are known to have remarkable properties of ultra-low interfacial tension between water and oil phases and a high solubility of both oil and water. This system can be divided into three types, which

are known as Winsor Type I, III and II microemulsions. A type I microemulsion corresponds to oil solubilized in aqueous micelles (surfactant aggregates having a hydrophobic interior and hydrophilic exterior). A type III microemulsion corresponds to an oil and water bicontinuous phase that is stabilized by a surfactant membrane. A type II microemulsion corresponds to water solubilized in reverse micelles present in the oil phase.

Microemulsion possesses superior characteristics of a relatively large interfacial area, Ultra-low interfacial tension (10^{-2}-10^{-3} mN/m), and large solubilization capacity for both water-soluble and oil-soluble compounds as compared with other colloidal systems (Bourrel, 1988).

The phase transition of microemulsion is related to the hydrophile-lipophile balance (HLB). The HLB is a parameter that shows the partitioning of surfactants between the oil and water phases relative to the surfactant's hydrophilicity. The transition of microemulsions and decreasing of the HLB for ionic surfactants is induced by increasing salinity, while for nonionic surfactants the transition occurs by raising the temperature of the system (Holmberg et al., 2003). Figure 2.6 shows the relationship between the types of microemulsion and interfacial tension. On the left hand side, Winsor Type I microemulsion is shown. The interfacial tension between oil and water decreases with increasing salinity for ionic surfactant systems and with increasing temperature for nonionic surfactant systems making oil solubilized in micelles. It shows oil in water microemulsion (o/w) equilibrating with an excess oil phase. The middle phase or Winsor Type III microemulsion is formed when the microemulsion structure becomes bicontinuous in equilibrium with excess water and excess oil phases. With continual decreases in salinity or temperature, the interfacial tension between the middle phase and excess oil ($\gamma_{o/m}$) equals the interfacial tension between the middle phase and excess water ($\gamma_{w/m}$) and is known as the lowest interfacial tension or the optimum salinity and phase inversion temperature or PIT. If the salinity or temperature is increased further, the interfacial tension between oil and water will increase, making water solubilized in reverse micelle. This is called Winsor type II microemulsion (Rosen, 2004). With these properties of low IFT and high solubilization, microemulsions are considered as an effective means to enhance oil remediation (Holmberg et al., 2003).
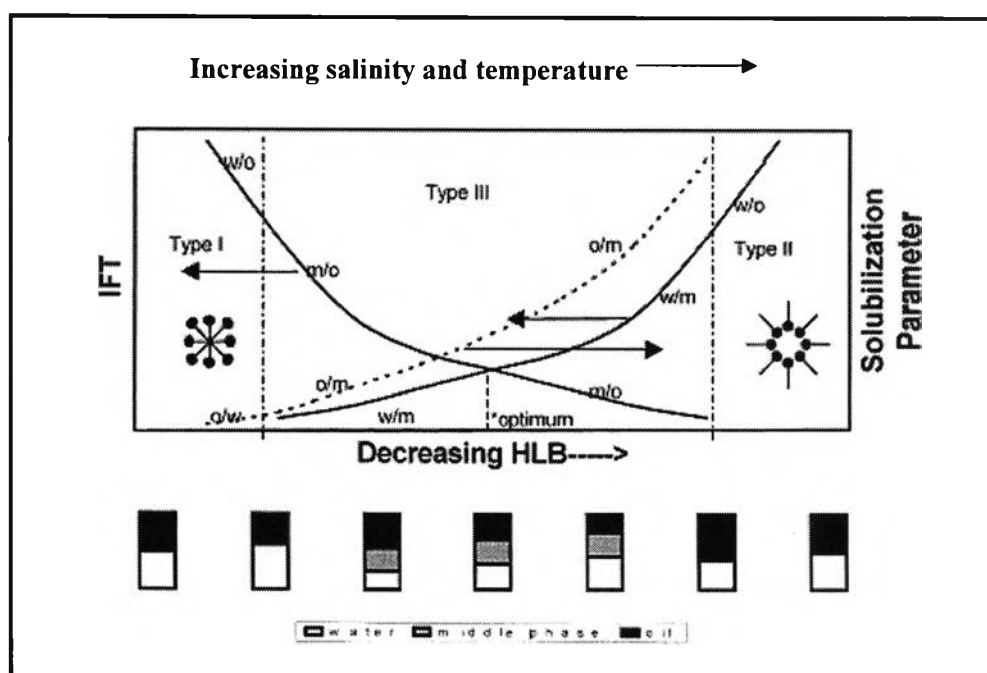
Figure 2.6 Winsor phase diagram (Sabatini et al., 2000).

2.7 Application of surfactant for oil removal

Surfactant enhanced aquifer remediation (SEAR) is a technique that uses surfactants to remediate subsurface contamination; such as those by chlorinated solvents and petroleum hydrocarbons. This enhancement is due to a reduction of IFT and a maximizing of oil solubilization. SEAR involves the injection of a micellar surfactant; and contaminants are subsequently extracted through strategically-placed pumping wells. Above ground processes are typically utilized to treat the contaminated groundwater and recycle the surfactant if necessary. Various design approaches may be taken to SEAR, depending upon the hydrogeological conditions and the physical-chemical properties of the DNAPL.

SEAR can be used in three ways: (a) it can increase contaminant mobility and solubility to improve the pump and treat performance, (b) it can decrease the mobility of contaminants to prevent its vertical migration, and (c) it can speed up the rate of biodegradation of the contaminant in soil (Pennell et al., 1994 and 1996). Surfactant enhanced aquifer remediation is categorized into two systems: solubilization and mobilization. Solubilization occurs from contaminant partitioning into the oil-like core of

the surfactant micelles. Mobilization is the displacement of oil from trapped residual oil resulting from a reduction of interfacial tension between NAPLs and water phases (Bedient et al., 1999).

The solubilization mechanism, which is at the heart of the SEAR process, is the formation of micelles in groundwater (i.e., colloidal clusters of nonionic surfactants), in which the molecules of the DNAPL are dissolved and then transported by the groundwater. In the field, SEAR works similarly to pump-and-treat operations except that dilute surfactant solutions are injected into the contaminated aquifer and withdrawn together with the solubilized DNAPLs for treatment (National Energy Technology Laboratory, 2002).

Surfactant based cleaning formulation by the formation of microemulsion is used to remove oily soil from substrate. The removal of petroleum product and vegetable oil from soil involves interactions between the surfactants, soil and the textile surface. Removal mechanisms applied to oily soils are the roll-up and snap-off or the emulsification and solubilization mechanisms. The roll-up mechanism is related to the contact angle between oily soil and fabric that has an affect on releasing oily soil from fabric. Emulsification and solubilization are mechanisms that decrease the interfacial tension between oil and surfactant solution and facilitates the solubilization of oily soil into surfactant micelles. Because minimum interfacial tension and maximum oil solubilization relate to microemulsion formation, oily soil detergency is highly dependent on the microemulsion system. For example, the phase inversion temperature (PIT) of an oil-water-surfactant system affects the detergency performance of a nonionic surfactant system (Holmberg, 2003).

2.8   Application of surfactant gradient system

Even though the SEAR technique effectively reduces interfacial tension between the oil and water phase, the use of this system must also consider the vertical migration of DNAPLs and the system must be controlled to achieve maximum removal at the lowest cost (Acosta et al., 2002).

Sabatini et al. (2000) identified that solubility enhancement, interfacial tension, viscosity and the density of selected surfactant systems were important variables

affecting remediation. Thus a surfactant gradient system was introduced to increase the solubilization potential while minimizing the mobilization of trapped oil.

The gradient approach is based on the concept of maximizing contaminant solubility while minimizing contaminant mobility by flushing different surfactant mixtures at different salinities or different temperature which provides different interfacial tensions between oil and the surfactant solution (Sabatini et al., 2000). From the change of the IFT, oil will become detached from the subsurface and subsequently, be trapped in the micelles (Childs et al., 2004). As a consequence, the problem of the mobilization of DNAPLs can be reduced. This means that surfactant systems can be formulated to obtain the maximum solubilization of oil in a surfactant solution without a middle phase formation. This phenomenon is believed to occur in the supersolubilization region. The supersolubilization region is a system operated near a type I/type III microemulsion boundary (Childs et al., 2004).

Tongcumpou et al. (2003) studied the comparison of the IFT between the supersolubilization region and Winsor type III microemulsion for detergency applications. They found that the supersolubilization region provides oil solubilization and water/oil IFT which are almost as good as the optimum condition in a middle phase system.

In 2004, Childs et al. developed a surfactant gradient approach to enhance DNAPL remediation. They used an electrolyte gradient to maximize the PCE solubilization while minimizing the potential for PCE mobilization. Column experiments were studied with selected surfactant systems from the phase behavior study. The additional gradient step with initial IFT above 1 mN/m can dramatically reduce the amount of PCE that mobilizes. They suggested that this approach can be effectively used to improve the efficiency of surfactant enhanced DNAPL remediation.

In addition, Pabute (2005) furthered this study by using the temperature gradient approach on a surfactant solution for the removal of different types of oil; e.g., decane and hexadecane stained on fabric in a batch study. The results showed that when the temperature gradient approach was used, it was able to remove both oils slightly better than when the temperature was fixed for the whole washing experiment.

For this present study, the experiment of soil column study using surfactant gradient approach to remove two types of NAPL oil, diesel and motor oil from substrate was adapted from Childs et al. (2004) and Pabute (2005). The surfactant gradient system along with varying an electrolyte of the selected surfactant system in continuous flushing by beginning the surfactant flush at a higher IFT and gradually lowering IFT in three or four stages was introduced through the column to maximize solubilization enhancement while minimizing the mobilization of free phase oil.