

CHAPTER I

INTRODUCTION



1.1 State of Problem

Nowadays, the presence of non-biodegradable contaminants in industrial wastewaters is a major concern. Ortho-dichlorobenzene, ethylbenzene, and diesel are known as hazardous substances which can be found extensively in groundwaters and soils as a result of improper designs of hazardous waste disposal facilities, accidental spills, and the leakage of underground storage tanks, among other commercial and industrial sources.

Based on the existing treatment methods for oil removal, there are two popular techniques employed to treat industrial wastewater. First, an oil-trap chamber is the most simple method to remove oil from wastewaters by gravitational force. The advantages of this technique are the lowest investment and operation costs as well as its simplicity in operation. However, it has a very low efficiency of oil removal and it is impractical to apply for a large quantity of wastewater. The second technique is a dissolved air flotation (DAF) system which is commonly used to treat various wastewaters since it can provide a very high oil removal efficiency. However, this process is required a relatively high pressure typically 5 atm resulting in high cost in both investment and operation. In contrast, froth flotation can be operated at atmospheric pressure leading to lowering both investment and operation costs. Therefore, it is very interesting to develop froth flotation to replace existing DAF units used widely to treat industrial wastewater.

Froth Flotation is widely used in several processes (Wungrattanasopon *et al.*, 1996, Koutlemani *et al.*, 1994, Zouboulis *et al.*, 1994, Clarke *et al.*, 1979, and Kabil *et al.*, 1994) including selective separation of minerals (Benn *et al.*, 1993, and Leu *et al.*, 1994), removing ink from paper fibers in paper recycling, and removal of emulsified oil from water (Pongstabodee *et al.*, 1998, and Feng *et al.*, 2000). The presence of emulsified oils, like ortho-dichlorobenzene, ethylbenzene, and diesel, in water is a serious problem for wastewater treatment since these substances are non-biodegradable. Froth flotation is an alternative technique to solve this problem

because it has several advantages including simplicity in operation, low space requirement, high efficiency of removal, flexibility of application to various pollutants at various scales, and low cost (Choi *et al.*, 1996). Based upon our previous works (Pongstabodee *et al.*, 1998), the maximum oil removal was achieved when the system was in Winsor Type III microemulsion. Hence, it is imperative to conduct experimental study on froth flotation in order to obtain better understanding and to apply for real applications.

1.2 Objectives

1. To study phase diagrams to form Winsor Type I-III-II microemulsions with ethylbenzene and diesel oil.
2. To study the effects of operating variables in the froth flotation column on the foam characteristic and the efficiency of oil removal.
3. To investigate the effect of foam formation and foam stability on the performance of froth flotation.
4. To determine the relationship between Winsor Type III microemulsion and the efficiency of froth flotation operation.

1.3 Scope of Work

In this study, ortho-dichlorobenzene, ethylbenzene, and diesel are studied as emulsified oils. Phase behaviors of all emulsified oils were studied in the first phase of this study in order to investigate the suitable systems to be operated in froth flotation and foam characteristic experiments. In addition, interfacial tensions of each system were measured. After the suitable systems were obtained from the first phase of the work, these selected systems were studied in froth flotation and foam characteristic experiments to determine the relationship between interfacial tensions, foam formation, foam stability, and performance of froth flotation in the second phase of the study. The last phase of the work was the investigation of the foam characteristic of selected systems in order to elucidate the correlation of foam characteristic and performance of froth flotation.

1.4 Surfactants

A surfactant is a substance which has a unique property of adsorbing onto the surfaces or interfaces of aqueous systems resulting in reducing the surface or interfacial free energies of those surfaces (or interfaces). The term of interface indicates a boundary between any two immiscible phases while the term of surface denotes an interface where one phase is a gas, usually air.

Surfactants have a basically molecular structure consisting of a head group that has very little attraction for a solvent but has strong attraction for water, known as a hydrophilic group, together with a tail group that has strong attraction for a solvent but has little attraction for water, called hydrophobic group. Surfactants are divided into four types which are

1. *Anionic Surfactants*: The surface-active portion of the molecule bears a negative charge.
2. *Cationic Surfactants*: The surface-active portion bears a positive charge.
3. *Zwitterionic Surfactants*: Both positive and negative charges are present in the surface-active portion.
4. *Nonionic Surfactants*: The surface-active portion bears no apparent ionic charge.

A single molecule of surfactant is called monomer and at a sufficient concentration in solution, monomers or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization that is illustrated in Figure 1.1 and the lowest total concentration at which micelles are present is called the critical micelle concentration (CMC).

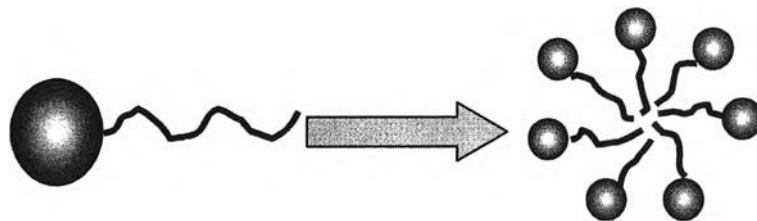


Figure 1.1 Formation of micelle.

There are two types of micelles which are normal and inverse (or reverse) micelles. For an aqueous solution, normal micelles are formed with the hydrophobic part (tail part) in the interior and the hydrophilic part (polar head) toward the aqueous phase. In contrast with the reverse micelles, they are formed in a non-polar solvent with the hydrophilic part in the interior and the hydrophobic part in the external. The picture of normal and reverse micelles is shown in Figure 1.2.

A great increase in solubility of a compound associated with the formation of micelles or reversed micelles has been termed “Solubilization” by McBain. The presence of micelles in the solution systems has a special advantage that is organic compounds, such as oils and hydrocarbons, or water can be solubilized more into the solutions. It is because the organic compounds or water can be dissolved into the center cores of micelles. Furthermore, the solubilization increases as a number of micelles in the solution increases.

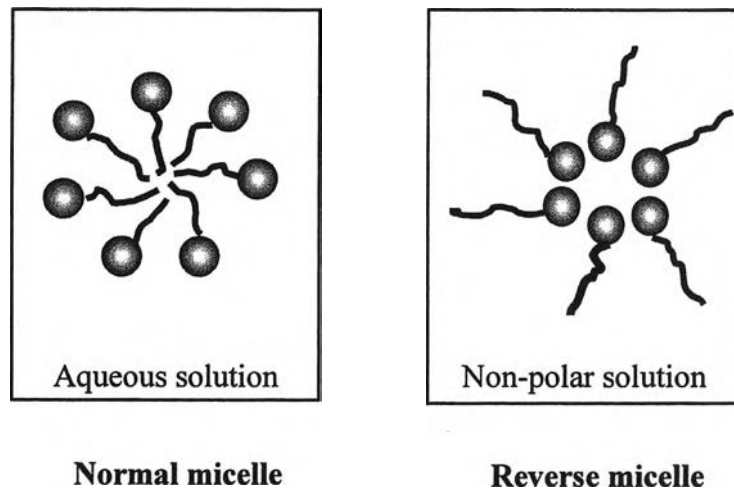


Figure 1.2 Normal micelles and inverses micelles.

Ref.: Bourrel *et al.*, 1988

1.5 Emulsion Systems

If two immiscible liquids are mixed well with a proper surfactant and left to reach equilibration, one of the two liquids will form tiny dispersing having droplets in the other liquid. This type of mixture is known as emulsion. Emulsions have long been of great practical interests because of their widespread occurrence in everyday

life. Some important and familiar emulsions include food products (e.g. milk, icecream, and mayonnaise), cosmetics (e.g. creams and lotions), pharmaceuticals (soluble vitamin and hormone products), and agricultural products (insecticide and herbicide emulsion formulations).

Emulsions are a special kind of colloidal dispersion: one liquid is dispersed in a continuous liquid phase of different compositions. The dispersed phase and the continuous phase are sometimes referred to as the internal (dispersed) phase and the external phase, respectively. There are three types of emulsions, based on the size of the dispersed particles. The first type is macroemulsion, the most well-known type. Macroemulsion is opaque in appearance with particle sizes larger than 400 nm (0.4 μm), and it is easily visible under a microscope. Microemulsion is the second type of emulsion. It is transparent with particle sizes smaller than 100 nm (0.1 μm). The last type is miniemulsion, a recently suggested type that is blue-white with particle size between the first two types (100 – 400 nm). Microemulsion is thermodynamically stable while the other two emulsions of macroemulsion and miniemulsion are unstable (Bourrel *et al.*, 1988).

1.5.1 Microemulsions

Microemulsions are transparent dispersion containing two immiscible liquids with particles of 10 – 100 nm diameters that are generally obtained upon mixing two immiscible liquid with a surfactant. Each droplet is separated from the continuous phase by forming a monolayer of surfactant at the interface. Bicontinuous microemulsions contain both oil and water layers a few molecules in thickness, separated by a monolayer of surfactant. Each layer may extend over a macroscopic distance, with many layers making up the microemulsion. Microemulsions may be water-external (o/w) or oil-external (w/o), or both. It can be generally prepared with more than one surfactant or with a mixture of a surfactant and a cosurfactant. The combination is usually required to obtain a proper balance between hydrophilic and hydrophobic properties for any particular oil to meet any specific applications. This balance can be determined experimentally by mixing an oil and water in various proportions with the surfactant-cosurfactant combination and noting whether a Winsor Type I, II, III, or IV system is obtained.

In some systems an addition of a fourth component, a cosurfactant, to an oil-water-surfactant system can cause the interfacial tension to drop to a near-zero value, typically in order of 10^{-3} to 10^{-4} mN/m. This ultralow interfacial tension allows spontaneous or nearly spontaneous emulsification with very small droplet sizes, ca. 10 nm or smaller. The droplets can be so small that they scatter little light; the emulsions appear to be transparent and do not break on standing or centrifuging.

The most studied phase equilibria of microemulsions are widely known as the Winsor-type microemulsion. The study is normally carried out by using a salinity scan, as shown in Figure 1.3. By increasing salinity, one can simply visualize a progressive change in the phase diagram and behavior.

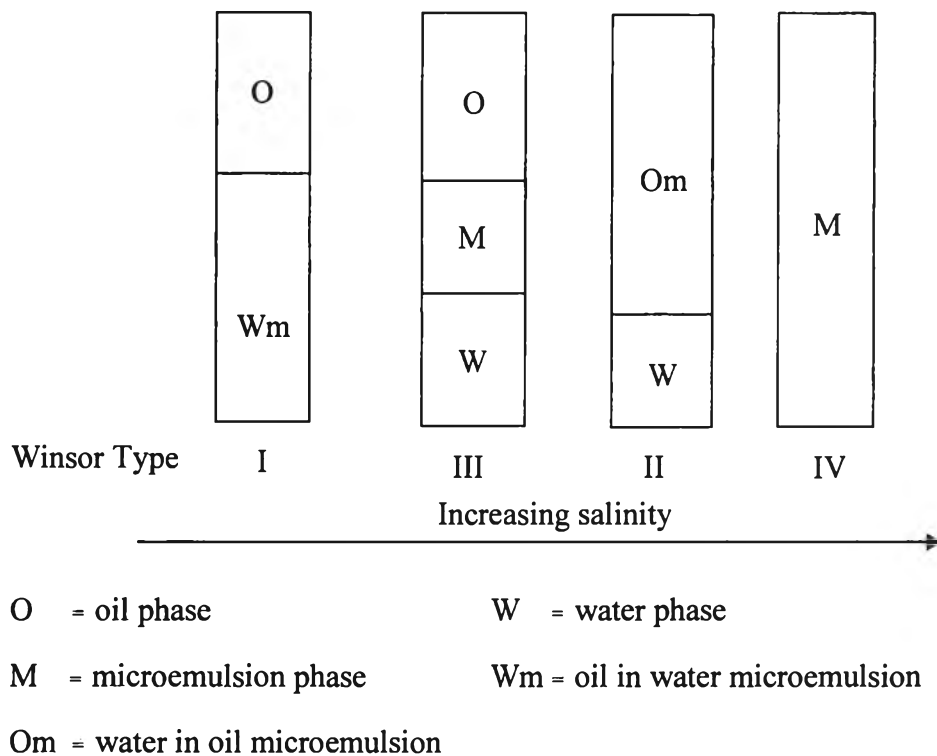


Figure 1.3 Schematic diagram of types of microemulsions.

Ref.: Winsor, 1954

In a low-salinity region, the Winsor type I system represents a lower-phase o/w microemulsion in equilibrium with an excess oil. In a high-salinity region, the Winsor type II system consists of an upper-phase w/o microemulsion in

equilibrium with an excess brine. It is clear that both Winsor type I and Winsor type II phase equilibria are driven by the bending stress of interfacial film. In an intermediate-salinity region, the Winsor type III system formed is composed of a middle-phase microemulsion in equilibrium with both excess oil and excess brine phases. The optimal salinity is defined as the salinity at which equal volumes of brine and oil are solubilized in the middle-phase microemulsion (Taylor *et al.*, 1992).

A number of factors can affect the phase type of microemulsion. These factors generally act by changing the partitioning of the surfactant between the brine and oil phases. In general, any change in the surfactant-oil-brine system that decreases the interfacial tensions between the excess oil and the excess water phases will cause the phase shift from Winsor type I to Winsor type III to Winsor type II as indicated in Figure 1.4.

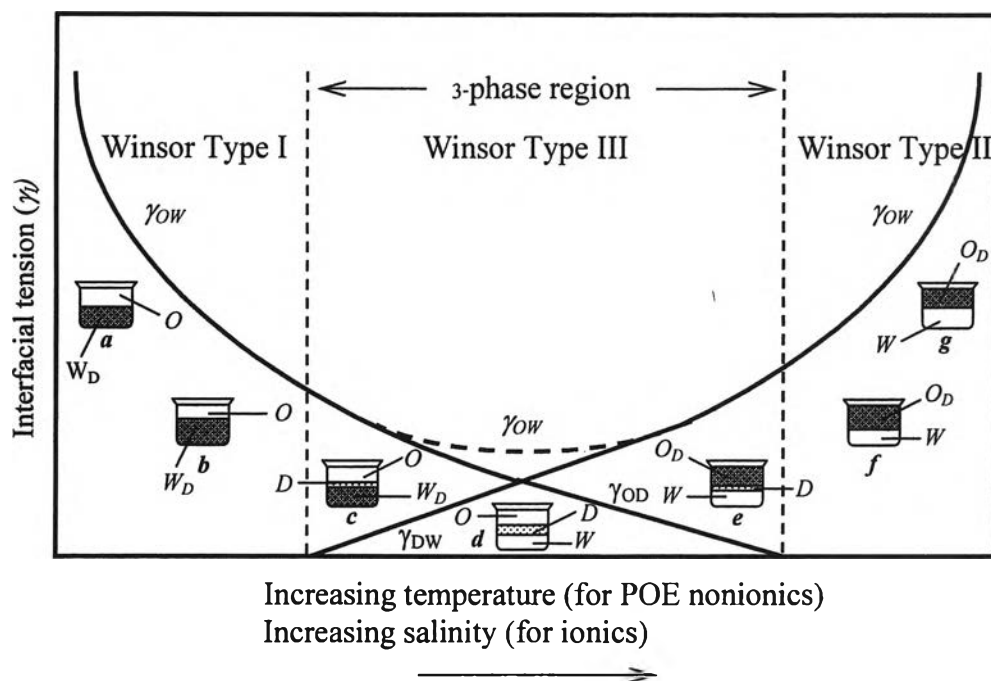


Figure 1.4 Relationship between interfacial tension and phase behavior.

Ref.: Wu *et al.*, 2000

Increasing salinity generally decreases the solubility of the surfactant in the aqueous phase. This decreased solubility tends to shift the phase behavior from Winsor type I to type III and then to type II. Changing oil type so that the surfactant

is more soluble in the oil will also shift the phase behavior from left to right. By increasing the molecular weight of the hydrophobic part of the surfactant, the oil solubility in the aqueous phase will generally decrease, and phase behavior will shift from left to right. Decreasing the amount of branches of the hydrophobic part will have the same effect. Similarly, decreasing polarity of the hydrophilic group will also decrease solubility in the aqueous phase (Taylor *et al.*, 1992).

The following changes will also shift phase behavior from Winsor Type I to Winsor Type III to Winsor Type II (Taylor *et al.*, 1992):

- Decrease in temperature for anionic surfactants
- Increase in temperature for nonionic surfactants
- Increase in alcohol concentration (alcohols of fewer than four carbons)
- Decrease in alcohol concentration (alcohols of more than four carbons)
- Increase in the divalent ion concentration of the brine

1.5.2 Solubilization Parameter

The solubilization parameters of oil (SP_o) and water (SP_w) are defined as

$$SP_o = \frac{V_o}{V_s} \quad \text{and} \quad SP_w = \frac{V_w}{V_s} \quad (1.1)$$

where V_o is the oil volume solubilized, V_s is the volume of surfactant, and V_w is the volume of water solubilized. All three variables are measured in the microemulsion phase. An interfacial tension (γ) can be measured between the microemulsion and excess oil phases (γ_{mo}) or between the microemulsion and excess water phases (γ_{mw}). As an interfacial tension decreases, the solubilization parameter increases as shown in Shun-Huh equation (Huh, 1979)

$$SP^2 \times \gamma = \text{Constant} \quad (1.2)$$

1.6 Principles of Froth Flotation

Flotation is a surfactant-based separation process in which surfactant is added to an aqueous solution and air is sparged through the solution. Consequently,

solid particles or droplets of oil are removed by adhering to the rising air bubbles. These particles adhered to the air bubbles are accumulated as foam or froth at the top of the flotation cell, and are skimmed off. The skimmed foam contains the removed substances in a higher concentration (after foam is broken) as compared to that in the feed solution. Generally, there are four basic steps in the flotation process for treating oily wastewater, namely bubble generation in oily water, contact between oil droplets suspended in the water and gas bubbles, attachment of oil droplets to gas bubbles, and rising of the bubble-droplets to assembly at the water surface where the oil can be removed by skimming off. Matis and Zouboulis (Matis *et al.*, 1995) reported that the stability of the froth was described by bubble coalescence and breakage parameters. The bubble coalescence is mainly due to the difference in pressure, which a smaller bubble has higher pressure than a bigger bubble, while the breakage is mainly dedicated to lowering the thickness of the film due to the force of gravity.

Surfactants play two important roles in flotation of mineral processing as collectors and frothers. As collectors, surfactants make the surface of oil droplets hydrophobic in character while they influence the kinetics of bubble-oil droplet attachment as frothers. Moreover, surfactants are used to promote foaming since absolutely pure liquids do not foam. The use of froth flotation for the removal of insoluble organic contaminants from water is shown in Figure 1.5.

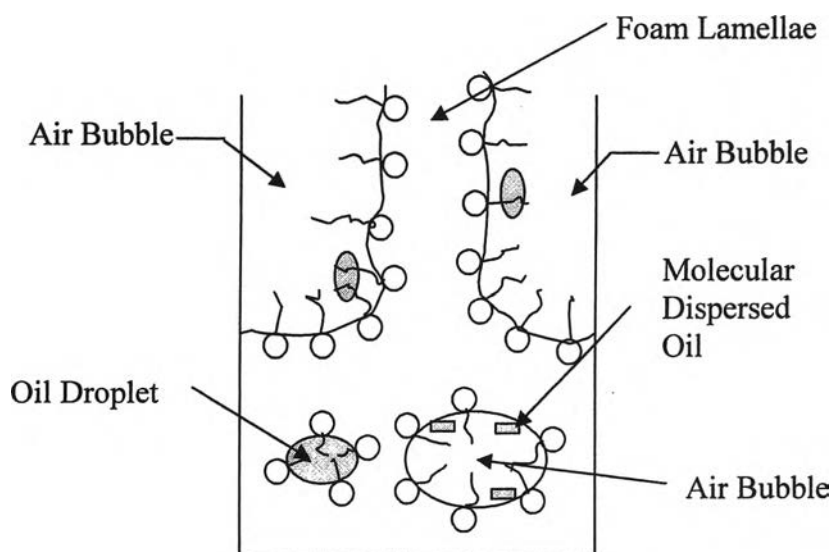


Figure 1.5 Schematic of the foam flotation process.

Ref.: Pongstabodee *et al.*, 1998

The surfactants tend to strongly adsorb at the air/water interface with the hydrophobic or tail groups in the air and the hydrophilic or head groups in the water. A closed-pack monolayer of surfactant is formed at the bubble surface under conditions normally employed. The hydrophobic region formed by the tail groups of the surfactant is compatible for dissolved organic solutes which tend to co-adsorb at the bubble surface. Polar regions of the solute molecule can also interact with the surfactant head groups, affecting solute adsorption at the air-water interface.

The effect of type, concentration of surfactant and NaCl on the removal efficiency of tert-butylphenol (TBP) by using foam flotation process was studied by Wungrattanasophon *et al.* (1996). This process was operated in a batch mode. Cetyl pyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) were used as surfactant to remove TBP from water in a flotation process. The TBP removal was maximized when the surfactant concentration was around the critical micelle concentration (CMC). The addition of NaCl affected the surfactant monolayer and micelle formation. It enhanced the removal ability of SDS, while reduced the removal ability of CPC.

In 1996, Tharapiwattannon *et al.* used foam fractionation to recover surfactant from water. A simple continuous mode foam fractionation was used in this work. Sodium dodecyl sulfate (SDS), Cetylpyridinium chloride (CPC), and Sodium n-hexadecyl diphenyloxide disulfonate (Dowfax 8390 or DADS) were studied. Under the suitable conditions, 90% removal of CPC could be obtained in a single stage with a liquid residence time of 375 minutes. From this study, the effectiveness of the foam fractionation process in recovering CPC was better than for DADS and SDS. In this study, the effects of air flow rate, foam height, liquid height, liquid feed surfactant concentration, and sparger porosity were studied. They found that an increase in the air flow resulted in a decrease in the enrichment ratio and an increase in the surfactant recovery rate while liquid height had little effect on the separation process. The enrichment ratio decreased and the surfactant recovery rate increased as feed liquid surfactant concentration increased. Moreover, a decrease in the pore size of the porous sparger resulted in a decrease in the enrichment ratio and an increase in the surfactant recovery rate.

Pongstabodee *et al.* (1998) studied about the removal of ortho-dichlorobenzene (ODCB) by froth flotation under Winsor Type III microemulsion. However, the studied system in this work did not reach the optimum condition because precipitation and liquid crystal occurred under the optimum condition. From the experimental results, the removal efficiency of ODCB increased as the surfactant concentration increased, salinity increased, causing a transition of Winsor Type I to Type III, and oil/water ratio decreased. The cationic surfactant was more effective than either the monosulfate or the disulfate anionic surfactant.

To improve the system to reach the optimum condition, Ratanarojanatam (1995) focused on the use of mixed anionic and nonionic surfactants which are sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)₁₀), respectively to remove ortho-dichlorobenzene (ODCB) from water. The optimum condition was achieved at 5% total surfactant concentration and fraction of SDS at 0.5. From the results in froth flotation experiment, the amount of oil removal from Winsor's type III microemulsion system was higher than that from Winsor's type I and II system. The highest oil removal of 91% was achieved at 7% total surfactant concentration and weight fraction of SDS at 0.8. In addition, Ratanarojanatam found that the overhead selectivity of oil to water is higher than the selectivity of oil to water in the feed when Winsor's type III was formed, *vice versa* in Winsor's type I regime. It can be concluded from this work that Winsor's type III has high advantage on performance of froth flotation because the maximum of oil removal and the separation is achieved in this regime.

Phoochinda (1999) studied the effect of Winsor's type III microemulsion on the amount of ortho-dichlorobenzene removal by using mixed surfactant systems which are sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)₁₀). Froth flotation experiment was studied at 3% and 5% total surfactant concentration. The results in this study confirmed that the highest oil removal corresponded to the formation of Winsor's type III microemulsion. Moreover, the combination of each phase in Winsor's type III microemulsion was studied to identify which phase is the main source of the removed oil. Interestingly, the oil removal from w-o systems is much higher than that from w-m systems. In addition, the effect of NaCl in the w-m-o system was studied and showed that adding 0.5 % by

weight of NaCl increased the ODCB removal but adding NaCl more than 1.0% by weight decreased the ODCB removal. The effect of volume of each phase was also studied. The results showed that when the volume of the oil phase decreased and the volume of the water phase increased in the w-o system, the ODCB removal decreased. When the volume of the middle phase increased and the volume of the water phase decreased in the w-m system, the ODCB removal increased.

In 2000, Feng and Aldrich studied the removal of diesel from aqueous emulsions by using flotation. The stability of these emulsions was characterized and factors such as Ph and salinity affecting the stability of emulsion were investigated. Moreover, they studied the effects of anionic and cationic surfactants, original diesel content, air flow rate, surfactant concentration and the air distributor sinter size. From the experimental results, it was concluded that when Ph exceeded 11, the emulsion stability decreased rapidly, leading to very rapid destruction of the emulsion and the removal of diesel by flotation increased rapidly. An addition of the electrolyte (NaCl) was found to have some influence on its stability. The cationic surfactant such as octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC) were effective collectors than the anionic surfactant which was sodium dodecyl sulfate (SDS). Under the optimal conditions, approximately 99% of the diesel removal could be obtained. The residual diesel concentration in the effluent was less than 10 ppm.

1.7 Studied Oils as Hazardous Substances

1.7.1 Ortho-dichlorobenzene

Ortho-dichlorobenzene is an aromatic substance. It is one kind of chlorobenzenes, which are widely used in several applications including solvents in paints, a raw material in the manufacture of phenol and aniline, an insecticide for termites, a degreasing agent for metals and as a heat transfer medium (Martin *et al.*, 1992). Ortho-dichlorobenzene is a starting material to produce 3, 4 dichloroaniline that is a raw material in the herbicide production. It can damage human's health such as depression of central nervous system, anesthesia and liver damage. It is a representative of pollutants in groundwater and rank twenty-fifth in the EPA list of

organic priority pollutants. Since ortho-dichlorobenzene is heavier than water, it will be a good representative of heavy oils in this study.

1.7.2 Ethylbenzene

Ethylbenzene is a colorless organic liquid with a sweet, gasoline-like odor. The greatest use (over 99 percent) of ethylbenzene is to make styrene which is another organic liquid used as a building block for many plastics. It is also used as a solvent for coatings, and in making rubber and plastic wrap. Ethylbenzene may be found in industrial discharges or leakage of underground storage tanks. From the EPA list of organic priority pollutants, only 0.7 parts per million (ppm) of ethylbenzene has a potential to damage the human's health. It can damage the liver, kidneys, central nervous system and eyes.

1.7.3 Diesel

Diesel is classified as middle distillates and is denser than gasoline, thus providing more energy per unit volume than gasoline. It is a complex combination of hydrocarbons produced by the distillation of crude oil. Diesel consists of hydrocarbons having carbon numbers predominantly in the range of C₉-C₂₀ and boiling in the range of approximately 163-357°C.

Apart from contamination of groundwater by diesel leakage, long-term potential hazards are resulted from the lighter, more volatile and water soluble compounds (such as toluene and xylenes) fractions. Chronic effects associated with middle distillates are mainly due to exposure to aromatic compounds.