CHAPTER 2

BACKGROUND AND RELATED WORKS

2.1 Literature Review

2.1.1 Surfactant and Soil Flushing

Ellis et al. (1985) tested several commercially available surfactants at the bench-scale experiment to treat soil that is contaminated with both PCB (polychlorinated biphenyl) and other hydrocarbons. Several surfactants and combinations of surfactants were used, including Richonate YLA (anionic) and Hyonic NP-90 (nonionic). The studies were performed using the batch shaker method, 100 g of contaminated soil was mixed with 200 ml of the surfactant solution containing various surfactant concentrations and then the mixer was agitated for one hour. Both soil and decanted leachate were analyzed. The ratio of 1:1 of the nonionic surfactants Adsee 799 and Hyonic NP-90 gave the highest removal of 93% for the hydrocarbons and 98% for the PCBs. These results were one to two orders of magnitude better than the removal efficiency using water alone. The optimum concentration of these was determined to be 0.75% by volume. The surfactant combination was then used to flood PCBs and chlorinated phenols contaminated soil in a packed column. It was concluded that after 3 and 10 pore volumes of surfactant solutions, the pollutant removal efficiency was 74.5% and 85.9%, respectively.

Abdul et al. (1990) studied the performance of commercially available anionic and nonionic surfactants to clean a sandy soil contaminated with automatic transmission fluid (ATF). The contaminated content was about 0.2385+/- 0.0199 g/5 g of soil. Using a batch shaker method, 5 g of contaminated soil was mixed with 100 ml of 0.5% by volume surfactant solution for 30 minutes. After settling for 10 minutes, the supernatant was decanted and then the settled soil was rinsed once with 100 ml surfactant solution, and twice with 50 ml water. The surfactant solutions and the rinsed water were analyzed for ATF. The experimental results showed that the removal efficiencies of ATF were 33% to 84% for nonionic surfactants and 56% to 81% for anionic surfactants, but for washing the

soil with water alone, the ATF reduction was only 23%. The effectiveness of the surfactants in removing ATF from the soil did not appear to be dependent on whether they were nonionic or anionic.

Grimberg et al. (1994) determined the influence of a surfactant on the rate of dissolution of phenanthrene, a model PAH. Phenanthrene dissolution kinetics depended on the observed mass transfer coefficient and the apparent saturation concentration, both of which depended on surfactant concentration. A simple two-step mass transfer model was developed to describe the relationship between dissolution rate and surfactant concentration. This approach may be useful in estimating effects on mass transfer kinetics for a variety of surfactants using data that are either available in the literature or are readily measured.

Shiau et al. (1994) established edible surfactant (those with FDA direct food additive status) systems capable of solubilizing (via micellar partitioning) and microemulsifying (via middle phase microemulsions) chlorinated solvents (PCE, TCE, and trans 1,2-DCE). The surfactants evaluated in this research were combinations of fatty acids and sugars and were selected based on their status as FDA direct food additive compounds and their hydrophile-lipophile balance (HLB). Solubilization studies were conducted in batch systems (40 ml EPA vials) by the excess additive method (excess organic phase present for equilibrium solubilization into micelles). Micellar partition coefficients with edible surfactants were observed to be a function of contaminant hydrophobicity and were comparable to values previously reported for other surfactants. It was noted that the most hydrophobic contaminant (PCE) evidenced the greatest partitioning between the micelles and the aqueous phase. The partitioning decreased as the hydrophobicity of the organic compound decreased (PCE> TCE> 1, 2-DCE). The solubilization potential (K_m) was noted to be affected more significantly by contaminant hydrophobicity than by surfactant selection. However, for a given organic compound, the partition coefficient is slightly higher for the nonionic surfactants than for the ionic surfactant.

Roy et al (1994) investigated and examined an innovative technique of in-situ flushing using colloidal gas aphron (CGA) suspensions generated from anionic surfactant solutions. The oily waste removal efficiency of CGAs was compared with that of conventional surfactant solutions and water flooding under different flow regimes. The CGAs and surfactant solutions produced from sodium dodecylsulfate (SDS), anionic surfactant that is commercially available and relatively non-toxic and biodegradable, were used to perform flooding experiments on a packed column of soil spiked with oily waste from a Superfund site north of Baton Rouge, Louisiana. The results shown that CGAs had a higher recovery of waste material (56%) than conventional solutions (47%) or water flooding (43%) in the downflow mode. The removal efficiency of CGAs was greater in the downflow mode than in upflow or horizontal modes, and increasing the surfactant concentration from 8 (CMC level) to 30 mM did not enhance the removal efficiency for either CGAs or conventional solutions. It can be seen that CGAs appeared to have better removal for the major chlorinated hydrocarbons present in the oily waste.

Thamsatitman (1995) investigated the role of nonionic, cationic and anionic surfactants on soil decontamination that used precipitated silica as a negatively charged soil model. The surfactants used were CTAB (cationic), Triton X-100 (nonionic) and Dowfax 8390 (anionic) and the target pollutants were 2 different DNAPLs, ortho-dichlorobenzene (ODCB) and tetrachloroethylene (PCE). The concentrations of surfactant used were varied at 1, 2, 5, and 10 times to the critical micelle concentrations (CMC) of each surfactant. The results shown that CTAB got the highest adsorption on the silica surface but Dowfax 8390 got no adsorption. For CTAB and Triton X-100 adsorption lowered the concentration below CMC. In soil washing, CTAB could remove ODCB and PCE about 6% and 3%, respectively. Triton X-100 could remove ODCB and PCE about 8% and 5%, respectively. Dowfax 8390 showed negative adsorption on the silica surface; it could form micelle in the wash system in equilibrium with the silica and could remove ODCB and PCE about 55% and 65%, respectively.

Roy et al. (1995) investigated the applicability of conventional surfactant solutions and colloidal gas aphron (CGA) suspensions to remove naphthalene from a contaminated soil matrix. Laboratory studies were conducted to evaluate the relative suitability of nonionic, cationic and anionic surfactants in removing naphthalene from the

soil. The nonionic surfactant used was Tergitol, HTAB was the cationic surfactant that was used and SDS was the anionic surfactants. Nonionic surfactant (Tergitol) was found to be more efficient than the ionic surfactants in removing naphthalene from a contaminated soil matrix in batch experiments and then was selected for further flushing studies. CGAs were generated with 0.15, 20 and 50 mM concentrations of Tergitol soluitons. The percent removal of naphthalene in six liquid pore volumes of CGAs was 1%, 11% and 51% with CGAs generated from 0.15, 20 and 50 mM Tergitol solution, respectively. Volatilization of naphthalene decreased with the increasing concentration of nonionic surfactant Tergitol. Micellar solubilization appeared to be the primary mechanism of removal using both surfactant solutions and CGAs. Increasing the concentration of the surfactant solution enhanced the percent removal of naphthalene. Using CGAs as a flushing medium may result in channeling and pore clogging in the soil matrix, thereby affecting the overall efficiency of the process.

Roy et al. (1995) studied the technology using CGAs to flush residual levels of a light non-aqueous phase liquid (LNAPL) such as automatic transmission fluid (ATF) from a Superfund site soil. Performance of CGA suspensions was compared with that of conventional aqueous anionic surfactant solutions under both stable gravity (downflow) and unstable gravity (upflow) conditions on a packed column of contaminated soil. The glass columns 10 cm long and 5.75 cm in diameter with a stainless steel top and bottom were used for all the experiments. A soil packing procedure was followed that achieved a bulk density range similar to the field soils (1.2-1.5 g/cm^3). It was found that CGA suspensions generated from 8 mM SDS solution removed about 50% ATF from the soil as compared to 42% by the conventional surfactant solution of the same concentration and to 20% by a water flood in downflow operation. CGAs were more effective in the downflow operation than in the upflow mode but for water floods and conventional surfactant solutions, the ATF removal in the upflow mode was higher than that in the downflow mode. In the upflow mode, both CGAs and conventional surfactant solution removed about 41% ATF from soil compared to 33% by water flood. They also indicated that increasing surfactant concentration beyond the CMC level did not increase the ATF removal efficiency for either CGAs or conventional surfactant solutions. The pressure required to pump the CGAs was much lower than that required for conventional surfactant solutions or water flood.

Yeom et al (1996) investigated dissolution of PAHs from soil contaminated with multi-component coal tar using a polymeric adsorbent, Tenax-TA and a nonionic surfactant, Brij 30. The results showed that Tenax created maximum concentration gradient at the soil/water interface, thus maximizing interfacial mass transfer. Even in the presence of Tenax, the release of PAHs from the weathered soil was a very slow, non-eqilibrium process. The rate-limiting step in the release of PAH was identified as diffusional mass transfer within the contaminant-soil matrix. Based on model analyses, the key parameter controlling dissolution of PAHs from the soil was found to be the diffusivities of PAHs within the soil/tar matrix. Brij 30 solution (5.5 g/L) substantially increased the rate of PAH dissolution from the soil. The enhanced mass transfer rates of PAHs by Brij 30 were attributed to their enhanced matrix diffusivities rather than their increased aqueous solubilities. Matrix diffusivities of PAHs in Brij 30 solution increased by two orders of magnitude compared with those with Tenax. Swelling of the weathered tar matrix of the soil by infiltrating surfactant molecules was suggested as the mechanism responsible for the observed diffusivity enhancement.

Roy et al (1997) studied the soil washing potential of a natural surfactant. The biodegradable plant-based surfactant was obtained from fruit pericarp of *Sapindus mukorossi*, a tree generally grown in tropical regions of Asia. A simple and economic method for the preparation of the surfactant was developed. The aqueous solubility of hexachlorobenzene (HCB) and naphthalene in the natural surfactant solutions were found to vary linearly with the concentration of the surfactant showing trends comparable to that of typical commercial surfactants. Natural surfactant solutions were also employed for flushing HCB from one-dimensional soil columns. A soil packing procedure was adopted to achieve a bulk density (1.6 g/cm^3) similar to that observed in the field. Experiments were conducted in the downflow mode with water and natural surfactant solutions at a flow rate of 2.5 ml/min (pore water velocity = 0.24 cm/min). The effluent samples were collected and analyzed for HCB. The results showed that HCB recoveries after 12 pore volumes of flushing with 0.5 and 1% of the surfactant solutions were 20 and 100 times more than that recovered by water flooding. It was clear that these promising results warranted further research to establish the usefulness of plant-based surfactants for soil washing.

In 1998, Kommalapati et al. investigated the ability of natural surfactant obtained from the fruit pericarp of *Sapindus mukorossi* to remove hydrophobic organic compounds (HOCs) from a representative soil. Soil was spiked with a chlorinated hydrocarbon, hexachlorobenzene (HCB), serving as a model HOC representative of contamination at a Superfund site north of Baton Rouge, LA. CGA suspensions generated from the surfactant were used in this study to flush HCB from the soil. CGAs generated with 1% natural surfactant removed 670 µg in 12 pore volumes compared to 8 µg by waterflood. They also found that natural surfactant performed better in the form of conventional solutions than CGAs at similar concentration in recovering HCB. Increase in natural surfactant concentration increased the removal of HCB significantly for both conventional surfactant solutions and CGA suspensions so the increased solubility of HCB was responsible for the enhanced recovery. The effect of alternating the introduction of flushing media with intermediate waterfloods on the removal of HCB and the pressure buildup across the soil column was also investigated. It was found that alternating the flushing media between CGA and water neither enhanced the recovery of HCB nor changed the pressure buildup across the soil column. In addition, the pressure buildup across the column remained fairly low when natural surfactant was used at concentrations up to 1% for both conventional solutions and CGA suspensions.

Yeom and Ghosh (1998) conducted batch experiments to determine the effects of Triton X-100, a nonionic phenolic ethoxylate surfactant, on the biodegradation of soil-bound naphthalene and phenanthrene. Two different types of soils, one contaminated with polynuclear aromatic hydrocarbons (PAHs) for different lengths of time, 2 days to 10 months, in the laboratory and the other, a field-contaminated soil from a manufactured gas plant (MGP) site, were used. Biodegradation of PAHs was measured by monitoring the $^{14}CO_2$ production for the artificially contaminated soils and the residual PAHs in soil phase for the MGP soil. Without adding surfactant, the mineralization rate of phenanthrene was significantly larger in the 10-month contaminated soil compared to that in the 2-day contaminated soil. Presumably, mineralization was mass-transfer limited in the soil with longer contamination period. Triton X-100 significantly enhanced mineralization in the 10 month-old soil but not in the 2-day old soil. The MGP soil, weathered over 2-3 decades, exhibited even greater enhancement of mineralization. Mineralization of PAHs in aged soils appears to be controlled by mass transfer rather than

the rate of biodegradation. Surfactants increase the rate of release of soil-bound contaminant and thus help promote biodegradation.

Bhandari et al. (2000) performed a soil washing study to evaluate the treatability of New Rover sand contaminated in the laboratory with a petroleum distillate. Unaltered and base-extracted sands were mixed with petroleum hydrocarbons, equilibrated, and washed with water or a commercial nonionic surfactant, Citrileen, at two different pH values (7 and 12). It was found that the surfactant had no significant effect on contaminant removal efficiencies at neutral pH. Washing the sand with distilled water at pH 7 resulted in 43% removal of total carbon from the sand particles. No major changes in carbon removal efficiencies were observed for water at pH 12 or for the surfactant solution at pH 7. However, removal of total soil carbon was significantly larger (53%) with the surfactant solution at pH 12. Treatment efficiencies of base-extracted sand particles were 10 to 13% higher than for the unaltered sand. Scanning electron microscopy (SEM) with elemental X-ray microscope was used to determine the distribution of iron and carbon on the New River sand surface. Low petroleum removal efficiencies were believed to be influenced by the high iron oxide content of the sand and the affinity of these metal oxides to bind natural and petroleum-derived organic carbon. Results suggested that the organic matter clearly played a role in the extent and intensity of hydrocarbon association. Removal of humic acids significantly improved total petroleum hydrocarbon (TPH) removal efficiency from the sand particles.

Sun and Puri (2001) investigated the role of some selected nonionic, anionic and cationic surfactants in solubilizing and mobilizing polycyclic aromatic hydrocarbons (PAHs) from soil. The data from the batch experiment showed that Brij 30 (a nonionic surfactant) started transporting the PAHs from soil to water at concentrations well below its apparent critical micelle concentration (ACMC). At its high concentrations, however, Brij 30 transported more PAHs to the aqueous phase. Thus, it showed a great potential in remediation of PAH-contaminated soil. The tested anionic and cationic surfactants did not show the solubilization effect until the concentrations reached their ACMCs. The experiment showed that the decomposition of the surfactants was more significant than that of the PAHs with the passage of time. A considerable portion of the solubilized

PAHs was either re-adsorbed by the soil particles or was hanging in the mobile phase after 170 days, depending on the nature and concentration of the individual surfactants. The data showed that the solubilized portion of the PAHs became more persistent in the soil-water system, and its transport was proportional to the concentration and nature of the surfactants studied.

Battke and Lieprlt (2000) examined the application of the non-toxic and readily biodegradable surfactant, Mulsifan RT 1 (Zschimmer & Schwarz Gmbh) to increase the PAH-extractability from soil and the amount of substrate. Use of pressurized batch-reactors overcame the oxygen limitation but reduced PAH-extractability. Simultaneous application of surfactant Mulsifan RT 1 and pressure in the batch reactors resulted in 95% PAH-biodegradation (parent removal of 1200 mg/kg dw EPA-PAH), application of surfactant only resulted in 81% biodegradation, application of the neither surfactant nor pressure resulted in 89% biodegradation after 66 days.

Hayes Thomas (2001) investigated a process for in-situ remediation of contaminated soil which provides enhanced mass transfer of pollutants from soils and non-aqueous phase liquids. Treating agents could be introduced into the contaminated soil and transported to an underground in-situ treatment zone of the contaminated soil by a foam-based fluid in a process for in-situ remediation. Treating agents employed in the process of this invention include bioenhancement chemicals such as nutrients, surfactants, oxidants and solvents, and bacterial cultures. The foam-based fluid was comprised of organic foam comprising between about 5% to 50% liquid and between about 50% to 95% gas. The foam was utilized as a carrier of the treating agents to the underground in-situ treatment zone, such as chemicals to reduce resistance to the mobile carrier phase in the subsurface, to provide chemical pretreatment in more concentrated forms, and to improve distribution of the treating agents in non-homogenous subsurface environments. The treating agents employed in the process of this invention promoted the controlled desorption of pollutants from the soil and non-aqueous phase liquids, thereby solubilizing the pollutants and making them available for biological attack.

Chun et al. (2002) investigated the solubilization of naphthalene and phenanthrene into the micelles formed by three different anionic surfactants for single, binary, and ternary mixtures including pyrene. The three surfactants were sodium dodecylbenzene sulfonate (SDDBS), monoalkylated disulfonated diphenyl oxide (MADS-C12), and dialkylated disulfonated diphenyl oxide (DADS-C12). The order of increasing solubility enhancement of naphthalene and phenanthrene was SDDBS < MADS-C12 << DADS-C12, which indicated that the hydrophobic chains in micellar core played a more important role for the solubilization of PAHs than the benzene rings in palisade layer of a micelle. The solubility enhancement of naphthalene was slightly changed in PAH mixtures. The solubility of phenanthrene was greatly enhanced in the presence of naphthalene but reduced in the presence of pyrene. The explanation for these results were that less hydrophobic compounds could be solubilized at the interfacial region of a hydrophobic core, which reduced the interfacial tension between the core and water, and then the reduced interfacial tension could support a larger core volume for the same interfacial energy.

2.1.2 Other Colloid Gas Ahprons Applications

Hasim and Gupta (1998) used CGAs to separate fine fibers from lean slurry of cellulosic pulp in a floatation column and the pulp fibers were recovered as foamate from the top. A pulp slurry, of concentration 1.0 kg/m^3 fiber, was used as the feed stream to recover pulp fibers. Sodium dodecylsulphate at a concentration of 2.0 kg/m^3 was used as a surfactant to generate the CGAs in a spinning disc apparatus at a rotation speed of 6000 rpm. The flotation cell was made of a perspex tube, 0.05 m in diameter and 1 m in height. The system worked in a counter-current fashion, where the feed was introduced at the top with the flow rate of 2.67 x 10^{-7} m^3/s and the CGAs were sparged from the bottom. The CGAs flow rates were varied from 2 x 10^{-7} m^3/c to 3.0 x 10^{-7} m^3/s. The results indicated that up to 70% flotation efficiency could be obtained within a short column height of 0.3-0.35 m and the separation efficiency improved with increasing flow rate of the CGAs. This technique can be applied to recover fine cellulosic pulp from paper-machine backwater.

Hasim et al. (1999) also used CGAs to clarify oily wastewater by flotation technique. Two important parameters in a floatation column, namely sparging rate of the CGAs and operating height on the concentration of palm oil, were studied in this work. A simple mass transfer correlation was proposed to evaluate the performance of a floatation column. Dilute surfactant solution (2 g/l) of SDS was stirred at a very high rotation speed of 6000 rpm to generate CGAs with a gas hold up of 61% (v/v). The flotation cell made of a perspex tube, 0.05 m in diameter and 1 m in height was used to separate oil-water emulsion. The oil droplets tended to adhere to the outside of this film, and being much smaller than the CGAs bubbles, a large number of droplets could be accommodated on each aphron and separated by floatation. As a result, high separation efficiencies could be achieved at relatively low residence time of the feed in the system. It was found that the CGAs sparging rate was an important factor in controlling the efficiency of the system and hence relatively high CGAs sparging rates should be employed for better performance.

2.2 Backgrounds

2.2.1 PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) are hydrocarbon compounds composed of benzene rings. PAHs generally occur as complex mixtures and not as single compounds. PAHs are primarily by-products of incomplete combustion. According to the Baseline National Toxics Inventory, the largest sources of air emissions are wildfires and prescribed burnings (73%), primary aluminum production (11%), coke ovens (charging, topside and door leaks) (5%), open burning of scrap tires (4%), on-road vehicles (3%), and coke ovens (pushing, quenching, and battery stacks) (2%). Additional sources include asphalt roofing manufacturing, industrial boilers, residential wood combustion, meat char boilers, and open trash burning. PAHs are also capable of undergoing long range transport, as vapor and particulate-phase material, although the contribution from long range sources is not known. (EPA, 1997)

The National Toxics Inventory for air toxics identified seven PAHs that have been identified as probable human carcinogens by EPA and as animal carcinogens by the International Agency for Research on Cancer (IARC). The seven PAHs comprising this subset are of similar molecular weight and are primarily found on particles in air emissions (EPA, 2000):

benz(a)anthracene	benzo(a)pyrene
chrysene	dibenz(a,h)anthracene
benzo(b)fluoranthene	indeno(1,2,3-cd)pyrene
benzo(k)fluoranthene	

Human exposure to PAHs occurs mainly through inhalation of air contaminated by cigarette and other tobacco smoke and through the consumption of foods, especially meats and fish that are smoked or charcoal-broiled. Exposure to PAHs may also occur in road sealing and roofing work involving coal tar and asphalt, in areas where high-temperature food fryers and broilers are in use, in homes that use wood fireplaces, wood-

stoves, or coal or oil furnaces, and where workers, vehicle occupants, or pedestrians are exposed to gasoline and diesel engine exhaust. Occupational exposures can also occur at workplaces such as coking plants, asphalt and aluminum production plants, or facilities that burn wood, coal, or oil (EPA, 2000).

Other exposure to PAHs may occur in the soil at or near hazardous waste sites, such as former manufactured-gas factory sites. PAHs have been found in some drinking water supplies in the United States. Background levels of PAHs in drinking water range from 4 to 24 nanograms per liter (ng/L) (EPA, 1997). Some PAHs may reasonably be expected to be carcinogenic and mutagenic substances. PAHs are in the rank 8-10 of 1999 CERCLA Priority List of Hazardous Substances (Agency for Toxic Substances and Disease Registry, 1999). The limit of PAHs in air is 0.2 milligrams per cubic meter of air (0.2 mg/m3) and the Permissible Exposure Limit (PEL) for mineral oil mist that contains PAHs is 5 mg/m3 averaged over an 8-hour exposure period (OSHA, 1994).

2.2.2 Soil Flushing

Soil flushing enhances contaminant recovery in conventional pump-and-treat systems by increasing the quantity of contaminants transported with the pumped water. Soil flushing systems use injection wells, drains, or filtration basins to flood the contaminated zone with chemical agents. The injected agents mobilize contaminants by increasing hydraulic gradients, reducing interfacial tension between NAPLs and water, increasing contaminant solubility, and reducing NAPL viscosity. Once the contaminants are mobilized, the system sweeps them to recovery wells or drains. At the conclusion of the flood, the flushing solution can be displaced to the recovery system by injecting water via the delivery system. Figure 2.1 shows a schematic of such a system.

Soil flushing can be used to enhance recovery of contaminants with low water solubility, pools and discontinuous ganglia or globules of NAPLs, and sorbed contaminants. Two types of chemical agents can enhance contaminant recovery: cosolvents and surfactants. The amount of organic contaminant mobilized during soil flushing depends on the chemical structure of the cosolvent or surfactant, the cosolvent or

surfactant concentration, geochemical conditions, the chemical structure of the contaminant, and temperature. Cosolvent concentrations must typically be greater than 20 percent to cause effective mobilization. Surfactants require much lower concentrations – an advantage over cosolvents (Committee on Ground Water Cleanup Alternative et al., 1994).
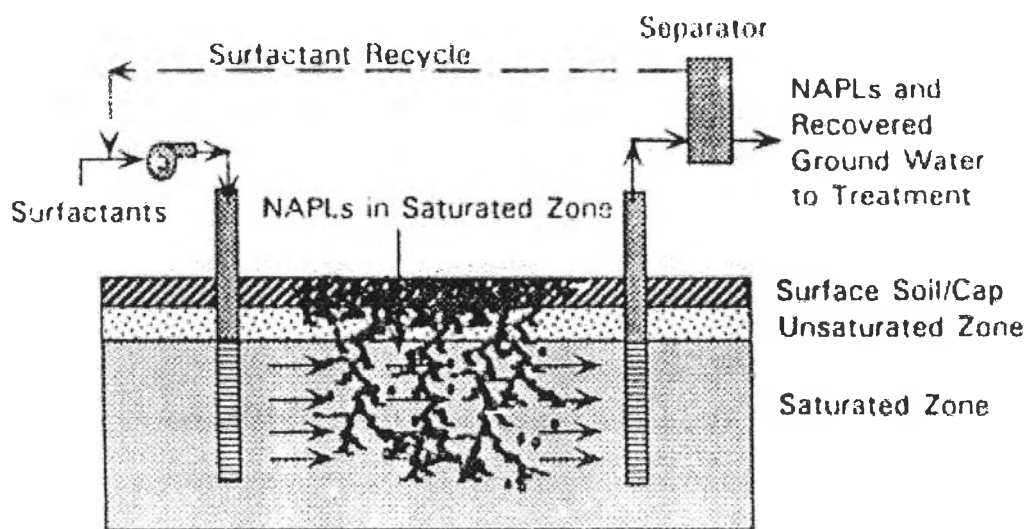

Figure 2.1 Process diagram for soil flushing (Committee on Ground Water Cleanup Alternative et al., 1994).

2.2.3 Surfactants

Because of the hydrophobic nature of the PAH compounds, conventional remedies such as pump-and-treat have proven to be of limited practical value. (Abdul et al., 1990; Roy et al., 1994) Therefore, significant efforts are being devoted to the development of efficacious approaches for the remediation of these contaminated sites. One of the methods to increase the solubility or to decrease the surface tension of the PAHs in water is the application of surfactants. Surfactants or surface active agents are chemical compounds that have the potential to alter the properties of fluid interfaces. Their molecules have two structural units: one with an affinity for water (the hydrophilic portion) and one with an aversion for water (the hydrophobic portion). The entire surfactant monomer is often referred to as amphiphilic because of its dual nature. The hydrophobic portion of the surfactant monomer is typically a long hydrocarbon chain, referred to as the "tail" of the molecule. The hydrophilic "head" group often includes anions or cations such as sodium, chloride, or bromide. The surfactant monomer is illustrated as a tadpole structure in Figure 2.2. The molecular weight of surfactants under consideration for environmental applications typically ranges from 200 g/mol to 2000 g/mol. Hydrophobic contaminants may partition into the hydrophobic core of a surfactant, increasing their mobility in the water. Surfactants are especially useful for dissolving non-aqueous phase liquid (NAPL) and enhancing NAPL mobility by lowering the interfacial tension between the NAPL and water, as shown in Figure 2.3. Surfactant solutions may also enhance recovery of sorbed contaminants. (Committee on Ground Water Cleanup Alternative et al., 1994)

Surfactant Monomer

Surfactant head | Surfactant tail

Hydrophilic | Hydrophobic

Surfactant Micelle

Amphiphile
in Palisade
Layer   Hydrophobic
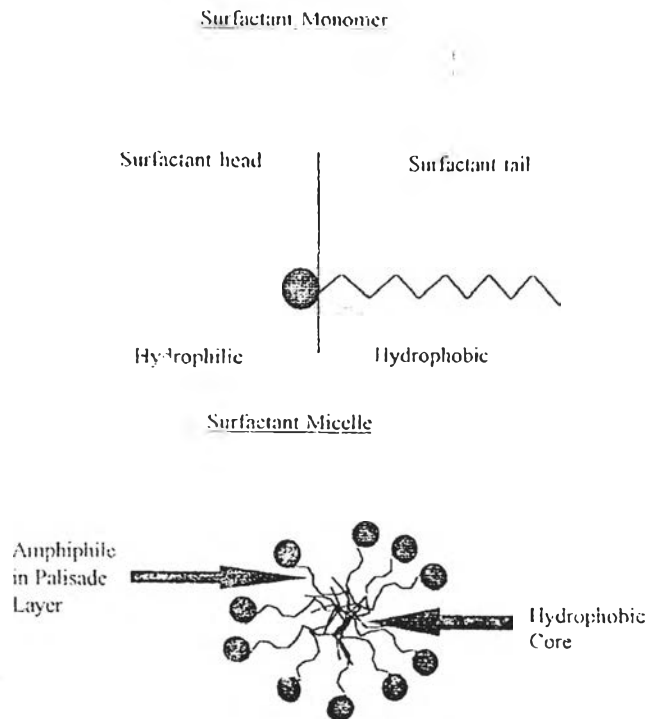   Core

Figure 2.2 Structure of the surfactant molecule, and a representation of a surfactant micelle in a surfactant solution somewhat above the critical micelle concentration (Wilson and Clarke, 1994).
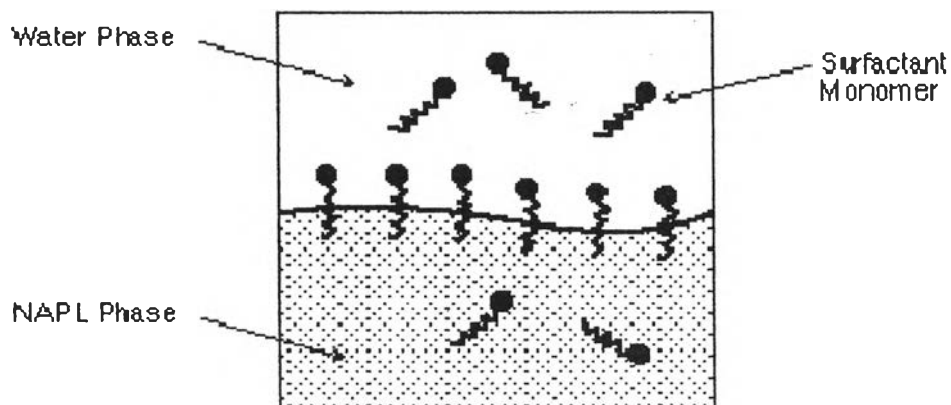
Water Phase   Surfactant
                                         Monomer

NAPL Phase

Figure 2.3 Performance of surfactant: surfactant monomers accumulate at the NAPL-water interface (Lowe, D., (1997).

2.2.3.1 Classification of surfactants

Surfactants can be generally classified according to the nature of their hydrophilic head group. **Anionic surfactants** give rise to a negatively charged surfactant ion (hence anionic) and a positively charged counterion upon dissolution in water. Examples of anionic surfactant groups include sulfonic acid salts, alcohol sulfates, alkylbenzene sulfonates, phosphoric acid esters, and carboxylic acid salts. Anionic surfactants tend to be good solubilizers and are relatively nontoxic. They have been used in petroleum oil recovery operations as well as in contaminant hydrogeology remediation applications.

Cationic surfactants yield a positively charged surfactant ion (hence cationic) and a negatively charged counterion upon dissolution in water. Examples include polyamines and their salts, quaternary ammonium salts, and amine oxides. Cationic surfactants tend to be toxic and are therefore not widely used in environmental applications at this time. Cationic surfactants also tend to sorb to anionic surfaces and so can be severely retarded in groundwater systems.

Nonionic surfactants are characterized by hydrophilic head groups that do not ionize appreciably in water. Examples include polyoxyethylenated alkylphenols, alcohol ethoxylates, alkylphenol ethoxylates, and alkanolamides. Nonionic surfactants tend to be good solubilizers and are relatively nontoxic. They are usually easily blended with other types of surfactants (i.e., used as cosurfactants) and therefore have found widespread use in petroleum and environmental applications. The performance of nonionic surfactants, unlike anionic surfactants, is relatively insensitive to the presence of salts in solution. (M.J. Schick, 1987)
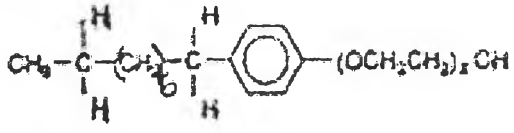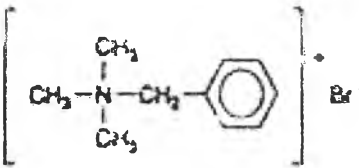
Surfactant	Ionic type	Molecular structure
Sodium dodecylsulfate	Anionic	$CH_3(CH_2)_{11}OSO_3^- Na^+$
Triton X-100	Nonionic	(structure)
Benzyltrimethyl-ammonium bromide	Cationic	(structure)
B-N-alkyl amino-propionic acid	Zwitterionic	$RNH_2CH_2CH_2COO^-$

Figure 2.4 Examples of surfactant types (Candida, 1992).

2.2.3.2 Micellization

A phenomenon unique to surfactants is the self-assembly of molecules into dynamic clusters called micelle (see Figure 2.5). It is important to distinguish that although all amphiphilic molecules are surface active and can be expected to be in excess at interfaces, not all amphiphilic compounds are commonly referred to as surfactants. As surfactants are added to an aqueous solution, they will tend to accumulate at fluid-fluid and fluid-solid interfaces. Some surfactant monomers also will exist in free solution in all phases present. Once a sufficient amount of surfactant has been added to aqueous solution, however, aggregations of surfactant monomers referred to as micelles will form. Micelles are often spherical in shape and can contain several hundred surfactant monomers. As shown in Figure 2.6, the threshold concentration at which micelles begin to form is termed the critical micelle concentration (CMC), which is different for every surfactant. CMCs typically range between 0.1 and 10 mM (Candida, 1992). Beyond the CMC, any surfactant added to aqueous solution will not increase the number of monomers in aqueous solution, but rather will contribute to the formation of additional micelles (Lowe, D., (1997).

A thermodynamically stable solution of micelles is referred to as a microemulsion. Contaminants can partition into the interior of the micelle, thereby increasing the total aqueous solubility of the contaminant by a process referred to as micellar solubilization. (Raghava R. *et al.,* 1998) The reduction in NAPL-water interfacial tension arising from the addition of a surfactant to an aqueous solution will reduce the influence of capillary forces. If the interfacial tension can be lowered sufficiently, physical mobilization of NAPL can occur. (D. Roy *et al,* 1995)
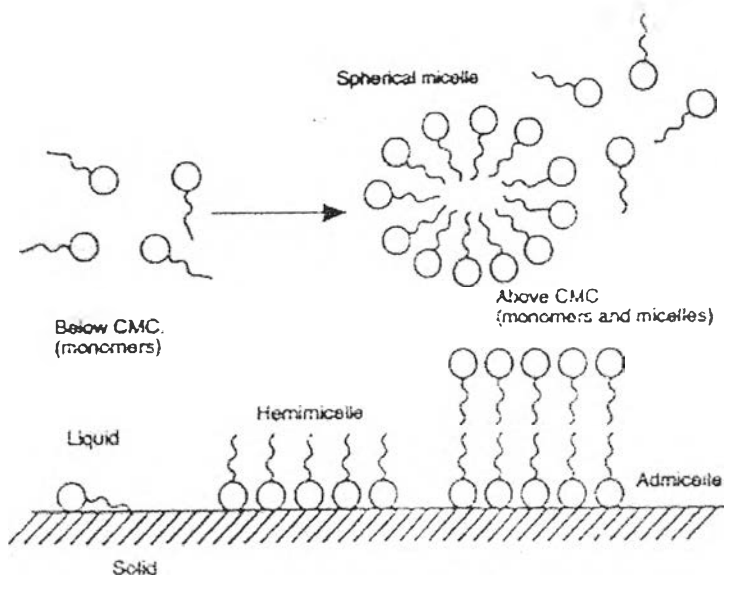
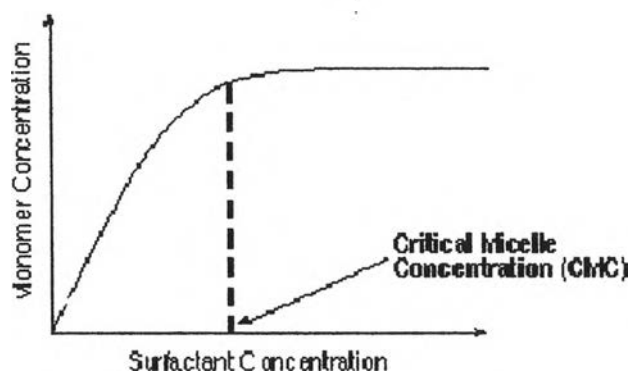Figure 2.5 Examples of surfactant micellization (Candida, 1992)

Figure 2.6 Formation of micelles at critical micelle concentration (CMC) (Lowe, D., (1997).

2.2.3.3 Soil Washing Mechanisms

There are two general mechanisms by which surfactants can enhance the removal of NAPL sources from the saturated zone. From an engineering standpoint, the easiest to apply is solubilization, which is a result of micelle formation. The second mechanism, mobilization of NAPLs, depends on the tendency of surfactants to lower interfacial tension between NAPLs and water (Candida, 1992)

Solubilization In pump-and-treat remediation, the amount of contaminant removed from the subsurface with each volume of groundwater pumped to the surface depends on the aqueous solubility of the contaminant. When surfactant is added to the aqueous phase, the organic interior of micelle acts as an organic pseudophase into which organic contaminants can be partitioned. This phenomenon is called solubilization as shown in Figure 2.7. Solubilization plays a major role in washing processes for surfactants that have concentrations above the critical micelle concentration. The solubilization of the organic compounds depends on the chemical structure of the surfactants, aggregation number, micelle geometry, ionic strength and chemistry of the surfactant solution, temperature, solubilizate chemistry and solubilizate size. (Lange, 1999) The apparent solubility

of slightly soluble hydrophobic organic compounds may be dramatically enhanced in solution of surfactants at concentrations greater than CMC.
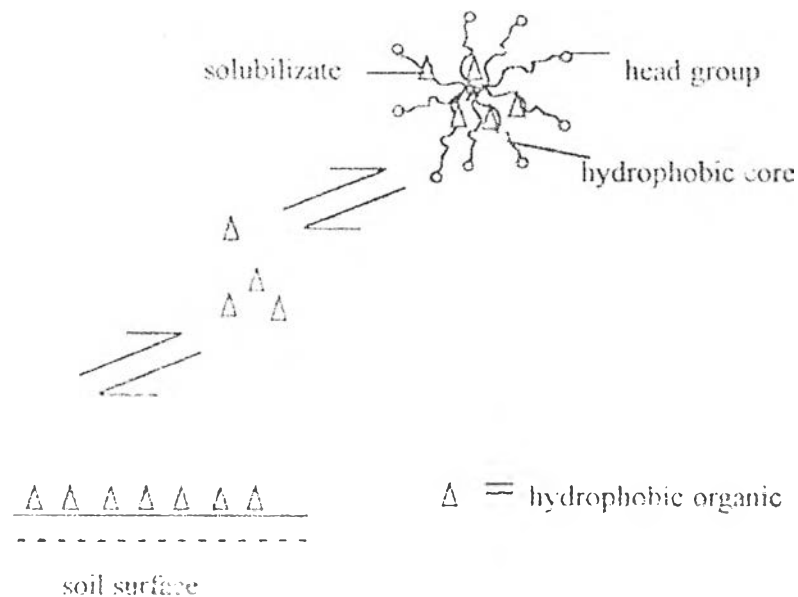

Figure 2.7 Schematic representation of micellar solubilization of a hydrophobic organic compound and the way that solubilization can remove the contaminant (Panida T., 1995).

The partition coefficient that described the partitioning equilibrium of the contaminant in the interior of the micelles and in the aqueous phase outside the micelle are related by the simple distribution law, K_{mw} (Wilson and Clarke, 1994) as

$$K_{mw} = C_m/C_w$$

Where: C_m = The contaminant concentration in the hydrophobic phase inside the micelles, mol/l

C_w = The contaminant concentration in the aqueous phase outside the micelles, mol/l

This formula is a good approximation for the distribution of solutes between water and solvents immiscible in water. Since the micellar interiors are

related like microdroplets of hexane or other hydrocarbon solvent, this would appear to be a reasonable model for calculating solubilizate concentrations in the micellar interiors (Thamsatitman, 1995).

Mobilization Surfactant-enhanced remediation can also be based on mobilization of the residual NAPL. This is the phenomenon on which surfactant-enhanced oil recovery work was based (Tadros, 1984). Mobilization has greater potential than solubilization to increase the rate of remediation, but can be riskier because of the movement of free-phase liquid.

In the saturated zone, the interface between the water-wet soil surface and NAPL is characterized by NAPL-water interfacial tension (IFT). The forces that trap organic liquids are dominated by capillarity (adhesive-cohesive forces), which is proportional to the IFT at the liquid (NAPL)-liquid (water) interface. An excellent discussion of capillary trapping is included in a report by Wilson and Clarke (1994). When the NAPL-groundwater IFT is high, a large pressure drop per unit of distance (hydraulic gradient) between the injection and extraction wells, $\Delta P/L$, is required to push a residual droplet of NAPL out of its pore space. Typical value of IFT for NAPLs and water are 30-50 dynes/cm. The product of the IFT multiplied by the increase in interfacial area that would result from the mobilization of the NAPL droplet represents an expenditure of energy. If the IFT were lower, less energy would be required to form the mew interfacial area and to push the residual saturation from the pore, and mobilization would occur at lower values of $\Delta P/L$. The ratio $[(\Delta P/L)/\gamma_{nw}]$ (where γ_{nw} is the NAPL-water IFT) is proportional to the capillary number, N_c. It is critical that the surfactant structure achieve a proper balance of hydrophilic and hydrophobic interactions at the interface to achieve large reductions in the IFT. This is distinct from solubilization, in which it is only necessary that surfactant micelles be present and remain stable in the aqueous phase (Candida, 1992).

2.2.3.4 Advantages and Limitation of surfactant in soil flushing

Advantages Soil flushing systems may significantly increase the mobility of NAPLs, improving their removal rate. Because they increase the quantity of contaminants extracted with water, these systems may reduce the cleanup time and total volume of water that must be extracted to achieve cleanup goals. Some researches have suggested that surfactants may improve bioremediation by increasing the accessibility of the contaminant to microorganisms. However, surfactant-contaminant interactions must be considered to determine whether the surfactant solutions are toxic to the microorganisms.

Limitations As with conventional pump-and-treat systems, geologic conditions can limit the performance of soil flushing systems. Soil flushing systems, like conventional pump-and-treat systems, are most effective in permeable, uniform media. Heterogeneous and low-permeability soils with mixtures of contaminants will generally result in reduced sweep efficiency, longer project duration, and less successful recovery. As a result, complete mobilization and removal of NAPLs has not been observed in the field with normal working concentrations of the chemical amendments, even though ongoing laboratory studies with pure solvents and controlled surfactant additions have demonstrated that near complete mobilization is possible.

Soil flushing systems also have other limitations. Fluids containing the large amount of cosolvent required for NAPL mobilization have densities and viscosities that differ substantially from those of water, complicating prediction of transport behavior. Further, the movement of contaminants mobilized by the surfactant must be carefully controlled. Controlling contaminant movement generally requires pumping a larger volume of extracted water must be treated and discharged elsewhere. Finally, other potential adverse reactions caused by the solution, such as permeability reduction, coating of aquifer solids, and water quality changes due to residual surfactant in the ground water, are also important to consider (Committee on Ground Water Cleanup Alternative et al., 1994)

The performance of a surfactant in the subsurface is dependent on temperature, sorption, degradation; the interaction of the compounds with the surfactants and soil, the partitioning of the compound with the surfactant micelle, the aqueous geochemistry of the injection water, and the surface chemistry of aquifer solids. (Z. Liu, *et al.*, 1991)

2.2.4 Colloidal Gas Aphrons (CGAs)

CGAs are micron size gas bubbles (25-30 μm in diameter) generated with a film of surfactant around them. CGAs are produced by a high-speed stirrer in a vessel containing dilute surfactant solution. CGA suspensions typically consist of 65% gas and hence, are a low density-fluid. The CGA suspensions have viscosity similar to water, which make them suitable for pumping without significant deterioration. Some of the applications of CGA suspensions are floatation of organic contaminants, soil flushing, and in-situ bioremediation. (Roy *et al.*, 1995; Raghava *et al.*, 1998; Hashim, 1998). Roy et al. (1992) found that CGA suspensions are more efficient than surfactant solutions on the basis of weight of contaminant removed per gram of surfactant.

2.2.4.1 The CGA generator

CGA generator involves a horizontal disc that rotates very rapidly (above 4000 rpm) and is positioned about 2 cm below the surface of the surfactant solution, as shown in Figure 2.8. The disc is mounted between two vertical baffles, which could be made of rigid plastic and which extended well above the surface of the solution. To avoid wobble, the shaft which carries the disc should be supported by bearings mounted below the stirring motor. The motor should be mounted on a sturdy support. If these precautions are taken, the disc can be spun at 6000 rpm continuously for very many hours without any untoward effects. If the disc rotates at less than about 4000 rpm, no CGA is formed, but once a critical speed is reached waves are produce on the surface. These beat up against the baffles and, having nowhere else to go, re-enter the liquid at the baffles. It was believe that the re-entering liquid carries with it a thin film of gas which becomes

sandwiched between the liquid and the baffles. Such a thin film of gas is unstable and will break up into minute droplets of gas encapsulated by the soapy shell, i.e. minute gas aphrons. The speed at which these are made is remarkable. The litres of CGA can be made in a few seconds. The unit has been run for many years without malfunction. If production of CGA is needed in larger quantities, several such generators should be used in parallel. The principal outlay is for the stirring motor. It has been estimated that the cost of electricity for 10,000 l of CGA would be less than the cost of 1 kWh of electricity (Sebba, 1987).
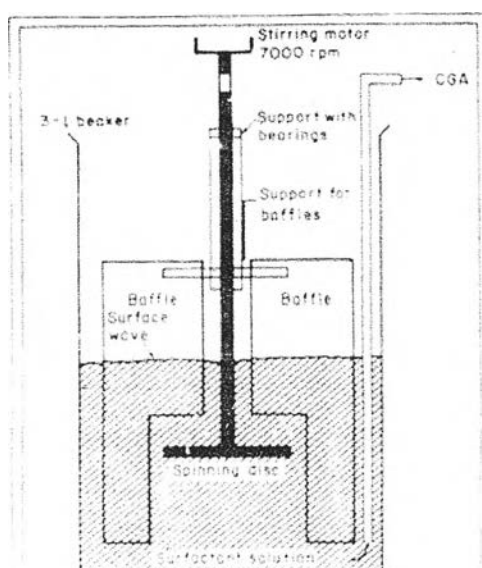

Figure 2.8 Spinning disc CGA generator (Sebba, 1987).

2.2.4.2 Properties of CGA

There are a number of remarkable properties of very small bubbles which could only be observed as a result of the development of CGA. After the CGA bubbles were closely examined, it was found that (Sebba, 1987):

1. The bubbles, rarely, if ever, coalesced as long as they were completely immersed in the water.

2. It the bubbles were below a certain critical size they rapidly contracted until they vanished.

3. Bubbles when they approached one another tended to bulge towards one another.

The CGAs carry an electrical charge depending on the surfactant used and combine well with oppositely charged particles to form a particle-bubble aggregate, which can be removed as an overflow. The entrapped liquid can be separated and recycled for further CGA generation. The CGAs have the following properties that are exploited in floatation process (Hashim, 1998):

1. Large surface area for particle-bubble contact
2. No significant coalescence in transportation by pumping
3. Adherence of particles to the outer shell of the bubbles by coulombic forces.

Pressure in a Bubble Consider a free floating spherical gas bubble in air, radius r. It can be expanded by increasing the pressure P inside it by blowing air in through a small capillary. The excess pressure is P_{ex}, which could be defined by the Laplace equation (Sebba, 1987);

$$P_{ex} = 4\gamma/r$$

Where, γ = surface tension of water

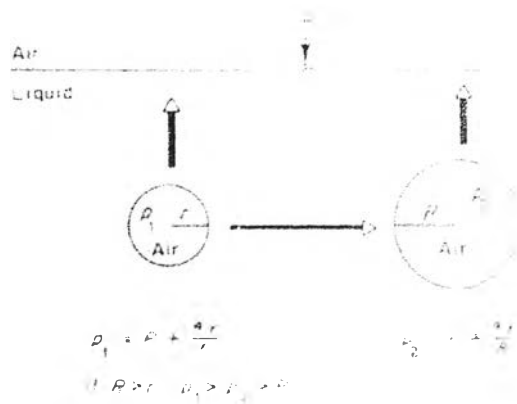r = radius of a free floating spherical gas bubble

Figure 2.9 Diffusion between bubbles (Sebba, 1987).

2.2.4.3 Density of CGA

One of the interesting properties of a CGA is that it provides one of the lightest liquids at ordinary temperatures and pressures. If one considers a CGA which is comprised of 65% gas in water, it will be seen that a litre of CGA would have a mass of 350 g, i.e. a specific gravity of 0.35. This property was made use of in the first experiments which led to the development of biliquid foams as it enables water made into a CGA to float on liquids such as hexane, as essential step in those early days. As will be seen it also has implications in fire-fighting.

2.2.4.4 Compressibility of CGA

Another interesting property of a CGA is that it can provide a compressible liquid, although no potential use for this property has yet been suggested. It arises because the gas which comprises about two thirds of the CGA still retains its characteristic gas properties, including compressibility. There has been no work done on how long this compressibility will last, but there is no obvious reason to expect it to be other than reversible. This may have some implication in the choice of what type of pump should be used if a CGA is to be transferred along a pipe. In practice, a peristaltic-type pump has been found to operate very well, but some difficulty has been experienced with displacement pumps.

2.2.4.5 Attachment of Particles

Perhaps one of the most useful properties of a CGA depends upon the structure at the interface between the bubble and the water in which it is dispersed. Figure 2.10 shows how a gas aphron is constituted at the molecular level. It should be noted that the encapsulating layer has an inner as well as an outer surface, though these surfaces have surfactant monolayers adsorbed on them, so that much of these surfaces consist of water. However, this water has different properties from bulk water being more hydrogen bonded. For that reason, it is quite permissible to consider this water as being a different phase from bulk water. This phase has oriented surfactant molecules at the surface that are hydrophil pointing inwards and hydrophobe outwards. This is easy to visualize for the surface in contact with the gas, but not so easy to understand for the surface exposed to bulk water. However, if it were a free-floating gas bubble, there would be no problem in recognized that the surfactant will be hydrophobe facing outwards.
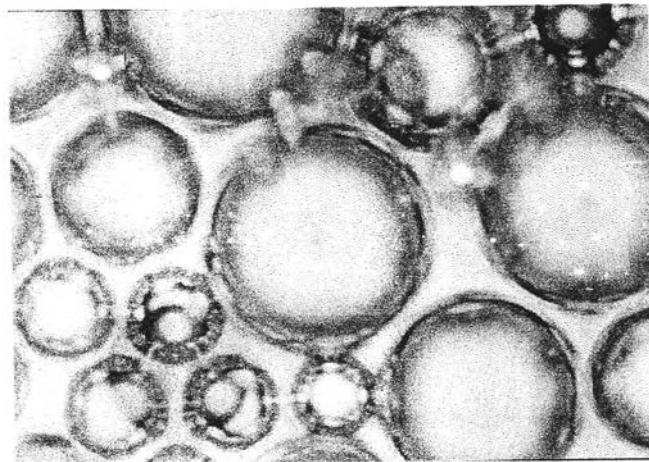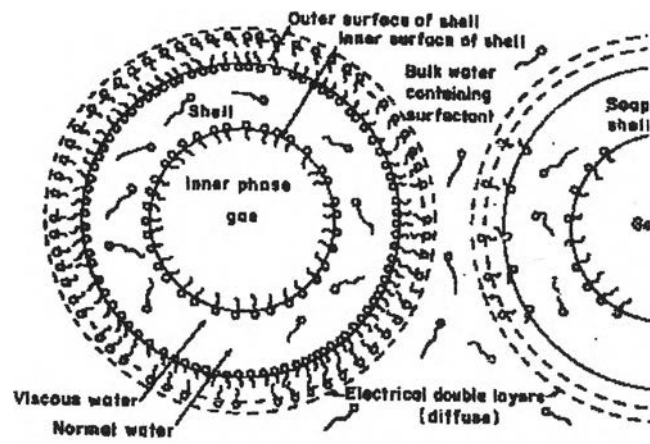
Figure 2.10 Structure of colloidal gas aphron (Sebba, 1987).

2.2.4.6 Applications of colloidal gas aphrons

Base on the mentioned CGA properties, some of the application, many of which are separation processes, are listed below (Sebba, 1987):

(1) stripping of dissolved gases from water

(2) floatation removal of finely divided suspensions of solids from water

(3) removal of dispersed oil droplets from water

(4) ion and precipitate floatation

(5) removal of ash forming materials from coal

(6) bubble-entrained floc floatation

(7) detergency

(8) separation of oil from sand

(9) floatation of micro-organisms

(10) fire-fighting

(11) frost protection

(12) fermentation.

For separation of oil from sand, an example where CGA could be applied would be in clean-up after oil or gasoline spills or where gasoline has leaked underground from faulty storage tanks. Some preliminary studies have shown the feasibility of the method. Bench studies have shown that an advancing front of CGA made of an ionic surfactant, percolating through a sand bed, carries with it most of the oil. The CGA must not be cationic as such a CGA will not move through the sand bed but is blocked. This is because the cationic surfactant is attracted to the negatively charged sand and makes it hydrophobic. This would be advantageous, however, if it is desired to introduce microorganisms with the CGA, whose function would be to destroy the oil by biological activity underground. In such cases there would be an advantage if the gas aphrons resided for a time in the sand bed.

The CGA bubbles are small enough to enter channels greater than 25 μm in diameter, but some channels are less than that. Until such time that CGA smaller than 25 μm can be made, which seems unlikely, there will always be some limitation to this method for scavenging oil underground. Nevertheless, as some of the oil is removed it may be useful for partial cleanup. Some hazardous oils, other than hydrocarbons, could also be removed in this way, such as for example PCB. The procedure would be to block the upper layers by prior percolation with a cationic surfactant solution and then to introduce a CGA underground through a borehole. The CGA loaded with organic contaminants could then be collected at boreholes some distance away. Because of the block ceiling the CGA has to move horizontally towards the wells (Sebba, 1987):