# 1. INTRODUCTION

Groundwater resources are the major source of fresh water for many regions and countries worldwide, including Turkey. The importance of groundwater as a source of water can be seen from Figure 1 which shows the global fresh water distribution. If one ignores polar ice because of its inaccessibility, about 96% of all the global freshwater is in the form of groundwater. Surface waters in the form of rivers, lakes and marshes form only about 1.1% of the accessible freshwater distribution (UNESCO, 1978).
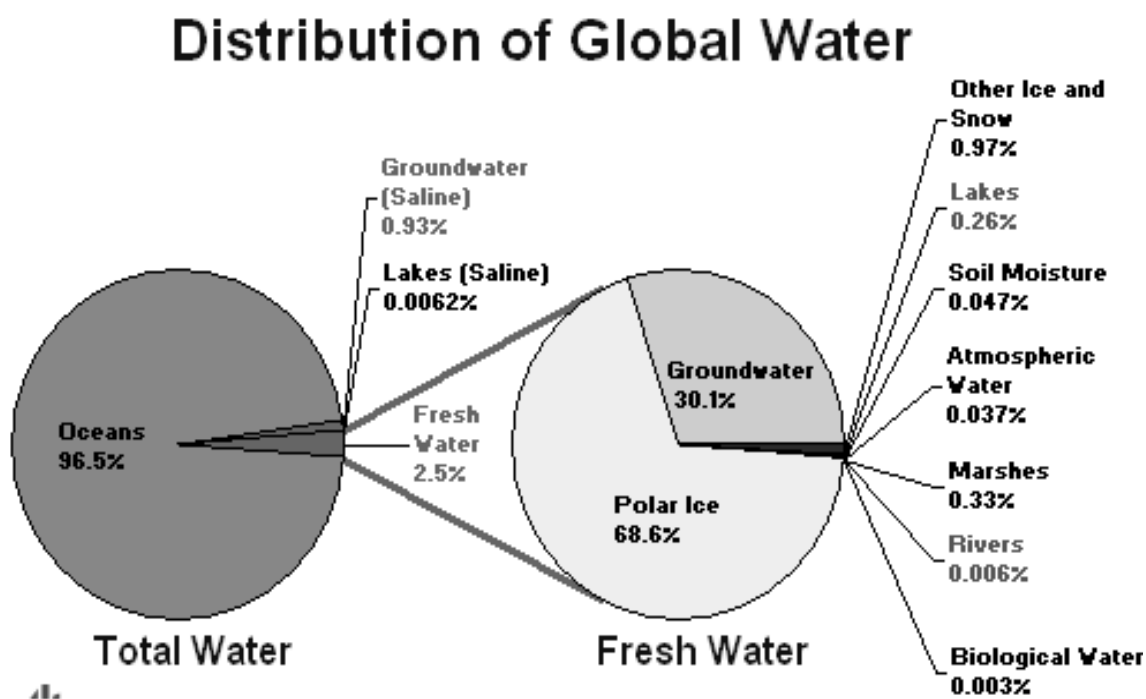


Figure 1.1. Distribution of global water (UNESCO, 1978).

Groundwater resources are however susceptible to various forms of contamination (Bedient et al., 1999). Examples of groundwater contaminants are: radionuclide materials used in nuclear power plants and nuclear weapons(e.g., U-235, P-239), inorganic compounds as a result of industrial activities(e.g., trace metals) or agricultural activities(e.g., pesticides, nutrients) and organic compounds due to gasoline use and industrial activities(e.g., aromatic compounds, halogenated compounds) and animal farms(e.g., viruses, bacteria, medicines). The focus of this research is on the remediation of

organic compounds from water saturated porous media. The focus of this research is on the remediation of a group of organic compounds known as BTEX (benzene, toluene, xylene and ethylbenzene etc.) compounds from water saturated porous media. These organic compounds are constituents of gasoline and other fuels, and used in nearly every industry. Among the hundreds of compounds which makeup gasoline, these are the most mobile and hence associated with a high exposure risk.

Because of their relative low aqueous solubility, organic compounds are often found in the form of Non-Aqueous Phase Liquids (NAPLs). The remediation of groundwater resources contaminated by NAPLs is a very difficult task because of the complex distribution of NAPLs in the subsurface, and their relative immobility (Oostrom et al., 2006). Despite the significant efforts that have been directed to this problem, currently no technology exists that can fully remediate groundwater contaminated with NAPLs.

NAPLs are often characterized into two categories as 1) Dense Non-Aqueous Phase Liquids (DNAPL) and 2) Light Non-Aqueous Phase Liquids (LNAPL). The term denser or lighter is due to comparison of their densities relative to that of water. The spread of NAPLs in subsurface waters is very much related to their densities. NAPLs which are lighter than water (LNAPL) tends to stay at the water table, while the DNAPLs if spilled in sufficient quantities, tend to migrate downward in subsurface waters till they reach a less permeable medium at the bottom of the aquifer. As a consequence DNAPL remediation is much more difficult compared to LNAPL. (Mercer et al., 1993)

Toluene and benzene, both LNAPLs existing in gasoline, wood processing oil, etc., have been chosen as the target contaminants in the proposed experimental work due to their wide usage in many industries. Both of these compounds have low solubilities in water but even that low concentration is thousands of times larger than the allowable drinking water level and hence can be very toxic to the environment. Benzene has adverse health effects on humans and can target the liver, kidney, lung, heart and the brain. Benzene is also a known carcinogenic.  Toluene on the other hand is not classifiable as a carcinogenic (IACR), exposure to high levels can cause light-headedness, sleepiness and loss of conciousness and can interfere with breathing and the beating of the heart.

Traditional remediation techniques such as Pump & Treat (P&T) have been used extensively at numerous contamination sites (Bedient et al., 1999). P&T involves the extraction of contaminated groundwater and its ex-situ treatment. P&T has been effective in limiting the spread of contamination and in the extraction of dissolved contamination plumes. However P&T technique has been found to be ineffective when NAPLs are present. (Pankow et al., 1988)   Because NAPLs tend to remain entrapped in the soil, they act as secondary sources continuously dissolving into the groundwater for many years and decades and possibly longer in some cases.  As a result, significant effort is being directed towards developing enhanced groundwater remediation techniques. In the late 1980's new technologies started to emerge in groundwater remediation.   Among the numerous technologies that have emerged, some researchers considered modifications to the basic P&T to enhance the contaminant recovery.  These enhancements include: "Surfactant addition", "Cosolvent addition", "Complexing agents", "Soil vapor extraction", "Heat augmented pumping" and "Air sparging" (Oostrom et al., 2006). In this study, the focus will be to investigate the recovery mechanisms and effectiveness of a cosolvent (ethanol) and a complexing agent (Hydroxypropyl beta cycodextrin, HPCD), on the recovery of Toluene (T), Benzene (B) and mixtures of T and B from porous media. In the literature the use of cosolvents and complexing agents are classified as "Enhanced Remediation Techniques".

There are numerous published studies which have considered different enhanced NAPL remediation techniques involving various flushing agents such as surfactant and cosolvents.  Surfactants typically increase the solubility of organic compounds due to the presence of a hydrophobic head and hydrophilic tail and have been used by many researchers due to this unique formation. Cosolvents such as alcohols  are another group of agents that have been studied extensively.  These compounds are fully miscible in water and tend to decrease the interfacial tension and increase the solubility of the NAPL into the aqueous phase. Another possible flushing agent, which has only recently been considered for NAPL recovery, is HPCD aqueous solutions. Although a number of studies have considered the use of HPCD as a remediation agent but none have yet investigated the effect of heat on the HPCD enhanced remediation. Further details on these agents and how

they can enhance the recovery of NAPLs from the subsurface is discussed in Chapters 3 and 4 of this thesis

The operating parameters which may potentially influence the NAPL recovery mechanisms in the porous media, either during ethanol or HPCD aqueous solution flushings, include temperature, cosolvent concentration, groundwater velocity, viscosity of both NAPL and flushing solution, density differences and ternary phase behavior etc. Understanding the impact of these parameters is important in order to optimize the remedial efficiency of the NAPL removal from the subsurface. The influences on the recovery mechanisms must be assessed one by one and jointly afterwards for the evaluation of fate and transport and ultimately the recovery of NAPL.

As found in the field NAPL contamination in the subsurface is commonly in the form of mixtures of organic compounds. The petroleum derived compounds especially exist together at contaminated sites. Apart from the aquifer parameters, the alterations, in the fate and transport of a target compound, is greatly depended on its formation at the contaminated site. The existence of these compounds together may alter the behavior of individual compounds. Significant progress has been achieved in the last 2 decades towards the use of chemical agents for the enhanced recovery of NAPLs from the subsurface. However, questions on the fate and transport of NAPLs during chemical agent flushing remain. This can have a significant impact on efficiency of the NAPL recovery. Specifically, two questions addressed in this study are; how does the NAPL behave when mixtures of NAPLs are present in the subsurface and can temperature be used in conjunction with various chemical agents to enhance NAPL recovery.

# 2. RESEARCH OBJECTIVES

The focus of this study will be on the use of ethanol and HPCD for the enhanced solubilization and mobilization of toluene, benzene and their behavior when they exist together. In the literature there are relatively few studies based on synthetically prepared mixtures. Most of the laboratory studies considered single NAPLs, while field investigations typically involved mixtures of numerous compounds (such as diesel and crude oil) often with unknown compositions. These latter studies focused on the removal of the total organic mass from the porous media, without considering the effect of the cosolvents on individual NAPL constituents. Hence, this study, which will investigate synthetically prepared mixtures at known amounts, will provide information about the relation between mixture's content and its behavior when flooded with an ethanol containing flushing solution.

The other part of this study focuses on the use of cyclodextrin solutions for the removal of NAPLs from porous media. Cyclodextrins have been considered in groundwater contamination studies for more than a decade. Most of the studies however, evaluated the use of cyclodextrins without any modification (such as heat) for remediation purposes. The effect of system temperature on the NAPL enhanced dissolution using hydroxypropyl-beta-cyclodextrin (HPCD) is assessed in this study.

Batch experiments will first be conducted to evaluate the effect of NAPL formation, and cosolvent on the physio-chemical parameters influencing NAPL recovery from porous media. These parameters include the interfacial tension, solubility and ternary phase diagram. The in-situ flushing experiments will be conducted in a one-dimensional sand column for relatively rapid evaluation of the different flushing agents and to identify the factors influencing NAPL recovery. Based on these experiments the recovery mechanisms for the two agents considered in this study will be evaluated. The effect of mixture formation of the organic phase and the validity of Raoult's law for cyclodextrin remediation at different temperatures will also be assessed in this section.
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# 3. THEORETICAL BACKGROUND

This chapter describes the factors responsible for the spread of NAPLs in the soil and groundwater in the event of a spill. It also discusses the different groups of chemical agents that have been used for groundwater contaminated with NAPLs. The different mechanisms responsible for NAPL recovery are also discussed.

## 3.1. Properties Influencing NAPL Movement

### 3.1.1. Interfacial Tension

Interfacial tension (IFT) is the force resulting from the difference in attraction between similar and different kinds of molecules(Lowe et al.,1999). For 2 immiscible liquids, IFT is the reason for the existence of two phases, and if the IFT between these two liquids is depressed to near zero, they make a single phase (miscible). In subsurface waters due to very low solubility of BTEX compounds, the NAPL forms. If IFT is not depressed to zero but to a certain low level, NAPL starts to move with water still being immiscible with water (mobilization), as shown in Figure 3.1.

The main reason that keeps the NAPL entrapped in the subsurface and not move through pores is the dislike of NAPL to soil (NAPL is the non-wetting fluid). This situation is due to inorganic content of aquifer and organic content of NAPL. By depressing the interfacial tension between water and NAPL (not till "0") they lose their dislike. Hereby the repulsion of soil to NAPL becomes closer to repulsion of soil to water and as a result NAPL starts to move with water.
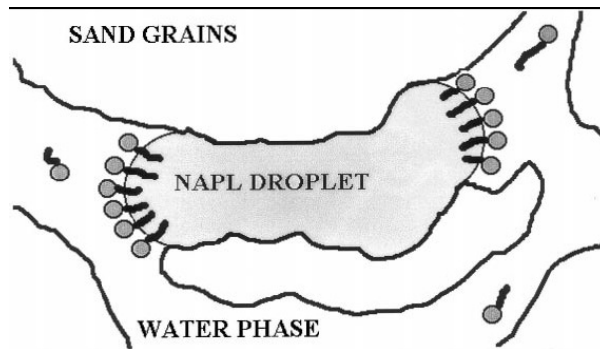
Figure 3.1 Depressed interfacial tension between water and NAPL by surfactant addition (Harwell et al., 1999).

### 3.1.2. Wettability

Wettability is the attraction of a fluid to a solid surface in the presence of another fluid. If the ends of that fluid make an angle smaller than 90 degrees with solid surface, it is referred to as the non-wetting phase. If that fluid establishes an angle bigger than 90 degrees with solid surface it is referred to as the wetting phase (Lowe et al., 1999). In the context of the present study, these two fluids and solid surface would be water, NAPL and aquifer soil, respectively. Since aquifer solids normally contain little or no organic matter, the non-wetting phase is the NAPL and the wetting one is water. That contact angle which is used to define the wetting phase, is also used to calculate the "capillary pressure" of the fluids in certain types of soils.

### 3.1.3. Solubility

Solubility is the ability of a compound to dissolve in a liquid. It is a function of both temperature and pressure. Some liquids are soluble in each other in all proportions as ethanol-water composition which will be used in this study as a flushing solution. These are called miscible liquids for each other. Solubility of a certain compound in a certain type of liquid can be altered also by chemical addition to the solution (such as hydroxypropyl-beta-cyclodextrin or surfactant addition). Solubility parameter has another particular effect on groundwater contamination since it has a major effect on plume size (St-Pierre et al., 2004).

### 3.1.4. Viscosity

The viscosity of a fluid is its resistance to flow. As seen in Table 3.1. the two NAPLs which will be used in this study are less viscous than water but the organic content of NAPL is keeping it entrapped in porous media. In groundwater remediation, it is known that heat may be used to achieve higher removal rates of NAPLs, by lessening the viscosity of the NAPL. Such technologies are referred to as heat-based technologies (see section 4.1).

Table 3.1. Viscosity of selected compounds.

| | |
|---|---|
| Toluene | 0.59 cP |
| Benzene | 0.652 cP |
| Water | 1.002 cP |

## 3.2. NAPL Remediation

In the use of chemical agents for subsurface remediation problems involving NAPLs, two basic mechanisms take place known as "mobilization" and "solubilization". For different remediation scenarios either one of the two mechanisms or both of them may occur at the same time. Each of these two mechanisms are discussed below.

### 3.2.1. Mobilization

In case the NAPL is entrapped in the subsurface, it has a resistance to move through the pores, which is due to the NAPL's hydrophobic nature and the NAPL's dislike to the mineral surface of the soil. The inorganic aquifer material is water surrounded, and the organic formation of the NAPL globule makes itself retain in the center of pores away from the soil surface. Hence a resistance to move through soil throats occurs for NAPL

when forced to move by hydraulic gradient. Mobilization is to depress this resistance and drive the contaminant through the pores as a NAPL.

### 3.2.2. Solubilization

This mechanism stands for driving out the NAPL from porous media by solubilizing it in water. But as mentioned before many NAPLs of concern have very low solubilities in water. Some cosolvents may be used to enhance their solubility. Yet the batch experiment solubility results for each organic compound may not be attained in the groundwater flow conditions. Thus the effect of solubilization especially for ethanol enhanced schemes is still a subject of investigation.

For remediation activities, an adequate knowledge of those mechanisms is necessary in order not to aggravate the contamination. Mobilization mechanism should be chosen with precaution when the contaminant is a DNAPL since DNAPL may migrate further downwards into the less permeable media at the bottom of aquifer (Stuart et al., 1999). But the difficulty of the situation is often due to possibility of both mechanisms occurring simultaneously. Therefore the basic ideas, which are responsible for both mechanisms, must be understood properly. The illustration below clarifies the distribution DNAPL into subsurface form an underground storage tank.
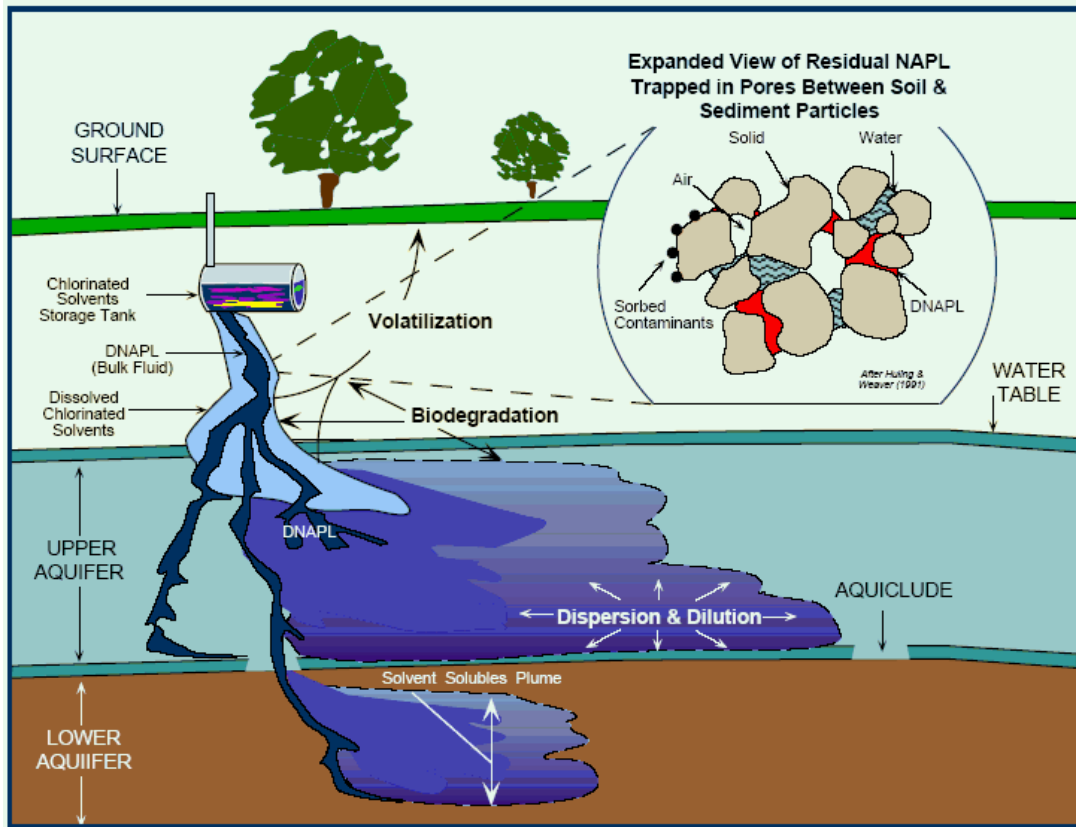
Figure 3.2. Distribution of DNAPL from an underground storage tank.

### 3.2.3. Ternary Phase Diagrams

The phase behaviour concept is a useful tool for describing the solubilization potential of the components within the various phases present in the system. A ternary diagram particularly quantifies the degree of solubilization (increase of the organic phase solubility in the aqueous phase) or partitioning (increase of the aqueous phase solubility in the organic phase). In order to visualize these relations, ternary phase diagrams are widely used (Falta, 1998; Martel et al., 1998; Roeder, 1998; Reitsma et al., 1998; Ramsburg et al., 2002; Parker, 2003; St-Pierre et al.,, 2004). The axes of a ternary phase diagram show the composition of water, NAPL and agent usually on mole basis. A ternary phase diagrams is hence particularly useful in that it shows all three components of a reaction system on one plot.
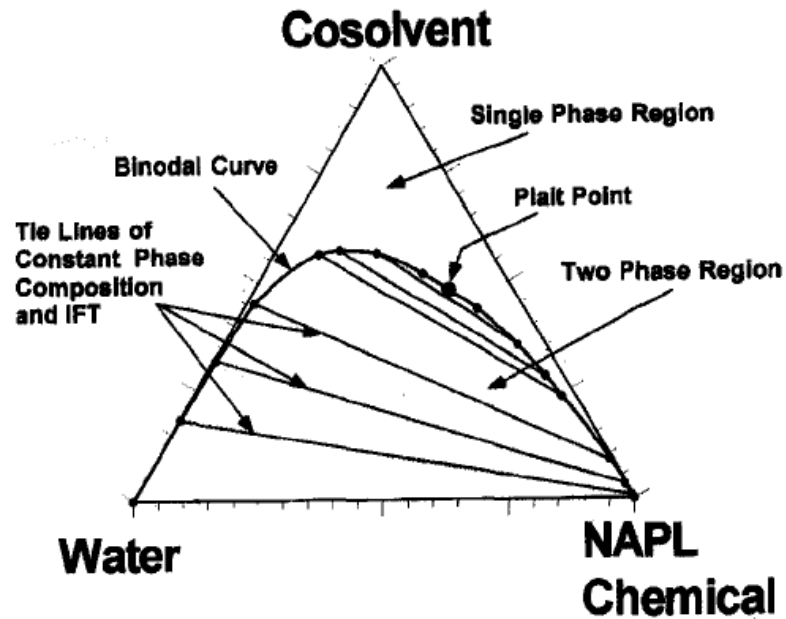
Figure 3.3. Representation of a ternary diagram (Falta, 1998).

A sample of ternary diagram is shown in Figure 3.3. A ternary phase diagram is composed of a miscibility curve or binodal curve and tie-lines. The region situated beneath of the binodal curve (corresponding to the mol fraction compositions of three components) implies that the system is immiscible (two phase system) however the region above of the binodal curve means a fully miscible system (one phase). At any point beneath the binodal curve, a tie line can be defined which passes through the point. The tie lines are constructed in a manner that firstly all three components are put in a vial, and each phase measured in terms of their composition. The aqueous phase composition and NAPL composition are marked as a single dot for each on the diagram and a tie line is drawn between them. The coordinates of the endpoints of this tie line with the binodal curve define the aqueous phase (left hand side) and NAPL (right hand side) compositions. Each tie line reflects an interfacial tension value. At the bottom of the diagram (water-NAPL axis, at zero content cosolvent) the IFT is at its water/NAPL value and the IFT on the binodal curve is "0", which means that two phases emerge into one phase on that curve.

The tie lines starting from the water–NAPL axis rise above to higher cosolvent contents with a positive or negative inclination. The slope of the tie lines is an indication of the partitioning characteristics of the cosolvent. A cosolvent is mostly partitioned into the aqueous phase when the tie lines have negative slopes where as it partitions to the NAPL

11

phase when the tie lines have positive slopes. At a single point (a particular composition) the tie line is tangent to the binodal curve. This point is called "plait point" and is particularly important in the interpretation of the ternary diagram in terms of dominating recovery mechanism.

## 3.3. Chemical Agents

The chemical agents that have been evaluated for NAPL recovery from the groundwater include mostly cosolvents such as alcohols, surfactants, and to a lesser extent, other agents such as HPCD and humic acid.

### 3.3.1. Alcohols

Alcohol is an organic compound in which a hydroxyl group (-OH) is bound to a carbon atom of an alkyl or substituted alkyl group (Petrucci et al., 2001).The most commonly tested alcohols are ethanol, methanol and propanol. They are also called as cosolvents. Alcohols can mainly partition into aqueous and organic phases at any proportions however some exceptions like n-butanol also exist (Ramsburg et al., 2003).

A commonly used agent for NAPL recovery ethanol is a primary alcohol. It is fully miscible with water but in addition it is also miscible with organic solvents like benzene, toluene, TCE, etc. It must be noted that due to its polar and non-polar ending, ethanol can dissolve ionic compounds and non-polar substances (oil etc.) respectively (Handbook of Chemistry, 44th ed). By the ability of mixing in water and also in other organic solvents, it reduces the surface tension of the solutions. The main use in groundwater remediation is related to its interfacial tension depression and solubility boost of organic compounds.

### 3.3.2. Surfactants

Surfactants are also known as surface acting agents. They are made of organic compounds which have a hydrophobic and a hydrophilic part. Due to that formation they can capsulate a hydrophobic compound in water. This complex is called as a "micelle"

(Figure 3.4.). In groundwater remediation their main use is due to their micelle formation capacities which is the reason of their interfacial tension depression (Harwell et al.,1999) Unlike alcohols,  surfactants can enhance the solubility of the NAPL in water only after their concentration exceeds the CMC (critical micelle concentration).
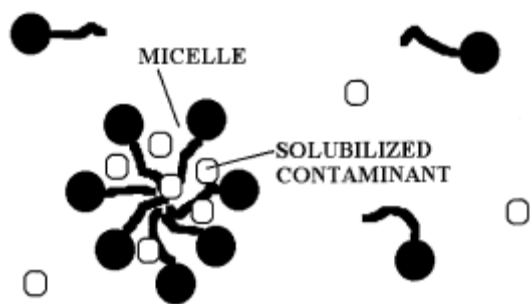


Figure 3.4. NAPL molecules capsulated by surfactant (Harwell et al., 1999).

### 3.3.3. Cyclodextrins

The most common modified sugars used in remediation activities are cyclodextrins. Cyclodextrins (CDs) are produced at commercial scale from the enzymatic transformation of starch by bacteria. The agent is a glucose-based toroidal-shaped molecule and has a hydrophobic cavity within which the organic compounds of appropriate shape and size can form inclusion complexes. This property was first used in the pharmaceutical research for the drug delivery (Boving and Brusseau, 2000). Over the last few years they have found a wide range of applications in food, pharmaceutical and chemical industries as well as agriculture and environmental engineering. The selected physical properties of cyclodextrin derivatives are given in Table 3.2. The chemical structures of the three main types of cyclodextrins are given in Figure 3.5.

Table 3.2. Selected physical properties of cyclodextrin derivatives (Szektli, 1998).

| Cyclodextrin | Substitution | MW (g/L) | Cavity volume ($nm^3$) |
|---|---|---|---|
| HP-α-CD | 0.6 | 1180 | 0.174 |
| HP-β-CD | 0.6 | 1380 | 0.262 |
| HP-γ-CD | 0.6 | 1576 | 0.427 |
| M-β-CD | 1.8 | 1312 | 0.262 |

Typical cyclodextrins contain a number of glucose monomers ranging from six to eight units in a ring and are named with respect to this ring size as below:

- α-cyclodextrin: six membered ring molecule

- β-cyclodextrin: seven membered ring molecule
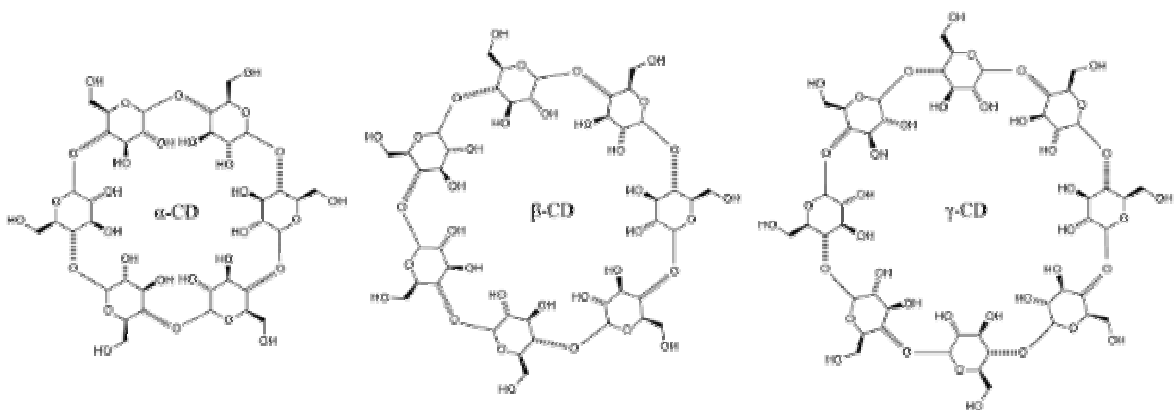
- γ-cyclodextrin: eight membered ring molecule



Figure 3.5. The chemical structures of the three main types of cyclodextrins.

Cyclodextrins, constituted only by 6-8 glucopyranoside units, can be topologically represented as toroids with the larger and the smaller openings of the toroid exposing to the solvent secondary and primary hydroxyl groups respectively. Because of this arrangement, the interior of the toroids is considerably less hydrophilic than the aqueous environment and thus able to host other hydrophobic molecules. On the contrary, the exterior is hydrophilic and impart the water solubility of cyclodextrins (Tuck et al.,, 2003). Nowadays, cyclodextrins are evaluated for their complexation performance with nonpolar organic pollutants such as chlorinated solvents. The nonpolar organic compounds are trapped in the central hydrophobic cavity of the cyclodextrin. Individual cyclodextrin molecules makes complex with molecules of contaminants, so this enables cyclodextrins to enhance solubility at all concentrations. One other advantage of using cyclodextrins is that their performance is not affected by the changes in pH, ionic strength and temperature. The beneficial properties of cyclodextrins in remediation include:

- low sorption to the aquifer solids (Brusseau et al.,, 1994)

- do not partition much to the organic phase (McCray, 1998) – regulatory concerns
- behave practically as conservative tracers
- generally nontoxic and nonreducing
- have a high solubility enhancing ability due to the polar exterior
- stable under typical environmental conditions
- do not appear to harm resident microbial populations during remediation (Wang et al.,, 1998)

### 3.3.4. Humic Acid

Eventhough there is not a concrete definition for humic acid, in molecular means; the general perception takes it as alkali-soluble humus fragments (Pena-Mendez et al., 2004).

Humic acid is one of three formations that make-up "humic substance". The other two constituents are "fulvic acid" and "humin" respectively. Humic substances have a wide variety use in industry and agriculture as in concrete and crop production. But for environmental and biomedical applications the main use is due to their binding ability with metals, radionuclides, anthropogenic organic chemicals etc. and forming of water soluble complexes (Pena-Mendez et al., 2004).

# 4. LITERATURE REVIEW

This section consist of three main parts including, a general review about the use of various agents for enhanced NAPL zone remediation, a detailed review of ethanol enhanced groundwater remediation and another detailed review of cyclodextrin enhanced groundwater remediation. These two agents (ethanol and cyclodextrin) are the considered in the current study.

## 4.1. Enhanced Groundwater Remediation

The existence of NAPL's in the subsurface is considered as one of the main reasons for groundwater contamination (Pankow et al., 1996). The relatively low solubility of NAPL's makes them act as a secondary source of continuous contamination. The dislike between organic compounds and inorganic aquifer material, prevents the extraction of NAPL from subsurface by Pump&Treat applications (Pennell et al., 1996).

The main in-situ enhanced remediation procedures for NAPL recovery includes; soil vapor extraction, surfactant flushing, alcohol flushing, surfactant+alcohol flushing, chemical oxidation, air sparging, heat based remediation, humic acid flushing and dense brine strategies and cyclodextrin enhanced recovery. Moreover given the limitations of individual technologies, a number of coupled technologies for NAPL recovery have also been investigated the recent years.

### 4.1.1. Soil Vapor Extraction

The main idea in this method is to drive out the NAPL in gaseous form and it is used mostly for decontamination of unconfined aquifers. The clean gas forced to an extraction well by a vacuum pump into subsurface, gathers inside the NAPL vapor and moves towards the extraction well (Heron et al., 1998). However it was observed at many field applications that, when air swept through the contaminated zone, the pool receded primarily from the upstream end, with less removal from the sides. In addition, the

geometry of both single and binary pools changed in the same manner (Ho and Udell 1992). This short coming of the method is a  major impediment for its usage when greater areas are to be recovered.

### 4.1.2. Air Sparging

Air sparging involves the injection of clean air into the saturated zone of a porous medium in an attempt to volatilize contaminants and transport them to the vadose zone to be removed by soil vapor extraction (Oostrom 2006). The most known application of air sparging is its coupled version with soil vapor extraction. Two wells; (similar to pump and treat) one extraction well and another pumping well are used to control the flow path of the vapor in the subsurface. The general idea founded on the greater partial pressure of gaseous organic contaminants can be very inefficient at heterogeneous subsurface formations (Waduge et al., 2004). In addition, Ji et al., (1993) showed that injected air typically flows in large channels, bypassing large areas of the contaminated zones (Heron et al., 2002).

### 4.1.3. Chemical Oxidation

In situ chemical treatment technologies include destroying organic chemicals in-situ either with oxidation or reduction. In situ oxidation involves the injection of reagents to stimulate degradative chemical reactions with the contaminants in the groundwater. Strong oxidizing agents such as hydrogen peroxide and iron (Fenton's reaction), potassium permanganate and ozone are used to chemically transform the contaminants into carbon dioxide, water and other byproducts. Chemical oxidation can be used to treat a wide range of organic contaminants (Conrad et al.,, 2002). The operations are largely unaffected by contaminant concentrations and is relatively inexpensive. Effective delivery of the oxidizing agent to contaminants is an important consideration in remediation design (Li and Schwartz 2004a).

### 4.1.4 Humic Acid

The compound known as humic acid, mostly found in surface waters due to degradation of organic material such as leaf etc., improves the aqueous solubility of metals

by bonding them to itself. The application of humic acid solutions in subsurface remediation applications were limited to chlorinated solvents (Brusseau et al., 2000, Johnson et al., 1999). The main mechanism used in these attempts was solubilization. The improvements in the aqueous solubility of organic chemicals resulted in faster Pump&Treat applications (Van Steempvort et al., 2002).

### 4.1.5. Heat Based Remediation

Heat Based Remediation involves the subsurface heating using electrical resistance or injection of hot fluids (water, stream etc) into the subsurface to render the NAPL more mobile or more susceptible to degradation. The effect of heat in groundwater is varying. The well known effects can be listed as; solubility enhancement, viscosity alteration, IFT alteration etc. (Oostrom 2006). However some other effects were also evaluated in the recent past, such as, alteration of microbiological degradation rate (Beyke et al., 2006), desorption of contaminants from soil particles and bioavalibility boost of contaminants (Wick et al., 2007). A recent work conducted by Aydin et al. (2008) focused on the effect of heat on alcohol enhanced remediation of LNAPL's. These different effects of heat made it useful in different remedial activities (Kaslusky and Udell, 2005; Wick et al., 2007).

### 4.2. Chemical Agent Flushing

Chemical agent flushing is one of the most promising technologies for NAPL zone remediation. The most tested chemicals are; surfactants, alcohols, cyclodextrins respectively. The last two will be reviewed in this section more broadly.

### 4.2.1. Surfactant Enhanced Remediation

In general, surfactants are used to increase the total aqueous solubility of a NAPL or to decrease NAPL–water interfacial tension to promote mobilization (Lowe, 1997). Numerous studies were directed to use of surfactants more than a decade both for LNAPL and DNAPL remediation. (Chu et al., 1996; Saba et al., 2001; Ramsburg and Pennell, 2001; Rathfelder et al., 2003; Schaerlaekens and Feyen, 2004; Taylor et al., 2001 etc.).

One of the interesting studies for DNAPL remediation is coupling of dense brine injection and surfactant use by Miller et al. (2001). The removal efficiencies of DNAPLs are directly related with the density modifications. The density of the flushing solution is increased by the injected brine hence DNAPL is converted to an LNAPL (Miller, 2000). The coupled effect of dense brine and surfactant flushing was tested by Miller et al., (2001). A surfactant solution was allowed to infiltrate before the brine was pushed upward. Because of the added mobilization due to interfacial tension reduction, this experiment yielded a 90% reduction in free TCE. The latter experiment seemed to be especially promising, because the researchers argued that the remaining residual TCE could easily be removed by soil vapor extraction in the vadose zone.

### 4.2.2. Alcohol Enhanced Remediation

Use of alcohols in the subsurface applications started with the petroleum industry in 1960's, to achieve better efficiencies in oil recovery processes. This method started to emerge in environmental activities in the 1990's. Field scale applications of this remedial technology have been conducted primarily in the last decade. Several researchers have studied the NAPL remediation efficiencies by different flushing agents such as surfactant and cosolvents (e.g., Boving and Brusseau, 2000; Johnson et al., 1999; St-Pierre et al., 2004). Some of these studies specifically focused on understanding the effects of ethanol because of its low toxicity, and availability on NAPL recovery from porous media (e.g. Taylor et al., 2004; Lunn et al., 1999; Grubb et al., 1999). Other researchers have investigated instability and fingering of NAPL that may develop during remediation operations. (e.g. Corapcioglu et al., 2003; Wang et al., 1998). Heat effect on immiscible NAPL-water system and phase behavior, physico-chemical properties of NAPL's were also subject to many studies in the recent past (e.g. O'Caroll et al., 2007; Hayden et al., 1999; Lee et al. 2004). Microbial activity on degradation of BTEX compounds were investigated too (Johnson et al., 2003).

Till now there have been considerable amount of studies for the assessment of alcohol enhanced recovery mechanisms of NAPL's. However the impact of various operating parameters and the important recovery mechanisms are still under investigation. Among the various alcohols, ethanol is widely used because of its availability and non-

toxicity and is therefore reviewed here. The most important investigations mostly involving ethanol as a flushing agent in subsurface applications are briefly discussed below.

An important research conducted by Grubb et al. (1997, 1998) used ethanol flooding to remove the LNAPL toluene from a 2-D flow cell. The aquifer matrix used in the first set of experiments was 0.85-0.60 mm Ottawa sand. The following experiment used layered systems including two fine-grained sand layers. Toluene amount used in the experiments was chosen as 20 ml and directly injected in the partly saturated flow cell.

Two different remediation schemes in the same experiment was tested (pure 50% ethanol-water flushing following pure ethanol flushing). The main advantage of the 50:50 blend is that it creates a viscous and dense fluid wedge below the toluene, enabling upward and downgradient mobilization (Grubb et al., 1998). The floods were introduced at the water table to minimize buoyancy flow of alcohol. During the first flood with pure ethanol, toluene mobilization was observed. The toluene moved downward, in a similar fashion that would have been expected for DNAPLs, to the ethanol– water interface. This location is expected based on the intermediate density of the toluene between ethanol and water. With time, toluene banking reduced the ability of the ethanol to remove additional toluene due to a reduced permeability. Trapped toluene was subsequently removed using a denser 50:50 (v/v) alcohol–water mixture. The removal rates of toluene in both the homogeneous and heterogeneous systems were estimated to be 80%.

A continuation of the study mentioned above was done by Palomino and Grubb (2004). The same dual flooding procedure was committed for dodecane, octane and toluene. Unlike the earlier research, this one was conducted with 500 ml of NAPL of each contaminant separately. This greater amount was chosen as a better representative of the field conditions. Apart from these differences, the experiment was conducted under the same conditions. In this research the authors particularly emphasized the economic value of the recovered petroleum products (toluene, octane etc.) in order to reduce the remediation cost.

As it was stated in the results section of their research, 50% of the recovery was attained by hydraulic movement before the introduction of pure ethanol into flow tank. The pure ethanol indicated a recovery around 30% and at last the blend resulted in with a 10% of recovery. The total recovery for all contaminants was between 80 and 90%. One main outcome of the study was the downward migration of every contaminant due to their greater density in comparison with pure ethanol. This condition was overcome by flushing with 50% ethanol-water solution which has a greater density than the contaminant. The photo below was taken during the pure ethanol flooding, showing the downward migration of toluene.
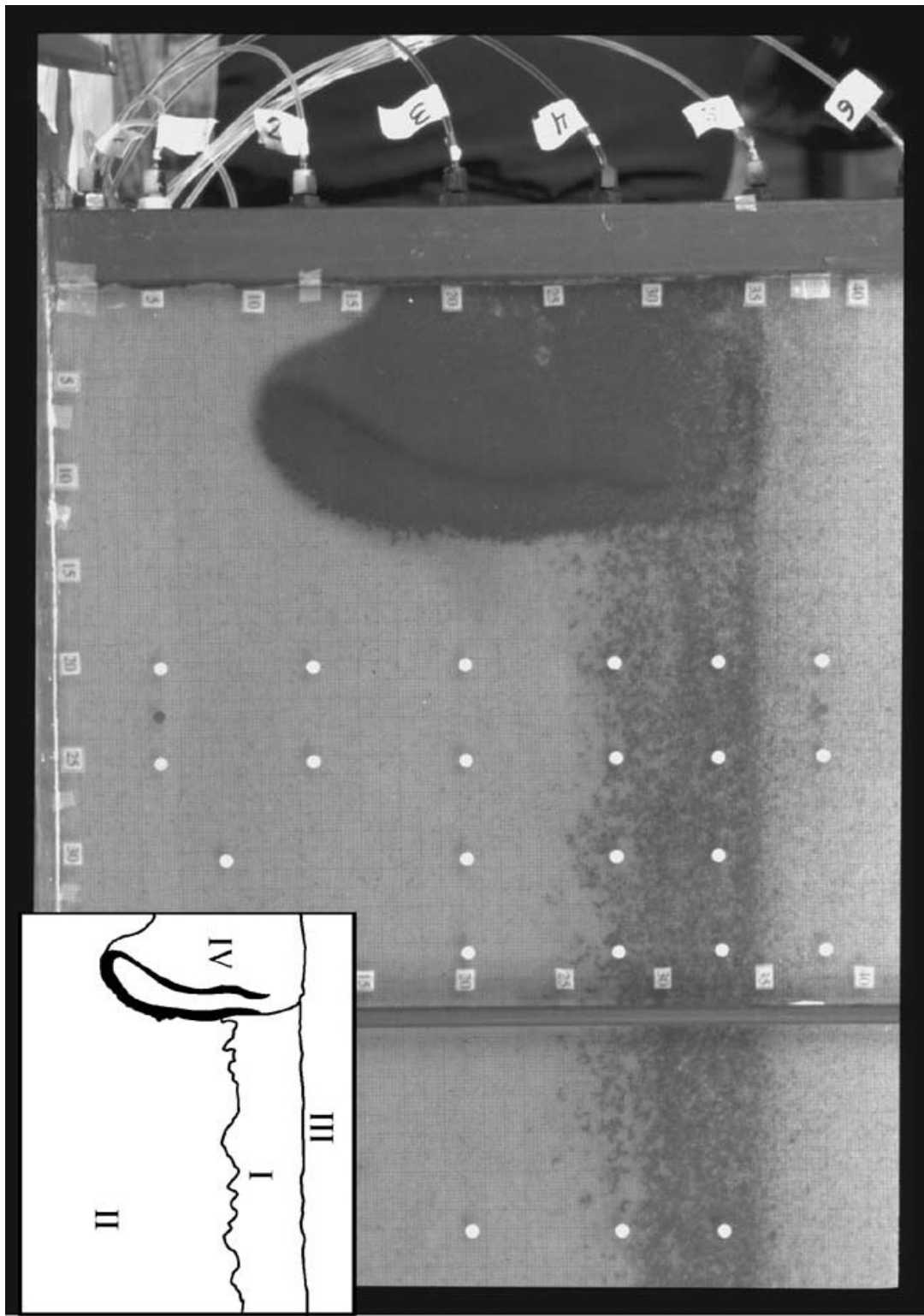
Figure 4.1. Horizontal migration of primary ethanol flood impeded by toluene (darkest band) situated along the ethanol–water interface (Palomino and Grubb, 2004).

Another research involving alcohol enhanced DNAPL remediation from saturated porous media was conducted by Lunn and Kueper (1997). In this study the focus was to

attempt to limit possible downward migration and worsening of the contamination during the flushing experiments. Two different alcohols (Ethanol and 1-propanol) were practiced and as DNAPL, PCE was selected.

The confined media containing pooled DNAPL was first flushed with 1-propanol and then by pure ethanol. The idea behind the use of 1-propanol was its preferential partitioning into organic phase and the density reduction of DNAPL. By this approach the authors tried to convert the DNAPL to an LNAPL. Since both 1-propanol and ethanol could reduce the IFT and start mobilization, the first flushing with 1-propanol was implemented with low concentrations in order to prevent mobilization. The mechanisms come into action with 1-propanol flushing were conversion of DNAPL to LNAPL and mobilization due to reduced IFT between phases. However ethanol, preferentially partitioning into aqueous phase, had only involved dissolution and mobility mechanisms. The researchers cautioned that downward PCE migration may still occur, both in free form with ethanol flooding (no density reduction) as well as during the initial stages with 1-propanol flooding. They recommended additional research with DNAPL-swelling alcohols and injection schemes where large alcohol slugs are delivered beneath the source zone.

The same researchers advanced their investigations by implementing the same two stage flooding but with different constituents. This new study conducted in 1999 (Lunn and Kueper, 1999b), involved 2-butanol followed by 1-propanol as flushing agents and PCE as the DNAPL. The relatively low miscibility of 2-butanol avoided the high concentrations in aqueous phase that may lead to downward migration of DNAPL. As the water- 2-butanol solution reached at DNAPL interface, 2-butanol shifted phase and reduced the density of DNAPL below that of water, by partitioning into DNAPL. The calculations developed by the authors indicated that with the given chemical properties of 2-butanol, it is unlikely to start downward mobilization.  The formula developed by the authors, relating the DNAPL pool height against interfacial tension as an adaptation of Brooks and Corey equation, had foreseen that, before the IFT was reduced to an amount enabling the downward mobilization, the density falls below of water hence the only mobilization occurs in upward and in the flow direction. For further mobilization, 1-propanol was used. The greater miscibility of 1-propanol in water made it possible for flooding. As it is with 2-butanol also 1-propanol partitions into NAPL when it reaches to water-NAPL interface.

Therefore without manipulating the density equilibria between phases, the mobilization of NAPL occurs at a greater extend. The total recovery rates attained from the column experiments were around 90% before the total amount of alcohol used in the experiment exceeded 1 pore volume which was very encouraging.

The hydrodynamic instabilities during alcohol flooding diminish the efficiency of DNAPL displacement (Lunn and Kueper, 1999b). Unstable behavior has been identified as one of the primary causes for bypassing of DNAPL, alcohol dilution, and inefficient miscible displacement. By using a three-step alcohol flooding process such like an isobutanol preflood, a composite alcohol main flood, and a polymer solution postflood, the fingering and bypassing of DNAPL was tried to be overcome. The preflood (10% isobutanol) accomplished a reduction in PCE density to approximately 1.0 kg/l. The main flood (65% ethylene glycol and 35% 1-propanol), which was neutrally buoyant, was used to mobilize the modified DNAPL with an inherently stable interface via reducing the IFT between phases. Finally, the main flood was displaced by a postflood consisting of a xanthan gum polymer solution, also with a density of approximately 1.0 kg/l, to reduce viscous fingering associated with water floods. Lunn and Kueper (1999b) reported a 99.8% mass recovery, using only 0.45 pore volumes of alcohol. The researchers recommended that future research focus on the delivery strategies for heterogeneous field situations.

. A similar idea about manipulation of density was developed by Roeder et al. (2001). However in this research in terms of density, the manipulated fluid was not only DNAPL but also aqueous phase. Density reduction of PCE was obtained by using tert-butyl alcohol. The main goal of the flow cell work was to investigate if phase density difference reversal could be applied for horizontal floods. Since the alcohol does not completely achieve phase density difference reversal, sucrose was added to the flushing solution to obtain concurrent density increases of the aqueous phase. The selected flooding solution of 40% tert-butyl alcohol, 15% sucrose, and 45% water had a density of 1.024 kg/l and a viscosity of 11.4 g/m*s. By manipulation of the aqueous density, the researchers attempted to avoid overriding of the alcohol flushing solution, which leads to lower remediation effectiveness. The bottom of the packing consisted of bentonite. A 56-cm zone of 0.30- to 0.50-mm sand was placed on the bentonite. A volume of 115 ml PCE was injected into the flow cell in sufficient amounts to create both entrapped and pooled

DNAPL. Most of the injected PCE moved to the bottom of the flow cell and migrated horizontally on sand layers; however, 25% of the PCE entered the bentonite. The horizontal displacement with the alcohol solution showed that density reversal did occur. In the swept zone, PCE removal was complete. In this particular case, the flushing solution caused underriding, which helped the mobilized NAPL rise to the top of the flow cell.

In the study conducted by Pennell et al. (1996) a mathematical expression was developed for the mobilization phenomena. This expression was then related with the desaturation curves of DNAPL, obtained from the column experiments. The mathematical approach was founded on the microforces acting on a NAPL globule in a single pore as depicted below.
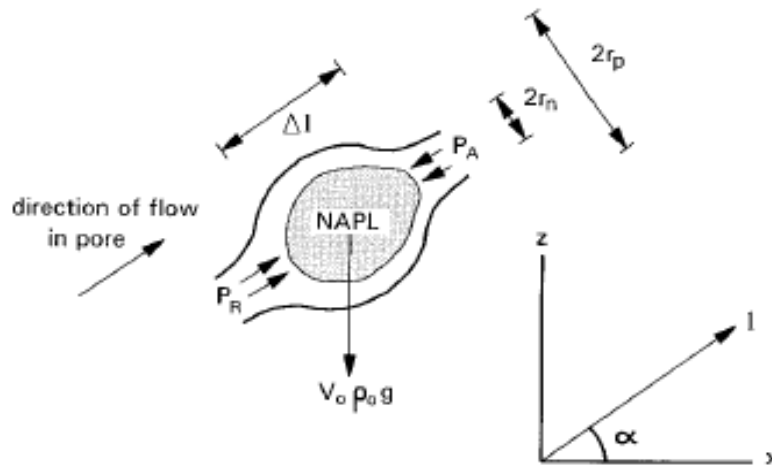


Figure 4.2. Schematic diagram of the pore entrapment model and corresponding coordinate system (Pennell et al, 1996).

Within this pore, pressure and gravity forces, which act to mobilize the globule, are balanced by capillary forces acting to retain the NAPL globule. The shear forces in between organic and aqueous phases and in between soil particle and surrounding fluid were neglected. The authors developed the following equation by the balance of pressure and gravity forces with capillary forces.

$$\frac{q_w \mu_w}{\sigma_{ow} \cos\theta} + \frac{\Delta\rho g k k_{rw}}{\sigma_{ow} \cos\theta} \sin\alpha = \frac{2\beta k k_{rw}}{\Delta l r_n}$$

(4.1.)

In this equation $\Delta l$ is the average length of the globule, $\Delta\rho$ is the density difference between phases, $g$ is the gravity acceleration constant, $q$w is the Darcy velocity of the aqueous phase, $k$ is the intrinsic permeability of the porous medium, $k$rw is the relative permeability to the aqueous phase, and $\mu$w is the dynamic viscosity of the aqueous phase, $\alpha$ is the angle of the flow with the horizontal axis, $\sigma$ow is the interfacial tension between the organic liquid and water, $\beta$ is the ratio between pore diameter (rp) and globule diameter (rn).

The left hand side of the equation was then renamed as Capillary and Bond numbers as follows;

$$N_{Ca} = \frac{q_w \mu_w}{\sigma_{ow} \cos\theta}, \quad N_B = \frac{\Delta\rho g k k_{rw}}{\sigma_{ow} \cos\theta} \qquad (4.2.)$$

Further manipulations of the equations eventuated as;

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B \sin\alpha + N_B^2} = \frac{2kk_{rw}\beta}{r_n d_b} \qquad (4.3.)$$

which in the end, for vertical flow, converted to;

$$N_T = \left| N_{Ca} + N_B \right| \qquad (4.4.)$$

The experimental section of the study was built with column experiments involving three different types of surfactants to start mobilization at different aquifer matrices. The surfactant formulations consisted of polyoxyethylene (POE) sorbitan monooleate (Witconol 2722), a 4:1 mixture of sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate (Aerosol MA/OT), and a 1:1 mixture of sodium diamyl sulfosuccinate and sodium dioctyl sulfosuccinate (Aerosol AY/OT). The selected contaminant was PCE and used at its residual saturation. The IFT between each flushing solution and water was measured and the Trapping number was calculated. The related saturation percentages

from the column experiments were also recorded for each flushing solution. With these inputs, desaturation curves were prepared for each flushing as the Trapping number on the x-axis.

From the desaturation curves, it was noticed that the mobilization of DNAPL at residual saturation starts when the Trapping number comes in between $2x10^-5$

$5x10^-5$. Further more, it was indicated that the whole mobilization of DNAPL was encountered when the Trapping number exceeds $1x10^-3$. This outcome was confirmed and used by many other researchers in subsequent studies (Oostrom, 2006).

In a series of studies conducted by Ramsburg and Pennell in years 2002, 2003 and 2004, techniques using prefloods with partitioning alcohols and main floods with surfactants were tested. The researchers used a 6% n-butanol aqueous solution to achieve the conversion of TCE and chlorobenzene (CB) to LNAPL, followed by a low-interfacial-tension surfactant solution containing 4% (4:1) Aerosol MA/Aerosol, 20% n-butanol, and 500 mg/l CaCl2.

It was concluded that, after the prefloods, the NAPL samples were always less dense than the aqueous phase samples. Only after 1.2 pore volume surfactant solution, 90% CB and 85% TCE were recovered. Ramsburg and Pennell (2002) stated that the minimal mobilization during the preflood and the near-complete intended mobilization during the main surfactant flood were consistent with trapping number calculations. They also noted that the results demonstrated the potential efficiency of their technique for DNAPL source remediation.

A substantial work about the use of ternary phase diagrams to predict performance of cosolvent flushing was performed by Falta (1998). The author attempted to develop a relationship between the phase diagram and the performance of the flushing. The method was developed by using the fractional flow theory, which had been established by petroleum engineering in the past. In the study to interpret the performance of the former experimental studies the developed method was applied and good correlation with the real results was obtained.

The main focus of the method is on the "plait point" of the ternary phase diagram. The tie line passing through the plait point is drawn (critical tie line) till it intersects to the water-cosolvent axis. The intersection point is called as "Critical tie line extension" and it divides the water-cosolvent axis into two parts as "Miscibility zone" and "Zone of tie line extensions". Figure 4.3. is an illustration of the above definitions.
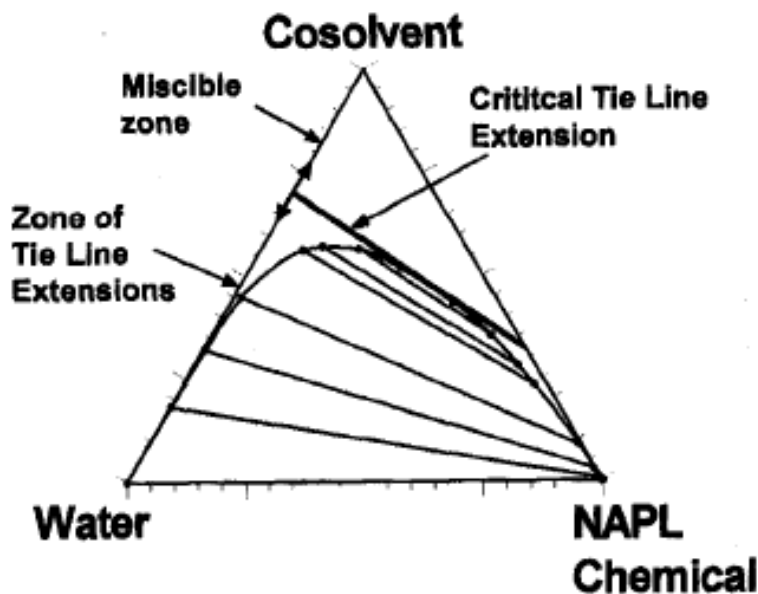


Figure 4.3. Important parameters for ternary diagram (Falta, 1998).

The author states that if the volume fraction of the flushing solution is in the "miscibility zone" the dominating recovery mechanism is mobilization and great improvements in the recovery are achieved. The author also points out that the developed method is comprised for the equilibrium conditions. One great shortcoming of the study is due to this assumption since it tries to explain NAPL remediation where non-equilibrium is a major parameter.

### 4.2.3. Cyclodextrin Enhanced Remediation

Studies that evaluated the use of cyclodextrin for enhanced groundwater remediation are briefly described below.

One of the first studies that focused on in-situ cyclodextrin enhanced remediation of groundwater is Wang and Brusseau (1993) which investigated the alteration of the solubilities of some organic compounds by HPCD in the aqueous phase. The target contaminants selected in this study were Trichloroethene (>99 % pure), chlorobenzene (>99%) naphthalene (>99%), anthracene (>99%) and DDT (98%). In the research it was concluded that the aqueous solubility enhancement of organic compounds was related to the HPCD concentration in the aqueous phase. The other main finding of the study was that there was a linear relationship between the solubility enhancement of the organic compounds and HPCD concentration. After evaluating the molecular volume of the five low-polarity organic chemicals (NOCs), the authors found out that the solubility enhancement was also related to the molecular volume of the target chemical since the dissolution by HPCD was occuring by inclusion of the chemical inside HPCD cavity. DDT having the biggest molecular volume in those five NOCs, which is even bigger than the cavity volume of HPCD, also had the lowest solubility enhancement. Apart from these indications the surface tension of the HPCD solution was presented as a logarithmic decrease from 72.8 till 50 dyne/cm with increasing amount of HPCD in the solution.

Boving et al. (1999), investigated the recovery of TCE and PCE using Hydroxypropyl-*beta*-cyclodextrin (HPCD; 90%) and methyl-beta-cyclodextrin (MCD; >99.8%) was investigated. The research included both batch and column experiments. The batch experiments included solubilization and interfacial tension measurements. Conducted column experiments involved two different flow schemes such as vertical and horizontal flow. The presence of the free phase TCE and PCE were adjusted at their residual saturations. To interpret the data of the column experiments and to have better insight of the recovery mechanisms, dimensionless Capillary and Bond numbers were calculated.

The outcome of the study was that the dissolution limit of the column experiments were in the solubility limit for the given flow rate. It was also clarified that mobility can not occur in any concentration of HPCD flushing experiments. However all of the column experiments, involving MCD as an agent, excluding only the one with %5 MCD, showed mobilization. This mobilization effect was also investigated through the dimensionless

numbers such as Capillary and Bond numbers to confirm this recovery process and the result of this calculation showed good correlation with the column experiment results.

The same researchers further investigated the subject and included numerical solutions for the given (Boving et al., 2001). The data attained from the batch experiments were used in the numerical simulations. 18 types of compounds, including some of the very important contaminants such as TCE, PCE DCB, Toluene etc., were investigated. The type of the cyclodextrin used in the experiments was "Hydroxypropyl-beta-cyclodextrin".

The linear relationship between LogKow and LogKcw was presented. The finding of this relationship confirmed that the more hydrophobic compounds have bigger enhancement factors. This outcome is explained with the hydrophobic structure of the HPCD cavity. However the more hydrophilic compounds, due to their higher aqueous solubility, end up with higher solubility in HPCD solutions. The interfacial tension measurements between TCE and HPCD solutions with increasing concentrations, gave a log linear decrease, yet this decrease can not initiate mobilization.

Three simulations were done for the compounds TCE, 1,2-DCB and Decane having the aqueous solubilities as 1150 mg/l, 137 mg/l and 0.0525 mg/l respectively. As can be understood from their aqueous solubility most hydrophobic compound DEC had the biggest solubility enhancement factor, 1200 times the TCE's enhancement factor. The enhanced solubility limit for the three compounds, were presented as 7502 mg/l, 4316 mg/l and 167 mg/l. The other major inputs for the simulation were selected as follows; flow velocity of 4 cm/hour, dispersivity of 10 cm, flow length scale of 100 cm with a volume of 1000 ml. The steady state conditions were assumed to be gained at 1.5 pore volume after the initiation of the run. The concentration of the effluent at the steady state was assumed to be equal to the enhanced solubility of the compound. The results of the simulations indicated that with the most hydrophobic compound, even with the biggest solubility enhancement factor, the time needed for the residual NAPL to be recovered from a contaminated field by HPCD solution, still tends to be greatest. The simulations yet did not cover the transient phase that happens to exist after certain amount of NAPL is recovered and the homogenous NAPL distribution is no more valid. As last it was indicated that the

given mechanism is readily valid for also NAPL mixture recovery schemes with consideration of the Raoult's law.

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Hanna et al. (2003) surveyed the interaction between different types of trichlorophenol(TCP), a commonly used wood preservative, and different types of cyclodextrin. Uncharged, electrostatically inert TCP and negatively charged TCP were evaluated in terms of solubility at different pH levels in different cyclodextrin solutions. The two pH levels subject to investigation were 3 and 8.8.

Underivatized beta-cyclodextrin which has a relatively low solubility in water at both pH levels did not make a significant improvement in any kind of TCP aqueous solubility. Moreover at pH 3, after a certain amount of cyclodextrin concentration, precipitation started to occur and the slowly increasing TCP concentration initiated to drop. At pH 8.8 not any precipitation was observed, however the TCP concentration could not reach to amounts as it did at pH 3. The solubility enhancement factors for both HPCD and MCD were much greater than the underivatized beta-cyclodextrin. Moreover the enhancement factor at pH 3 happened to be 10 times of the solubility limit at ph 8.8. It was previously known that the TCP concentration in the aqueous phase was related to pH level such that the TCP concentration follows a 10-fold increase for every pH unit increment above 6 and is constant for pH values below 5 (300 mg/l). Another representative of this condition could be the different octanol-water partition coefficients at two different pH levels. The cyclodextrin usage would be more beneficial for this low solubility circumstances in acidic conditions.

Bizzigotti et al. (1997) focused on the enhanced solubilization of PCE maintained by HPCD and the degradation of the solublized PCE by zero valent iron powder or iron fillings. The selected contaminant was PCE, and 4 types of cyclodextrin; HPCD, beta-cyclodextrin, *alpha*-cyclodextrin, and *gamma*-cyclodextrin were investigated in the research. Batch solubility and column recovery experiments were conducted to evaluate the observed degradation rate constants. The column experiment set up was particularly interesting for the two columns were linked in series. The first "Generator column" having free phase PCE was flushed with different concentrations of cyclodextrin solutions to maintain the solubility limit and linked to the second "Reaction column" containing iron

fillings or iron powder in the different amounts for the dechlorination to occur. The samples were collected after and before the "Reaction column".

Regular applications of zero-valent iron for dechlorination of chlorinated solvents have limitations due to solubility limit of the solvent in the aqueous phase. The degradation process which is enhanced by cyclodextrin brought about by zero valent iron is presented below;
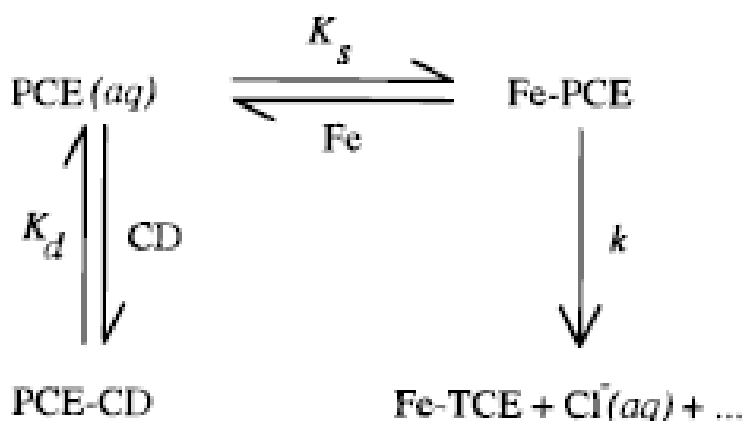
$$PCE\ (aq) \underset{Fe}{\overset{K_s}{\rightleftharpoons}} Fe\text{-}PCE$$

$$K_d \Updownarrow CD \qquad \qquad \Big\downarrow k$$

$$PCE\text{-}CD \qquad \qquad Fe\text{-}TCE + Cl^-(aq) + ...$$

Figure 4.4.. Reaction of Cyclodextrin-Complexed PCE with Solid Phase Iron (Bizzigotti et al., 1997).

It was concluded that only HPCD complexed PCE stays in the aqueous form while the underivatized cyclodextrin-PCE complexes precipitates. The interfacial tension was also investigated and alteration with increasing amount of cyclodextrin in the solution claimed to show unstability such as a decrease at the low concentrations and an increase after some certain concentrations.

As a result of the study it was indicated that the degradation rate of chlorinated solvents was decreased with the increasing amount of cyclodextrin in the solution confirmed both from batch and column experiments. Yet even the degradation rate was decreased, the amount that was degraded by zero-valent iron was increased due to increased solubility of PCE. One other outcome of the study was due to recycling process which was pursued after a certain time of experimentation in the column floodings. For iron degrades the chlorinated solvents in the second column (or as a field approximation in

the "permeable reactive barrier") the extracted cyclodextrin could be used over and over, lapping over the contaminated sites, hence decreasing the cost of remediation.

Lindsey et al. (2003) focused on the targeting of hydrophobic compounds in fenton reaction in the coexistence of cyclodextrins. The degradation of hydrophobic compounds by hydroxyl radicals obtained from the fenton reactions was investigated in terms of the possible scavenger effects due to non-pollutant compounds such as chloride, ethyl ether and methanol.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \hspace{3cm} (4.5.)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH\cdot + H^+ \hspace{3cm} (4.6.)$$
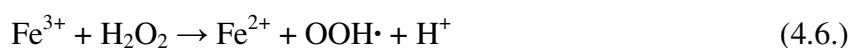
The above fenton reaction producing hydroxyl radicals is generally applicable to the contaminated fluids. The mentioned scavenger effect; reaction of a non-pollutant chemical with hydroxyl radical before the radical reacts with the pollutant being a major short coming of the oxidation process. To overcome this short coming the authors tried to capsulate Ferrous iron(II) and the organic pollutant in the cavity of carboxymethyl-beta-cyclodextrin (CMCD). The selected organic contaminants were the compounds such as phenanthrene, phenol, pyrene, (>%98) PCB-54 (2,29,6,69-tetrachlorobiphenyl, 99%), and PCB-80 (3,39,5,59-tetrachlorobiphenyl, 99%) respectively.

The outcome of the study was encouraging due to enhanced degradation rate constants obtained with CMCD. Even at worse scenarios with many scavengers in the environment the degradation constants kept increasing with the increased CMCD concentrations in the solutions. This effect was represented as a result of inclusion of organic compounds and ferrous iron(II) inside the torodial shape of CMCD. The fenton reaction starting at a very close proximity of the organic contaminant near to the CMCD due to its bondage with iron prevented the decrease of the degradation rate constants by scavengers. Another minor finding of the study was that the solubilization process of PCB's in cyclodextrin solution could be accelerated easily by sonification. The presence of humic acid in the solution was also investigated to represent similar environmental characteristics of the surface waters. Without CMCD, humic acid decreased the degradation rate constants of the contaminants however when the CMCD were put in the

scenario, the effect of the humic acid became invisible, and the rate constants gave similar results as they had given in clean water. The effect of the sorption preventing the bioavalibility of the contaminants such as PCB's hence the recovery percentage, was also reduced with increasing amount of CMCD in the solution.

The use of cyclodextrins for bioremediation purposes has been subject to several investigations. Bardi et al. (2000) investigated the effect of cyclodextrins on the biological processes. In the bioremediation schemes till now, surfactants have been used for their ability to increase the bioavailibility of the contaminant in the aqueous phase. However in many applications their usage is up to some extend since they may have toxic characteristics, especially when the remediation procedure is performed in in-situ cases. With this consideration, any improvements in the biodegradation procedures by non-toxic cyclodextrins are substantially noteworthy.

In the research, the compounds degraded by the microorganisms were; dodecane, tetracosane, naphthalene and anthracene respectively. The cyclodextrin that was subject to investigation was underivatized beta-cyclodextrin at a concentration of 1% weight per volume, which is sold cheapest in the market.

The main outcome of the study was that the underivatized beta-cyclodextrin enhances the degradation of aliphatic and polycyclic aromatic hydrocarbons by increasing their bioavailability.  The greater reduction of the organic contaminants in same time period has resulted in a greater amount of biomass which corresponds to that the greater substrate consumption was directed to the biomass production instead of energy consumption. The reduction in the degradation time was much greater for the aromatic compounds than long chain aliphatic hydrocarbons. The maximum degradation rate was observed in the early stages of degradation. One other possible advantage of using beta-cyclodextrin is that when volatile hydrocarbons are released into the environment, this procedure helps to reduce atmospheric pollution by accelerating their degradation.

Wang et al. (1998) focused on the degradation of single compound "Phenanthrene". The effect of HPCD on to desorption and solubilization of hydrophobic organic

compounds was the main motivation for this research. Two types of cyclodextrin were used in the study, each of them being hydroxypropyl-beta-cyclodextrin but one at analytical grade and other at technical. The examination of two HPCD at different purities was due to costly price of analytical grade where in the field scale cases application of big amounts would be prohibitive. The technical grade HPCD contained 3.2% propylene glycol. The effect of this compound was also investigated. Control samples with HPCD and without phenanthrene were analyzed in order to conceive any interactions between phenanthrene degrading bacterias and HPCD molecules. Investigations on different inoculum densities were performed to comprehend their effect on the degradation process.

This study revealed that HPCD enhances the biodegradation of phenanthrene even at relatively low concentrations such as 10 g/l. The increased concentration of HPCD increased the substrate utilization rate, however the lag phase of the higher concentration HPCD samples were longer, implying that the time needed for the bacteria to start degradation was longer either due to the high concentration of HPCD or phenanthrene. The inoculum density did not have any effect on the substrate utilization rate yet the lag phase for the low inoculum densities were longer. Control samples were analyzed in terms of cell densities with HPCD and the bacterial colonies inside, and it was clarified that the HPCD does not affect the phenanthrene degrading bacterias in any terms. The impact of biggest impurity in technical grade HPCD; propylene glycol, was determined as it was a competitor of Phenanthrene. The degrading bacterias showed cell growths only with technical grade HPCD. The comparison of technical and analytical grade HPCD showed that the technical grade usage resulted in smaller substrate utilization rates for phenanthrene degradation. Despite this reduction in the efficacy of phenanthrene degradation, the technical grade HPCD application still brings about greater substrate utilization rates.

A field scale assessment of cyclodextrin enhanced groundwater remediation was performed by Mcray and Brusseau (1999). A control cell of 3m to 5m with an aquifer depth of 9m, situated in OU1 site at Hill AFB in Layton, UT, USA was flushed with analytical grade (90% purity) Hydroxypropyl-beta-cyclodextrin for 8 pore volumes (corresponding to 10 days). 65000 liters of flushing solution was used during the whole experiment. The complex structure of the NAPL was also investigated for the

determination of its dissolution behavior in the subsurface. 12 different compounds including the very common contaminants such as TCE, DCB, Toluene and Benzene etc. were subject to examination. The remediation procedure was interrupted at day $8^{th}$ for 24 hours to see if the equilibrium concentrations were reached at the given groundwater velocity.

The results of the experiment were in good correlation with the prior lab scale experiments. The dissolution behavior was ideal (explicable by Raoult's law). The control of equilibrium process indicated that the equilibrium conditions were achieved with the given flow rate. The main outcome of the study was that any field scale remediation activity with HPCD could be evaluated prior to remediation with the batch solubility experiment results. However the uncertainty due to site formation should always be considered.

# 5. MATERIALS AND METHODS

The experimental work that has been performed to evaluate the removal efficiencies of benzene and toluene from porous media consists of two components; batch experiments, column flushing experiments as listed below.

## 5.1. Batch Experiments

As indicated in chapter 2, the purpose of this study was to evaluate the performance of two agents: ethanol and HPCD for the removal of NAPLs from the subsurface. The NAPLs considered was toluene, benzene and a mixture of the two. The experiments conducted with ethanol were used to assess the significance of the various mechanisms-namely enhanced solubilization vs. mobilization on the overall NAPL recovery efficiency. The experiments involving HPCD also focused on the impact of temperature of the flushing solution on NAPL removal

To achieve these objectives, the following batch experiments were conducted:

### 5.1.1. Interfacial Tension (IFT) Measurement

- IFT of the NAPL (toluene) water system as a function of ethanol content at 20 ℃.
- IFT of the NAPL (benzene) water system as a function of ethanol content at 20 ℃.
- IFT of the NAPL (benzene + toluene mixture) water system as a function of ethanol content at 20 ℃.

### 5.1.2. Solubility Measurement

- Solubility of toluene as a function of ethanol content at 20 ℃.
- Solubility of toluene in water-HPCD solution at 20 ℃.
- Solubility of benzene in water-HPCD solution at 20 ℃.
- Solubility of benzene + toluene mixture in water-HPCD solution at 20 ℃.

- Solubility of toluene in water-HPCD solution at 40 ℃.
- Solubility of benzene in water-HPCD solution at 40 ℃.
- Solubility of benzene + toluene mixture in water-HPCD solution at 40 ℃.

### 5.1.5. Ternary Phase Diagrams (TPD)

- Development of the toluene-ethanol-water at 20 ℃.
- Development of the benzene-ethanol-water at 20 ℃.
- Development of the mixture (toluene + benzene) -ethanol-water at 20 ℃.

## 5.2. Column Experiments

A total of 7 flushing experiments were conducted:

- Flushing of NAPL (toluene) with an ethanol-water solution (50%-50% by volume) at 20 ℃.
- Flushing of NAPL (benzene) with an ethanol-water solution (50%-50% by volume) at 20 ℃.
- Flushing of NAPL (50% toluene+ 50 % benzene by mass) with an ethanol-water solution (50%-50% by volume) at 20 ℃.
- Flushing of NAPL (toluene) with a 50 g/L HPCD aqueous solution at 20 ℃.
- Flushing of NAPL (benzene) with a 50 g/L HPCD aqueous solution at 20 ℃.
- Flushing of NAPL (50% toluene+ 50 % benzene by mass) with a 50 g/L HPCD aqueous solution at 20 ℃.
- Flushing of NAPL (50% toluene+ 50 % benzene by mass) with a 50 g/L HPCD aqueous solution at 40 ℃.

## 5.3. Equipments

The instruments used in this study for the batch and flushing experiments are listed below.

### 5.3.1. Batch Experiments

Gas Chromatography 1: Agilent 6980N Gas Chromatography including FID, ECD detectors, auto-injectors with split/splitless mode, capillary column of 50 m, purge-trap. Gas Chromatography is controlled by software from a personal computer.

Gas Chromatography 2 : Perkin Elmer Gas Chromatography including FID, ECD, MS detectors, auto-injectors with split/splitless mode, Head space auto sampler, capillary column of 50 m, purge-trap. Gas Chromatography is controlled by software from a personal computer.

Interfacial Tension Meter: Manually operated IFT measurer (KSV 703 Digital Tensiometer) using Du-Nouy ring with different size sample vessels.

### 5.3.2. Flushing Experiments

Column: Cole Palmer Kontes chromaflex glass column (diameter: 5cm, length: 30cm) standard borosilicate glass column for visual observation of 1-Dimensional flow.

Pump: Masterflex peristaltic pump used with a viton tubing which has a diameter of 0.8 mm enabling very low flow rates similar to groundwater.

Centifuge: Nuve NF 1200.
Water bath Shaker: Julabo shake Temp SW22.
Sensitive balance: Denver instruments APX-200.
Other laboratory instruments: Injectors, vials, flasks, etc.

## 5.4. Experimental Procedures

### 5.4.1. Solubility Measurements

The method used for the solubility measurement of Hydrophobic Organic Compounds (HOC) in the ethanol water solution or the Hydroxypropyl-beta-cyclodextrin (HPCD) solution was performed as explained in the related literature (Wang et al., 1993). 2ml NAPL of benzene, toluene and their mixture were put in vials containing 20 ml of flushing solution at different concentrations. The NAPL contained either pure benzene, pure toluene or 50% mixture of toluene and benzene by mass, which corresponds to a mol fraction of 46% toluene and 54% benzene, regarding the experiment. The vials were then settled into a water bath reciprocating shaker with temperature set, for 72 hours at 150rpm. At the end of 72 hours, to achieve the phase separation, the vials were centrifuged at 3000rpm for 20min. Finally the aqueous phase was extracted from the vials for GC-headspace analysis.

The dissolved concentrations were measured after 48 hours to determine whether the time needed for equilibrium is achieved. The GC-headspace analysis is identical to that used for the 72-hours samples.

### 5.4.2. Solubility Calculation

The measured solubility data were also compared to the log-linear model developed by Yalkowsky et al. (1972). Yalkowsky's method for the calculation of solubility is originally developed for pure hydrophobic organic compound (HOC) solubility in a cosolvent+water system. The equations used in the calculations are (Yalkowsky et al., 1972).

Log $S_m$= log $S_w$+ r*f   (Yalkowsky's calculation for pure liquid HOC)        (5.1.)

$$r=a*\log K_{ow} + b;$$        (5.2.)

where; Sm: solubility of HOC in ethanol+water system. Sw: Solubility of Hoc in pure water. r: Cosolvency power. f: volume fraction of ethanol in aqueous phase. a, b: Emprirical constants unique to the cosolvent.

The cosolvency power, a variable unique for each HOC is directly proportional to the octanol water partition coefficient of the compound (Yalkowsky et al., 2002). This variable is essential for the formula and also calculated separately. However the aqueous solubility of HOC with zero ethanol is also an influential parameter in the formula. Thus, an HOC with lower octanol water partition coefficient (lower cosolvency power) may still have greater solubility at a higher cosolvent content.

### 5.4.3. Measurement of Interfacial Tension

The Interfacial tension was measured with the tensiometer (Figure 5.1.) using Du Nouy Ring method. The platinum ring was immersed into the liquid and IFT is measured while the ring is being pulled up. The sensitivity of the equipment was very important in determining the effect of changes in the phase behaviour. All the measurements were performed in triplicates due to this sensitivity. The Interfacial tension (IFT) of a "HOC-alcohol-water" system is also strongly influenced by th temperature. This influence is increased when the alcohol content of the system is increased (Aydin et al., 2008). Therefore all of the experiments were carefully conducted at the same temperature.

The basic steps of the IFT measurement can be summarized as (Figure 5.2.):

1. The ring was placed above the surface and the force was set to zero from the equipment.
2. The ring hit the surface. The positive force was noticed as a result of the adhesive force between the ring and the surface.
3. The ring was pushed through the surface and this caused a small negative force.
4. The ring broke through the surface and a small positive force was measured due to the supporting wires of the ring.
5. When lifted through the surface the measured force started to increase.
6. The force kept increasing.

7. The maximum force is reached

8. After the maximum value was reached there was a small decrease of in the force until the lamella breaks.



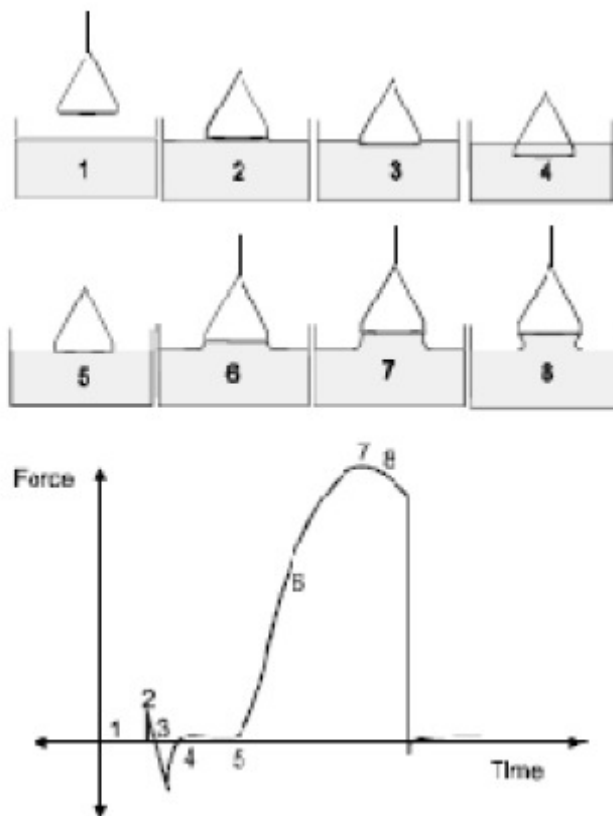Figure 5.1. Interfacial tension meter (KSV 703 Digital Tensiometer).



Figure 5.2. The steps of measurement of Interfacial tension with Du-nouy ring.

### 5.4.4. Construction of Ternary Phase Diagram

The location of the miscibility curve on the ternary phase diagram was determined using the "Cloud Point Titration Method". The titrations conducted for the determination of the turnover points between one-phase and two-phase regions were accomplished in mini-titration vials. All equilibrium phase behavior experiments were conducted at room temperature around 24ºC. The titration set-up was used for the determination of miscibility points. A known amount of a chemical solution (containing alcohol, surfactant, organic contaminant, etc.) was placed in a glass vial capped with a Teflon mini-valve to minimize contaminant losses due to evaporation. The components of the ternary phase diagram (contaminant, water and chemical agents) were added gradually to the solution using gastight macro-syringes. The turning point was observed directly from the change in transparency. After the determination of the first point, chemical solution was further added to move the mixture out of the cloudy zone to reach the one phase zone again. The second point of the miscibility curve was obtained by adding water to reach again a cloudy zone. The miscibility curve was drawn with 18 of the determined values. Phase diagrams were established on molar basis.

### 5.4.5. Column Experiments

Column experiments were conducted with a vertically installed chromaflex glass column which also enables visual detection of NAPL movement. The column was connected to peristaltic pump with viton tubing and packed with homogeneous sand with a porosity of 0.35. For the uniform distribution of the sand into column, sand was compacted after every 2 cm increments. The column was then saturated upwards by distilled water for 1 day at a flow rate less than 1ml/min to prevent the formation of air bubbles. Experiments were conducted with flushing solutions containing 50% ethanol by mass or 50g/l HPCD. The organic contaminants were dyed with oil-red with a concentration of $4x10^-4$ M for visual detection. The flow rate of the every experiment was kept uniform at 3.1 ml/min, corresponding to a groundwater velocity of 2.27 m/day.

Ten grams of the contaminant was introduced into the column via viton tubing from the bottom end of the column. 4 pore volumes of flushing was performed for each

experiment. The last 100 ml of the flushing was completed by distilled water for HPCD floodings.

The experiments conducted at raised temperature were done with the same glass column and peristaltic pump. To increase the temperature of the flushing solution prior to introduction into column, a water bath was used. To heat the column (aquifer) and reduce the heat losses a strip heater was used and column was insulated with an aluminium foil. All heating instruments were set to the desired temperature. Once the samples are obtained, they are immediately analyzed by Gas Chromatography either using head space or direct injection method regarding the contaminant formation. Figure 5.3 is a representative of the conducted flushing experiment at raised temperature.



Figure 5.3. The experimental setup for increased temperature.

# 6. RESULT AND DISCUSSION

## 6.1. Ethanol Enhanced Remediation

This chapter presents the results of the laboratory experiments conducted to evaluate the removal of NAPL (toluene, benzene, or a mixture of the two) using the two agents ethanol and HPCD. Section 6.1 presents the results of the batch and flushing experiments using ethanol flushing solution, while section 6.2 presents the results using HPCD.

### 6.1.1. Solubility

For the assessment of solubility degrees in cosolvent system, Yalkowsky's method was used (Yalkowsky et al., 1972). However to validate this method a batch experiment involving toluene solubility in ethanol-water solution was performed. In the first stage, solubility of Hydrophobic organic compounds (HOC) in ethanol+water systems was evaluated. Figure 6.1 is the log-scale comparison of concentration data obtained from batch experiment and Yalkowsky's method. As seen from the graph Yalkowsky's method is in good agreement with the real data. This is consistent with other papers in the literature such as Corseuil et al. (2004).
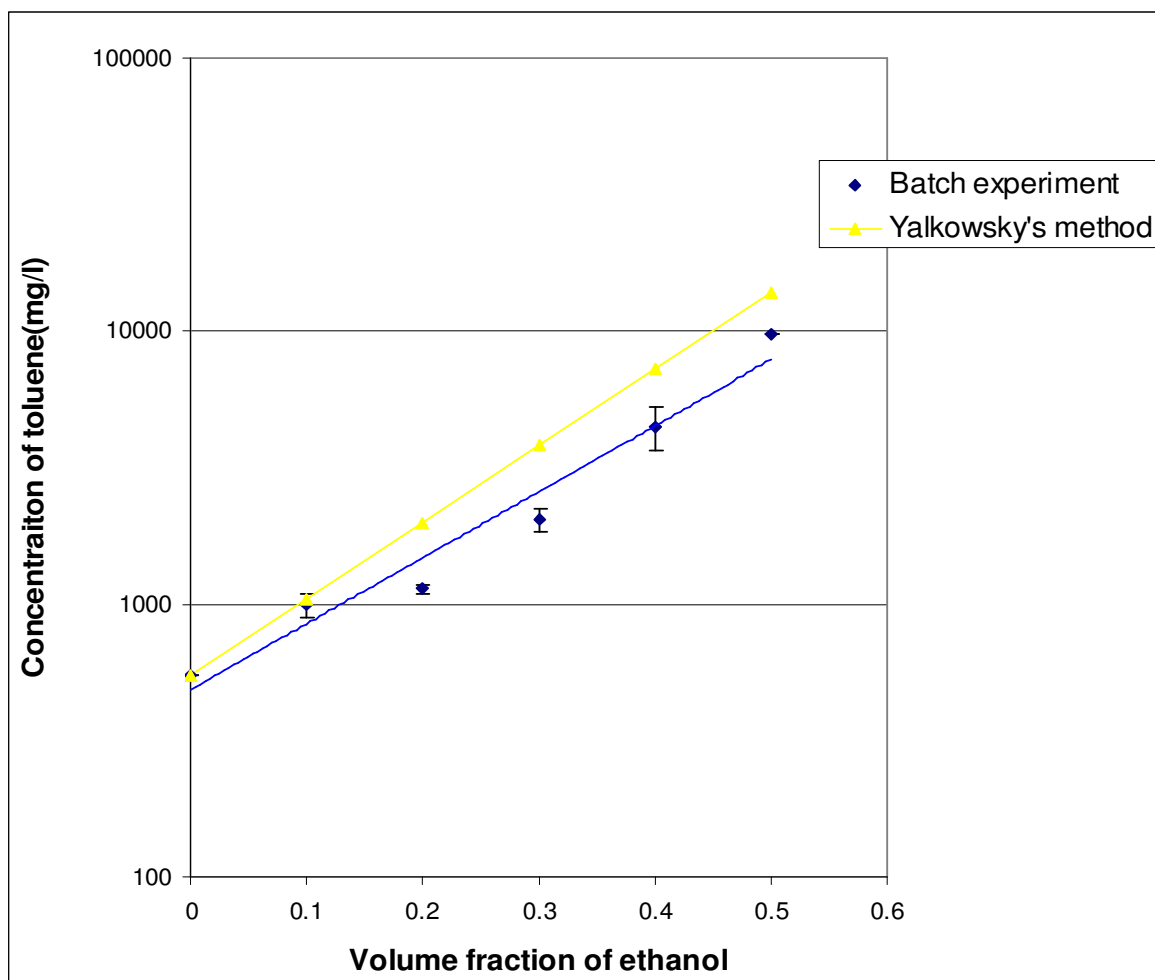
Figure 6.1. Comparison of toluene concentrations obtained from Yalkowsky's method with the real data.

6.1.1.1. Solubility of Toluene in Ethanol-Water Solution: The addition of ethanol into aqueous phase yields an increase in the concentration of toluene. This increase was relatively low for low amounts of ethanol however as the ethanol amount increased the effect of ethanol on the toluene solubility increased. A logarithmic increase of the toluene solubility was encountered with respect to volume fraction of ethanol in the aqueous phase and the cosolvency power for toluene was found as 2.85. The solubility of pure toluene in ethanol water system is drawn in Figure 6.2.
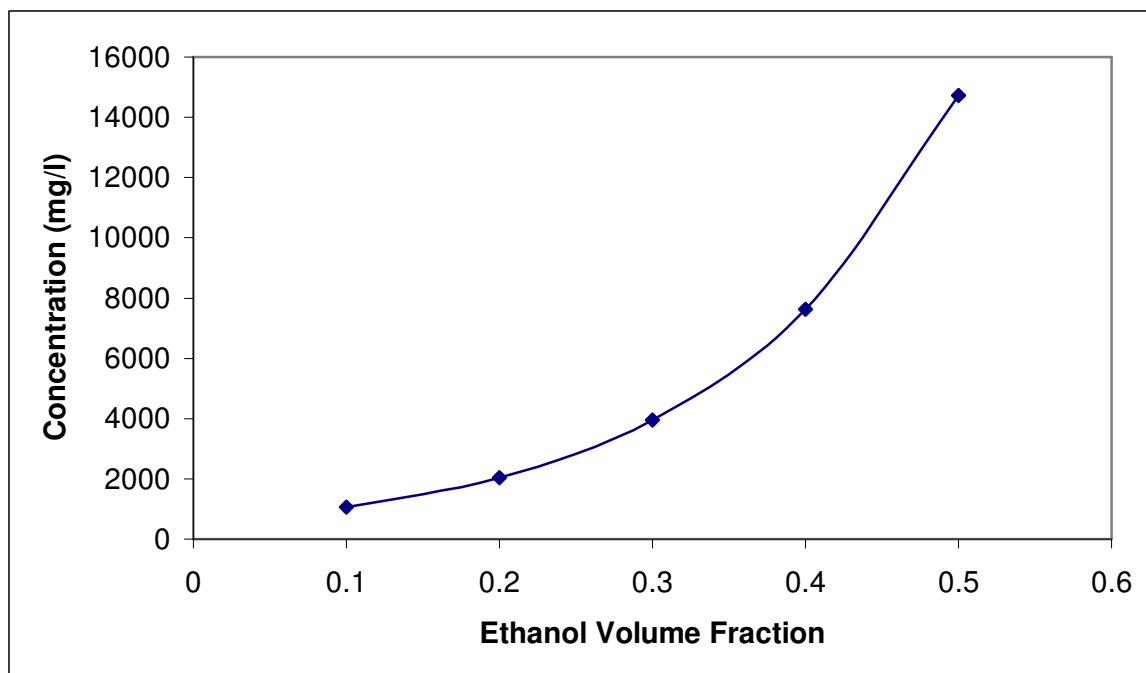
Figure 6.2. Solubility of toluene in ethanol+water system, with respect to volume fraction of ethanol in the aqueous phase.

6.1.1.2. Solubility of Benzene in Ethanol-Water Solution: The solubility of pure benzene in ethanol water system is drawn in Figure 6.3. The solubility was determined using the Yalkowsky model (Yalkowsky et al., 1972). As the case of toluene solubility, solubility of benzene exhibits a similar logarithm increase as the volume fraction of ethanol in the aqueous phase increases. However, benzene has a lower octanol water partition coefficient, and a lower cosolvency power compared to toluene found as 2.39, did not mean a lower solubility as seen from the figure below.
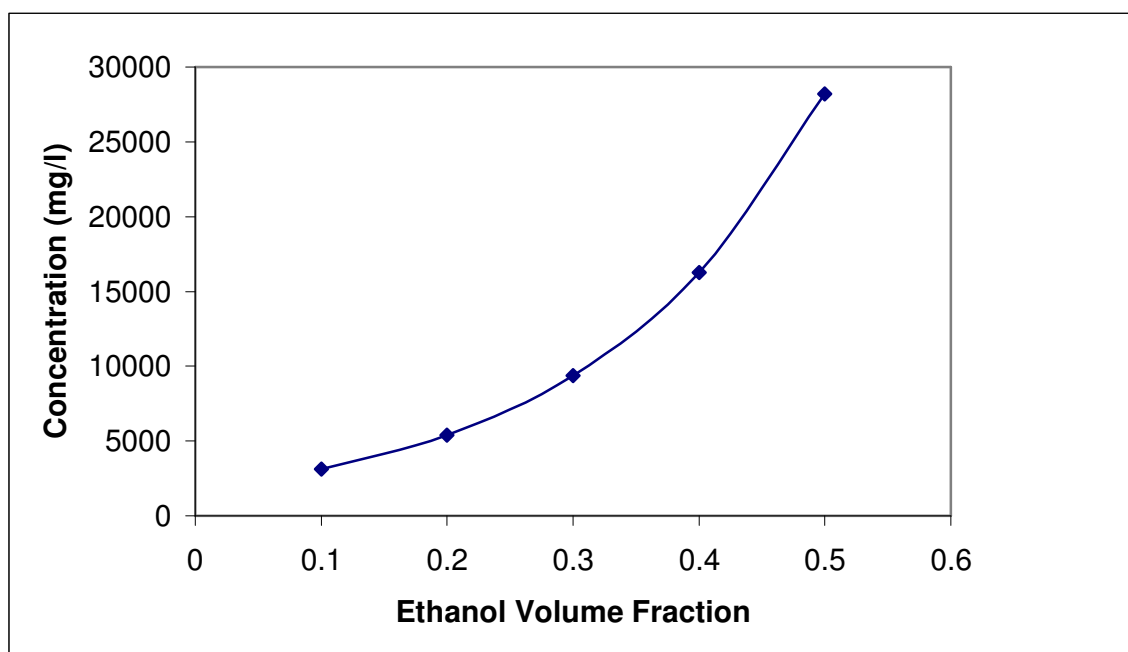
Figure 6.3. Solubility of benzene in ethanol+water system, with respect to volume fraction of ethanol in the aqueous phase.

6.1.1.3. Solubility of Toluene and Benzene from Mixture Organic Phase: Figure 6.4. depicts the aqueous solubility of benzene and toluene from a mixture NAPL both at 50% by mass. For the following calculation Raoult's law was applied to the Yalkowsky's prediction. The mol fractions of toluene and benzene were 0.46 and 0.54 respectively. As seen in the following graph, the solubilities of toluene and benzene in the aqueous phase with 50% ethanol by volume are 6700 mg/l and 15000 mg/l respectively. Based on these values, it is reasonable to expect benzene having a recovery rate 2 times greater than toluene, provided that enhanced solubilization is the only transport mechanism and that multiphase equilibrium is maintained in the NAPL-water-ethanol system.
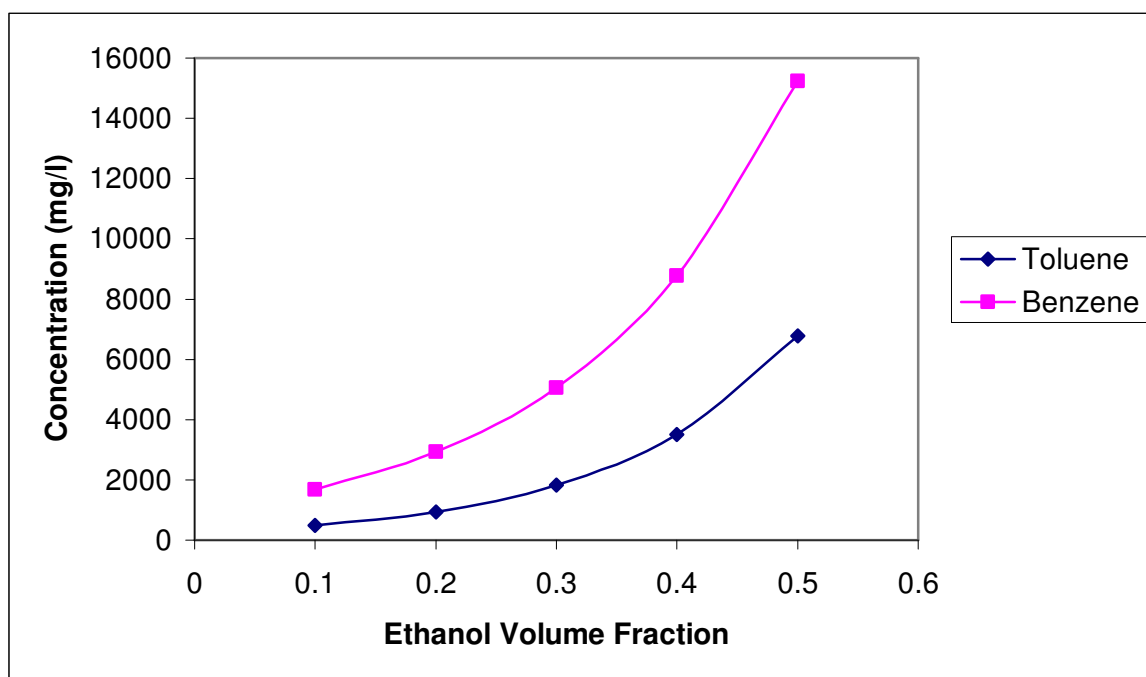
Figure 6.4. Solubility of toluene and benzene in mixture (50% by mass) with respect to ethanol volume fraction in the aqueous phase.

## 6.1.2. Interfacial Tension

IFT between NAPL and aqueous phases is altered by the addition of a cosolvent to the system (Falta, 1998). The IFT term is very crucial for the assessment of mobility mechanism in the recovery. Furthermore IFT is an essential variable for the non-dimensional "Trapping number" which is also helpful to evaluate the mobility degree of NAPL in the porous media (Pennell et al., 1996). When the IFT is sufficiently depressed, the movement of the residual organic phase starts to occur (Grubb et al., 1997).

6.1.2.1. IFT between Toluene and Aqueous phase: Figure 6.5. shows the IFT between toluene and ethanol-water solution with respect to ethanol volume fraction in the aqueous phase. The IFT between toluene and water with zero ethanol is 32.4 dyne/cm. Direct measurements of interfacial tensions between two phases shows a logarithmic decrease on the IFT with increase in ethanol of the system. The experiment was conducted at 20ºC. Zero IFT is reached when the two phase become totally miscible. As approached to the zero IFT with increasing amount of ethanol in the system, the measurements showed

greater variance which is due to increased miscibility of the system. Therefore the experiment was stopped when the ethanol volume fraction reached to 0.38.
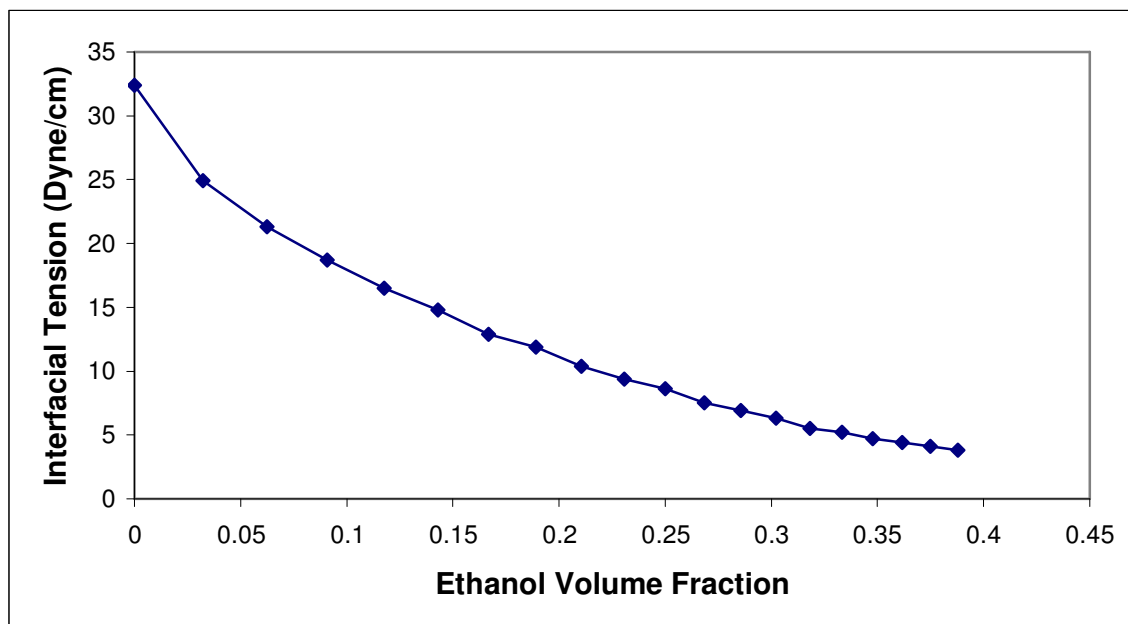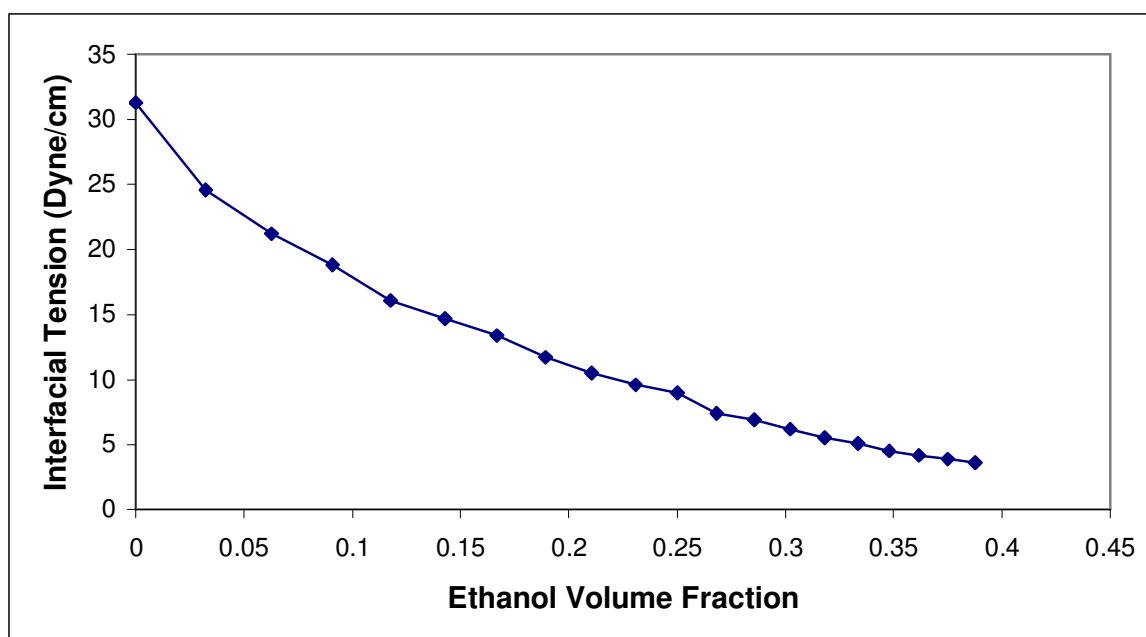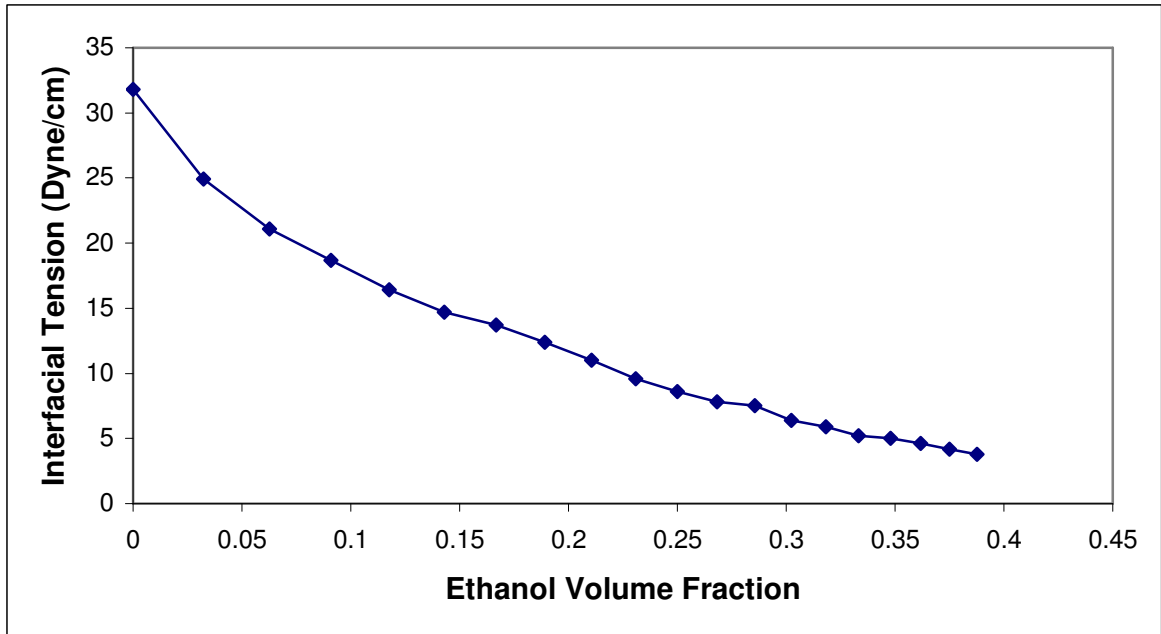


Figure 6.5. Interfacial tension between toluene and water+ethanol, as a function of ethanol volume fraction in the aqueous phase at 20ºC .

6.1.2.2. IFT between Benzene and Aqueous Phase: Figure 6.6. shows the IFT between benzene and ethanol-water solution as a function of ethanol volume fraction in the aqueous phase. The IFT between benzene and pure water is 31.3 dyne/cm, slightly less than toluene. The same logarithmical decrease in the IFT between benzene and aqueous phase was also observed. Similar behavior in the variance of the measurements at increased ethanol content due to increased miscibility was encountered.

Figure 6.6. Interfacial tension between benzene and water+ethanol, as a function of ethanol volume fraction in the aqueous phase at 20ºC .

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6.1.2.3. IFT between Mixture Aqueous Phase: Figure 6.7. shows the IFT between the NAPL mixture (benzene and toluene) and ethanol-water solution with respect to ethanol volume fraction in the aqueous phase. The content of the mixture NAPL was 50% toluene and benzene by mass. The IFT between mixture and pure water is 31.8 dyne/cm, slightly less than toluene and slightly more than benzene. Similar logarithmical decrease in the IFT of the system was observed, hence the effect of ethanol on the IFT between the mixture NAPL and aqueous phase was similar to the effect on toluene and benzene.

Figure 6.7. Interfacial tension between the NAPL mixture (toluene + benzene) and water+ethanol, as a function of ethanol volume fraction in the aqueous phase at 20°C

IFT decrease between the pure organic compounds (benzene, toluene) and water was very similar to each other with the increasing amount of ethanol. The mixture of these compounds at the same mass amounts gave no different IFT measurements either. However benzene gave slightly lower IFT measurements than toluene, which is not easily measured due to precision of the Ring method especially when the miscibility of the system increased with the high ethanol contents. Figure 6.8 depicts the resemblance of three different IFT curves.
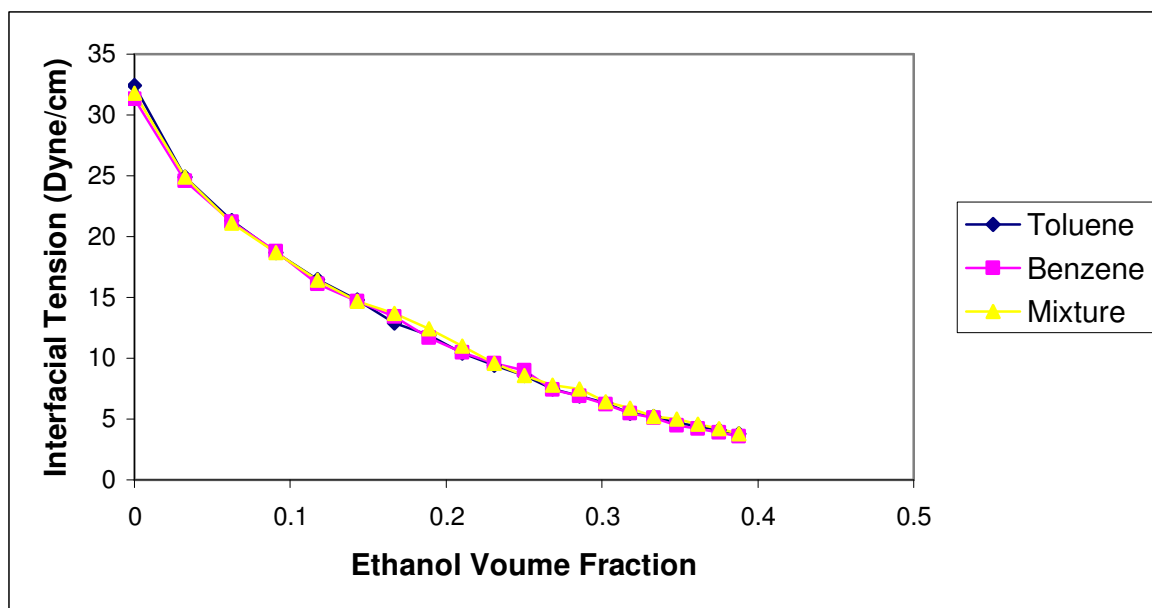
Figure 6.8. Comparison of IFT of Toluene, benzene and the mixture of the two as a function of ethanol volume fraction in the aqueous phase at 20ºC .

### 6.1.3. Ternary Phase Diagrams

In the first stage of the experimentation miscibility curves for benzene, toluene and mixture were prepared. Due to temperature sensitivity of the experimental procedure, all three experiments were performed under same conditions and to overcome the evaporation effect vials were sealed with gas tight caps. The tie lines for benzene and toluene were obtained from literature data.

6.1.3.1. Ternary Diagram for Toluene-Ethanol-Water: The Ternary phase diagrams determined from the cloud point titration method for the toluene-ethanol-water system at 20ºC are shown in figure 6.9.a. The miscibility curve was constructed, starting from the two ends, (toluene and water) of the diagram, which enabled a better precision of the procedure. The diagrams are based on the mol fractions of the components. Figure 6.9.b. was obtained from the literature and includes the tie lines (Shaw, 1989). Comparison of the two ternary plots shows that the experimentally determined miscibility curve and that from Shaw (1989) are in good agreement. The tie lines having negative slopes in the second diagram indicates that there is a preferential partitioning of the alcohol into the aqueous phase.

For toluene flushing experiment, the ethanol mass content has been chosen as 50% (55% by volume) of the aqueous phase. This point is located in the "miscibility zone" and therefore mobility is dominant recovery mechanism as defined by Falta 1998.
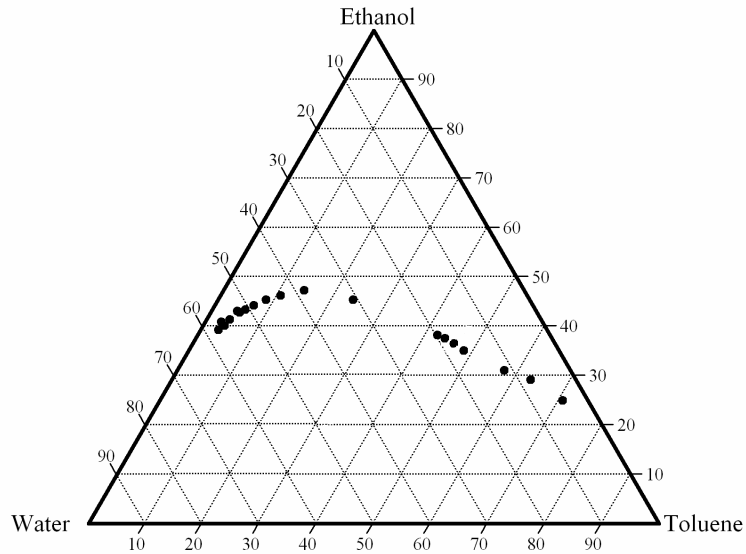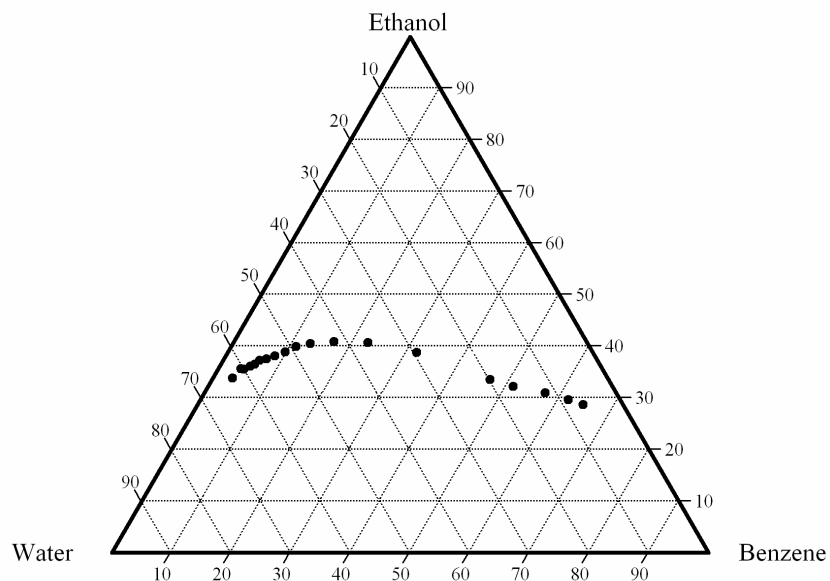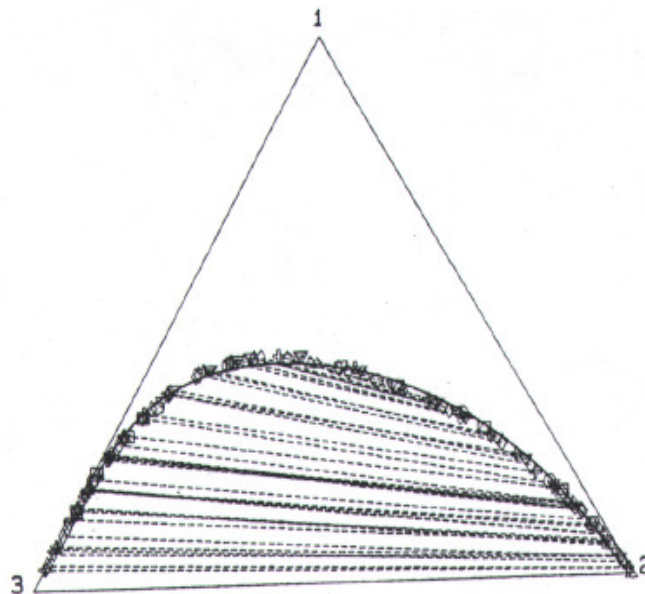


a)
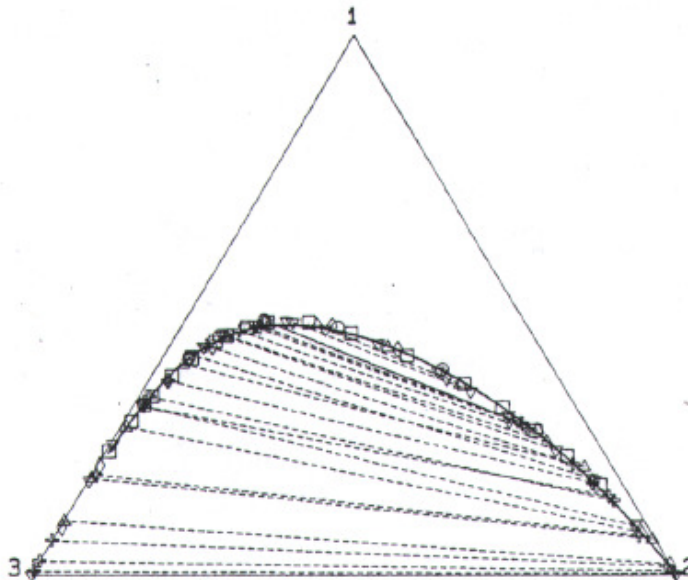


b)

Figure 6.9. a) Experimentally-determined miscibility curve for Toluene-ethanol-water system at 20ºC b) Miscibility curve for Toluene-ethanol-water system including the tie lines, data obtained from literature (Shaw, 1989).

6.1.3.2. Ternary Diagram for Benzene-Ethanol-Water: The experimentally-determined ternary phase diagram for the benzene-ethanol-water system is shown in Figure 6.10.a. The diagrams are based on the mol fractions of the components. Figure 6.11.b was obtained from literature and includes the tie lines (Shaw, 1989). The miscibility curve from the literature data is in good agreement with the experimental data.

For benzene flushing experiment, the ethanol mass content has been chosen as 50% (55% by volume) of the aqueous phase, which also refers to mobility dominated recovery based on the ternary diagrams. In comparison with the ternary diagram of toluene, the critical tie line extension of the benzene is at a slightly lower value, thus benzene is expected ot be recovered at a slightly greater rate than toluene.

a)



b)

Figure 6.10. a) Experimentally-determined miscibility curve for Benzene-ethanol-water system at 20ºC b) Miscibility curve for Benzene-ethanol-water system including the tie lines, data obtained from literature (Shaw, 1989).

6.1.3.3. Ternary Diagram for Mixture-Ethanol-Water: The experimentally-determined ternary phase diagram for the NAPL mixture (benzene + toluene)-ethanol-water system is shown in Figure 6.11. The diagram is based on the mol fractions of the components. The

molar mass of the mixture was assumed as the weighted average of the molar masses of the components. A similar ternary phase diagram is not found in the literature. However from the similarity of mixture phase diagram to the single NAPL (benzene or toluene), it can be assumed that the volume fraction of the flushing solution (55%) is above the critical tie line extension (in the "miscibility zone") hence the recovery mechanism will be dominated by mobilization.
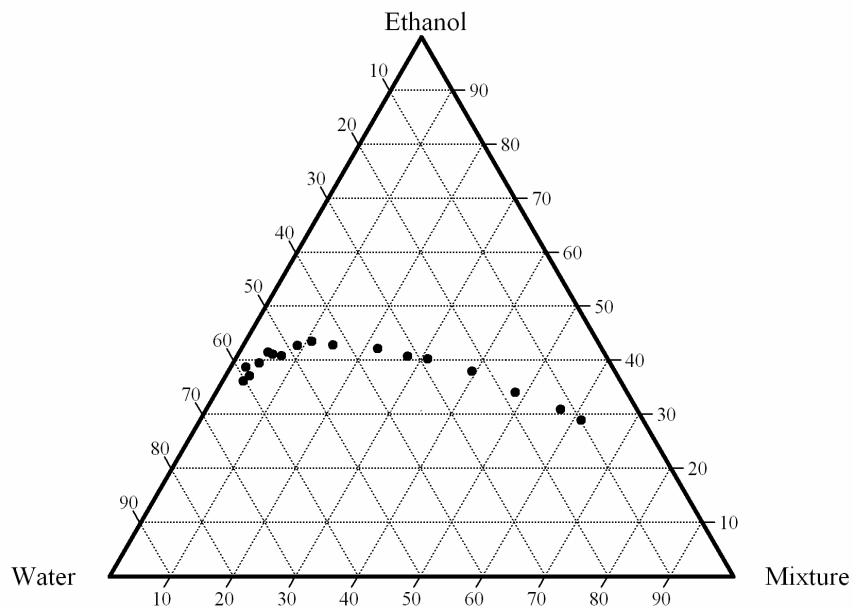


Figure 6.11 Miscibility curve for the NAPL Mixture-ethanol-water system at 20ºC

The ternary diagrams imply that in all flushing experiments mobilization will be the dominant recovery mechanism. However the enhanced solubility due to the presence of ethanol in the flushing solution may still be significant on the NAPL recovery efficiency. Because the IFT and ternary diagrams of all three NAPLs are close to each other, similar recovery due to mobility is expected in all three flushing experiments. The difference in recovery would be due to the difference in the enhanced solubility of the NAPL due to the presence of ethanol in the flushing solution.

### 6.1.4. Capillary, Bond and Trapping Number

The Capillary, Bond and Trapping non-dimensional numbers are useful tools for the evaluation of the mobility degree of NAPL in idealized flushing experiments. The trapping number is a combination of the capillary and bond numbers. The capillary number is the ratio of the viscous forces to capillary forces where as the bond number is the ratio of buoyancy forces to capillary forces. Mobilization of residual NAPL has been observed to occur for the range of trapping number between $2 \times 10^{-5}$ and $5 \times 10^{-5}$ (Pennell et al., 1996).

Due to the increased miscibility of the system IFT between HOC and the 50% ethanol-water solution could not be measured yet the IFT between NAPL and the aqueous solution containing 33% ethanol by mass, was measured as 3.8 for toluene and 3.6 for benzene. It is assumable that benzene would have a slightly lower IFT than toluene when the aqueous phase contains 50% ethanol by mass. Other parameters in the capillary and bond numbers are same for both benzene and toluene. Densities of toluene and benzene are 0.86g/ml, viscosity of the aqueous solution containing 50% ethanol by mass is 1.069 centipoise, the relative permeability is assumed to be about 0.9. The intrinsic permeability of the clean sand was measured previously as 0.0000001 cm². Contact angles at the interphase are also same. Below is the graph of Trapping number with respect to increasing amount of ethanol in the system. The graph was developed till 33% ethanol by mass (corresponding to 38% by volume), since the IFT could not be measured reliably for higher ethanol contents.
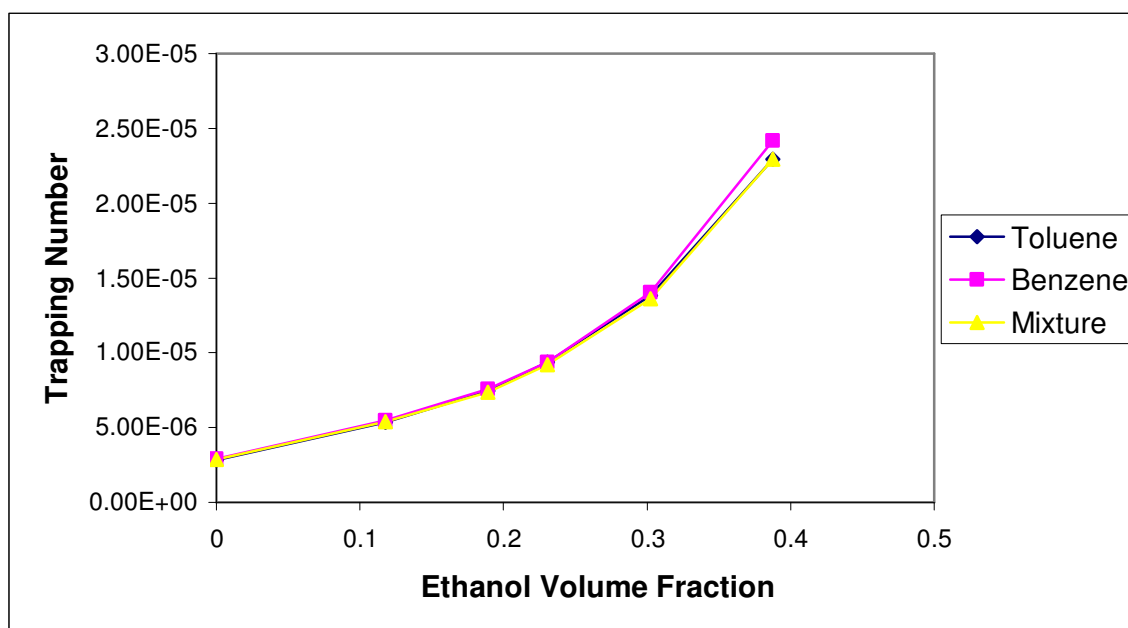
Figure 6.12 .Trapping Number with respect to volume fraction of ethanol in the flushing solution.

For benzene, toluene and mixture the trapping number, which is a measure of mobility, seems similar. Benzene shows slightly greater Trapping numbers, due to its lower IFT in comparison with toluene and mixture yet this difference is not significant.

**6.1.5. Flushing Experiments**

First two experiments were performed with toluene and benzene where as the third one was with a mixture of benzene and toluene at the same mass amounts. In all experiments, the content of the flushing solution was in the miscibility zone. The temperature kept constant at 20ºC degrees for all three experiments.

6.1.5.1. Toluene Flushing Experiment: 10 gram of toluene was introduced into sand column which had been saturated with deionized water for 1 day prior to experiment with a flow rate less than 1 ml/min. The toluene was injected from the bottom end of the column. After the injection of toluene, the column was flushed with water-ethanol solution containing 50% ethanol by mass. At the end of first pore volume, the flow rate decreased for several minutes when the free phase toluene first started to arrive to the top end. This

decrease continued no more then 5 minutes and the flow rate turned into normal conditions.

The free phase toluene started to migrate immediately after the start of the flushing procedure. This free-phase or "bank" movement was visible particularly in the first half length of the column because the NAPL was dyed red prior to injection. Beyond that point no more toluene mobility was visualized through the glass column. However the effluent continued to contain free phase toluene, which implies that the small toluene blobs that can't be visualized through naked eye, were still moving towards the top end of the column. The effluent concentration of the toluene is given in Figure 6.13.a as a function of the volume of flushing solution injected into the system. The pore volume inside the column is estimated to be about 200 ml. The cumulative toluene removal as a function of volume is presented in Figure 6.13.b.
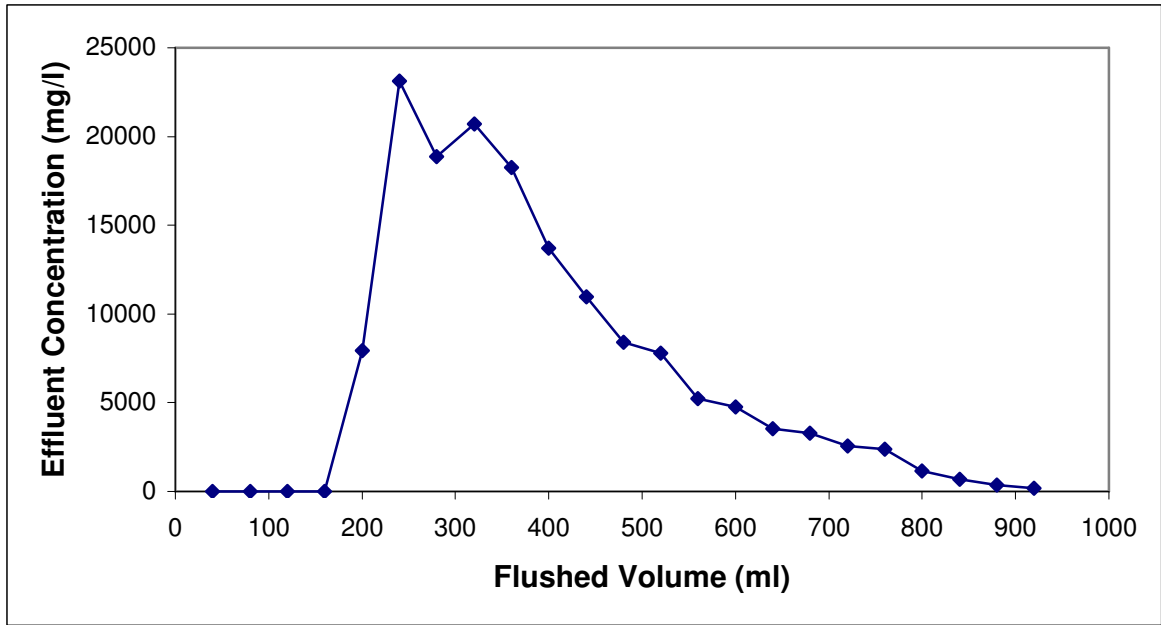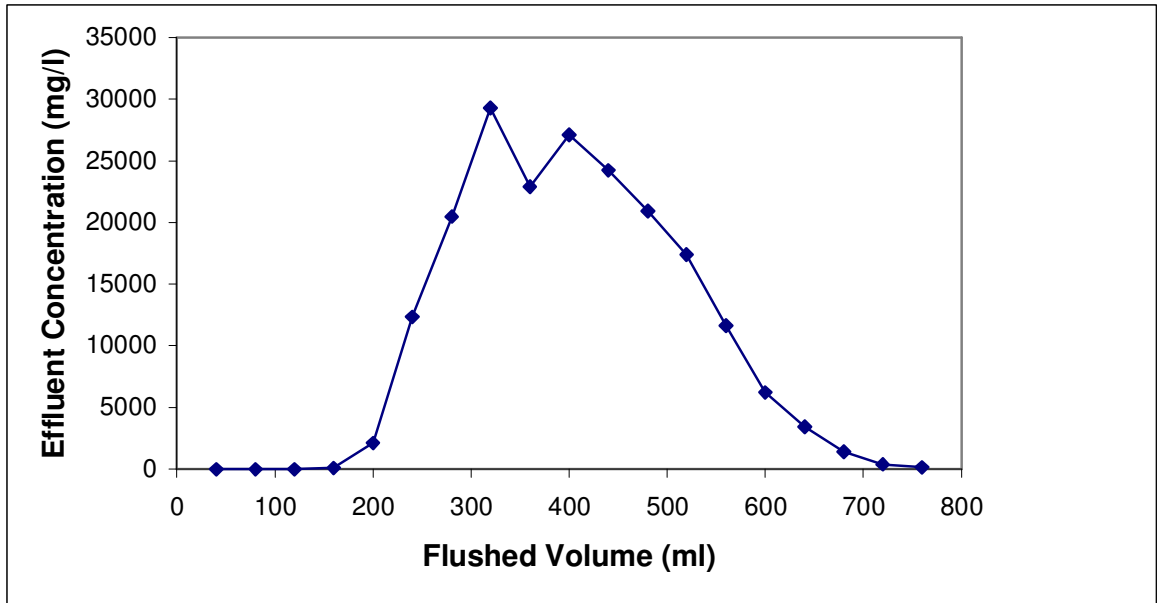
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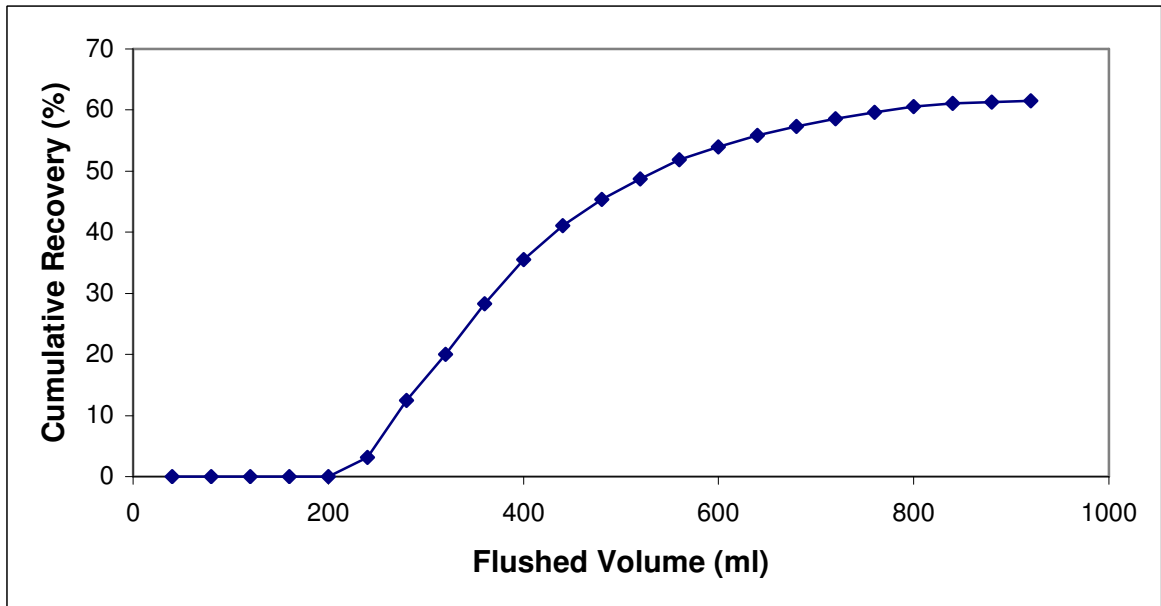


b

Figure 6.13. a) Effluent toluene concentration b) and cumulative toluene recovery due to flushing with a 50 % ethanol solution at 20ºC

The effluent color and transparency changed with in the end of the first pore volume. This was an indication of the arrival of the free phase toluene. The cloudy effluent arriving at the 180 ml vial was an indication of the dispersion in the column that ethanol migrated into column depths and drive out free phase toluene before all the water left the system. The GC analysis verified that the greatest toluene recovery was observe just after
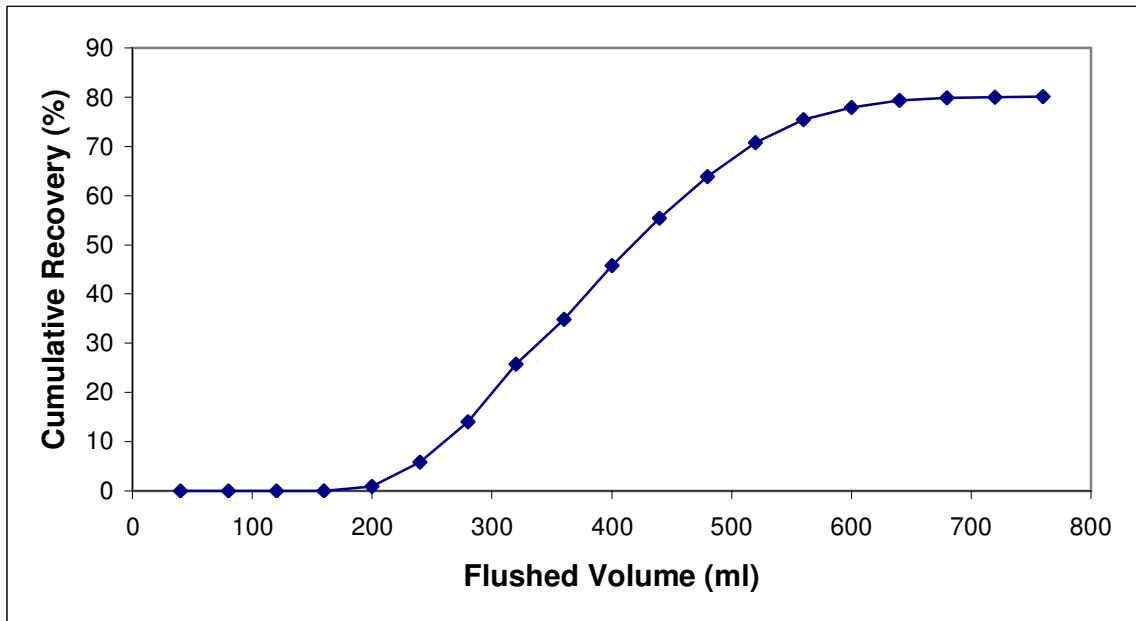
the first pore volume, which was also detected as free phase toluene in the effluent vials by the naked eye. The peak concentration observed in the effluent vials was approximately 23000 mg/l. The recovery rate of toluene after 900 ml of flushing was 61%. The steady line obtained at the beginning of $5^{th}$ pore volume at 61% recovery, is due to the mass transfer limitations encountered in the column.

6.1.5.2. Benzene Flushing Experiment: 10 gram of benzene was introduced into sand column which had been saturated with deionized water for 1 day prior to experiment with a flow rate less than 1 ml/min. The benzene was injected from the bottom end of the column. After the injection of Benzene, the column was flushed with water-ethanol solution containing 50% ethanol by mass.

As it was also observed in toluene experiment, the free phase benzene started to migrate immediately after the initiation of the flushing procedure and detected by naked eye till the half length of the column was reached. The free phase benzene continued to be seen at the effluent end for 1 more pore volume. The effluent concentration of the benzene is given in Figure 6.14.a as a function of the volume of the flushing solution injected into the column. Figure 6.14.b shows the cumulative benzene removal as a function of the volume of the flushing solution.

a



b

Figure 6.14. a) Effluent toluene concentration b) and cumulative toluene recovery due to flushing with a 50 % ethanol solution at 20ºC.

As in the toluene flushing experiment the effluent color and transparency has changed at the end of the first pore volume (about 190 ml). The cloudy effluent arriving at 180 ml vial, implied that some fingering of flushing solution similar to toluene experiment, was observed. The GC analysis verified that the greatest benzene recovery was performed in the middle of the second pore volume, which was also detected as free phase toluene in

the effluent vials by naked eye. The highest concentration observed in the effluent vials was around 29000 mg/l. The recovery rate of toluene after 800 ml of flushing was 80%. The steady line obtained at the end of 4th pore volume at 80%, is due to mass transfer limitations encountered in the column. The steady line in benzene experiment was observed at 800 ml vial. However in the toluene flushing experiment this steady line was at 900 ml vial.

6.1.5.3. Mixture Flushing Experiment: A mixture of 5 gram benzene and 5 gram toluene was introduced into the sand column which had been saturated with deionized water for 1 day prior to experiment with a flow rate less than 1 ml/min. The mixture was injected from the bottom end of the column. After the injection of mixture, the column was flushed with water-ethanol solution containing 50% ethanol by mass. The delay similar to toluene and benzene experiments after the initiation of the experiment was also observed.

Similar to the two earlier experiments, the free phase mixture started to migrate immediately after the initiation of the flushing procedure and detected by naked eye till the half length of the column was reached. The free phase mixture continued to be seen at the effluent end for 1 more pore volume. The cumulative benzene and toluene removal in mixture is given in Figure 6.15.a with respect to volume of the flushing solution passed through the system and the effluent concentration of the benzene and toluene is presented in Figure 6.15.b.
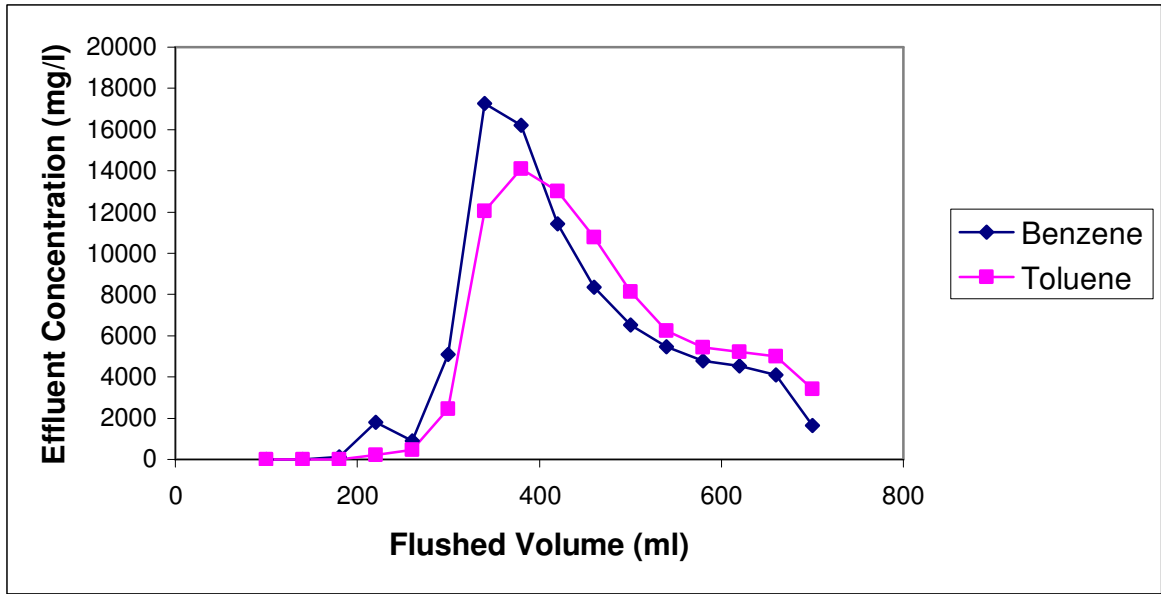
a
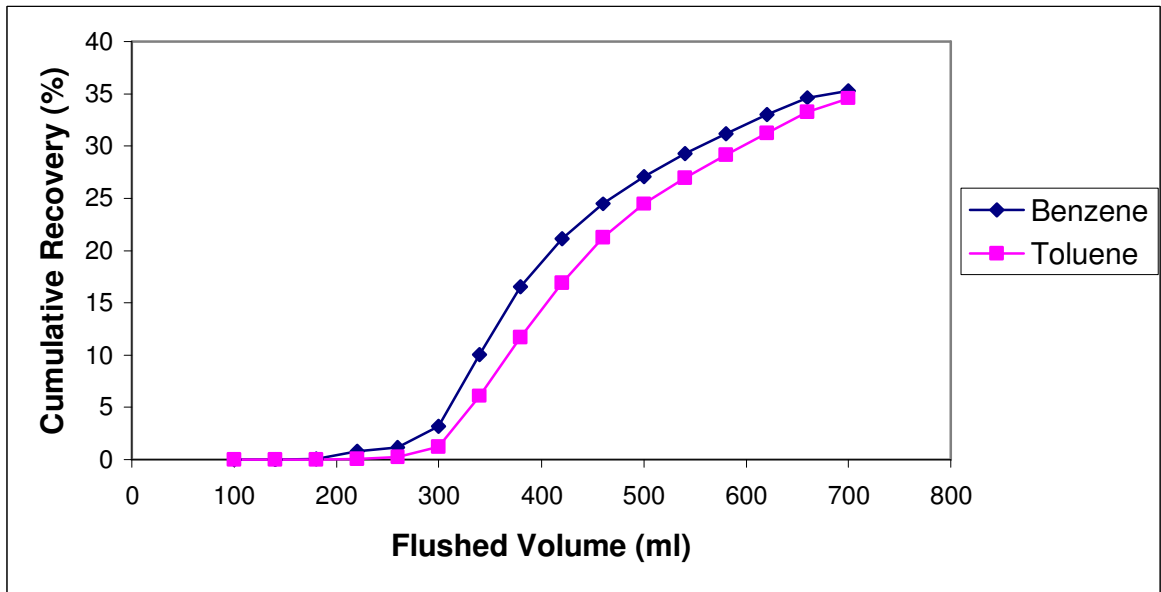


b

Figure 6.15. a) Effluent toluene and benzene concentration (mixture) b) and cumulative toluene recovery due to flushing with a 50 % ethanol solution at 20ºC.

The effluent color and transparency has changed with at the end of the first pore volume similar to earlier experiments. If the only mechanism was mobility the two curves should be close to each other. However at the initiation of flushing experiment, benzene was recovered at a greater rate than toluene. As the flushing experiment progressed and right after the peak concentrations were attained, toluene started to get recovered at a greater rate. The possible explanation is that at the beginning of the experiment benzene,

having a greater mol fraction in the mixture and the greater solubility, was recovered at a greater rate but with the progress of the experiment toluene mol fraction was raised due to depletion of benzene and toluene concentration in the vials exceeded benzene.

From the preceding studies it is known that due to mass transfer limitations, equilibrium solubility levels obtained from batch experiments or using Yalkowsky's model can not be achieved in the flushing procedures (Aydin et al., 2008, Van Valkenburg and Annable, 2002, Lunn and Kueper, 1999b). More precisely; depending on the flow rates and soil type, sufficient contact between the NAPL and the injected flushing solution may not be sufficient to reach equilibrium conditions. However, if the flushing solution also causes the NAPL to be mobilized, the added mixing and contact time between the flushing solution and the NAPL may lead to enhanced solubility. In other words, mass transfer would be enhanced when mobility occurs. The cumulative recoveries of only toluene and only benzene flushing experiments were 61% and 80% respectively. The latest finding shows that this difference was due to increased dissolution of NAPLs when mobility comes into scene. Moreover, the earlier steady line obtained in only benzene flushing experiments in comparison with toluene, is due to this dissolution potential. The greater solubility levels of benzene made it possible that it was recovered at a greater recovery rate (%80) and earlier.

## 6.2. HPCD Enhanced Remediation

This section describes the batch and column experiments conducted to assess the effectiveness of HPCD for the recovery of NAPL benzene, toluene and a mixture of the two in the form of NAPL from media. The effect of system temperature on the recovered NAPL is also evaluated. Results of the batch experiments are presented first, followed by the results of the flushing experiment.
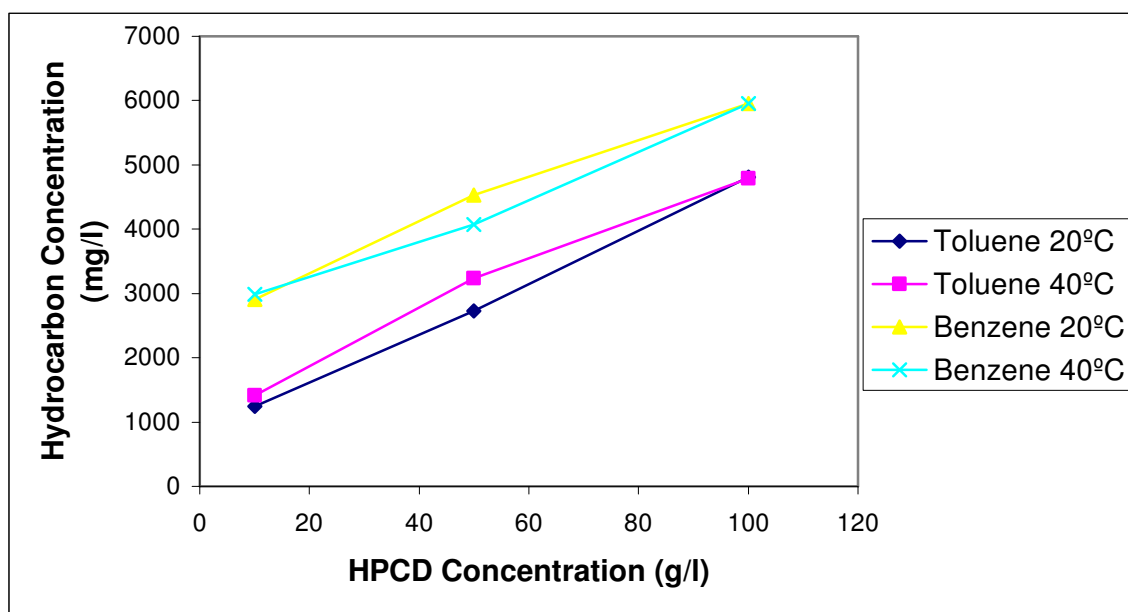
### 6.2.1. Solubility

Inclusion of hydrophobic organic compounds (HOC) in the cyclodextrin cavity brings about an increase in their aqueous solubility (Tanada et al., 1999). This is the

fundamental reason for the usage of cyclodextrin in the groundwater remediation and many other industrial and medical activities. The IFT between NAPL and aqueous solution is decreased with respect to HPCD amount in the aqueous solution however this reduction of IFT by HPCD is not enough to start mobilization of NAPL (Boving and McCray, 2000).

The possible alteration of the HOC solubility as a function of HPCD concentration in the solution and due to increase in temperature is investigated below. Data on the solubility of toluene and benzene in HPCD solution from the literature was not used due to their inconsistency with each other which also may be a result of different purity cyclodextrin usage by different researchers (Boving et al., 2000, Carroll et al., 2009, Tanada et al., 1999). However it is expected that the aqueous solubility of HOC would increase linearly with increase in HPCD concentration in the aqueous solution.

The solubility of benzene and toluene were measured for HPCD concentrations of 10 g/l, 50 g/l and 100g/l at 20 and 40ºC. The solubility of a mixture of the two HOCs (benzene and toluene, each 50% by mass) was also measured.

6.2.1.1. Solubility of HOC's: Figure 6.16.a shows the solubility of toluene and benzene as a function of HPDC concentration at 20 and 40ºC. The results show a linear increase with HPDC concentration in the aqueous solution which is consistent with published data using HPDC (Caroll et al., 2009). Solubility of both NAPLs tend to increase with increase in HPCD concentration, however benzene had higher solubility than toluene. Moreover, for the range of temperatures considered here, heat did not have a significant impact on benzene and toluene solubility.

a
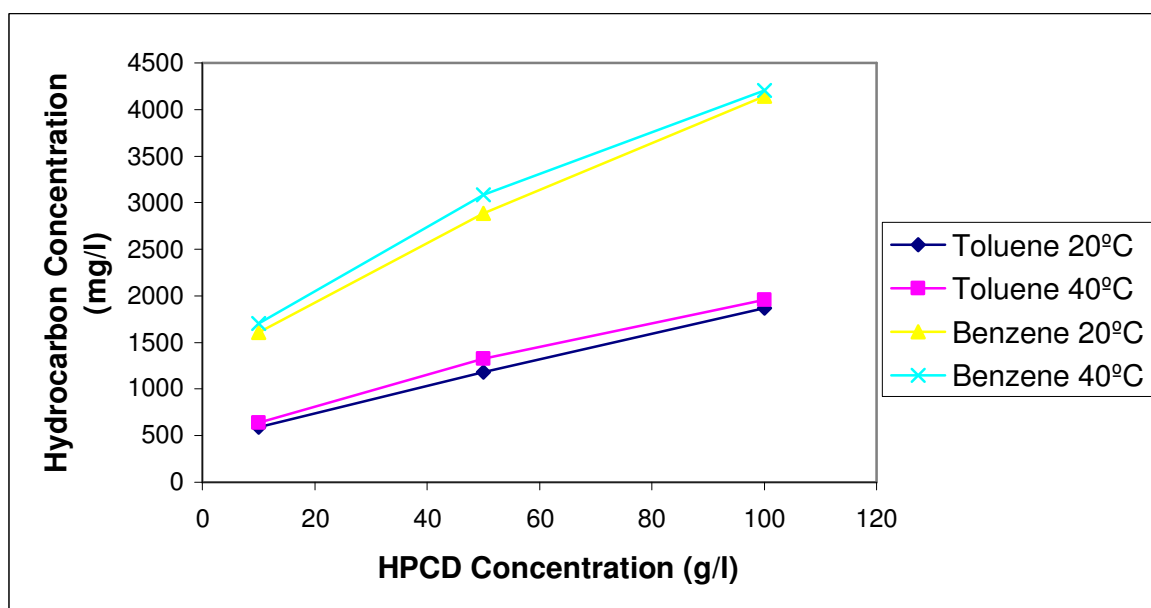


b

Figure 6.16 a) Solubility of benzene, toluene from pure NAPL b) Aqueous solubility of benzene, toluene from mixture NAPL as a function of HPCD concentration at 20 and 40ºC.

The results of the solubility experiment for a NAPL mixture consisting of benzene and toluene (each 50 % by mass) also showed a similar trend with HPCD concentration and temperature (Figure 6.16.b). The linear dependency of the solubility of the mixture on NAPL composition (by mole fraction) shows that Raoult's law is valid for a benzene/toluene NAPL in an HPCD solution. This has been also noted in a recently

published study is (Carroll et al., 2009). However, in this study the validity of Raoult's law was observed at both 20ºC and 40ºC.

All the above solubility results were observed after the samples were left to equilibrate in the reciprocating shaker for 72 hours (Wang et al., 1993). To evaluate the rate of dissolution at the two temperatures considered, the dissolved NAPL concentration were also measured after 48 hours. This experiment was only performed for the mixture NAPL. Figure 6.17 shows the observed aqueous concentrations at 48th hour as a function of HPCD concentration and temperature.
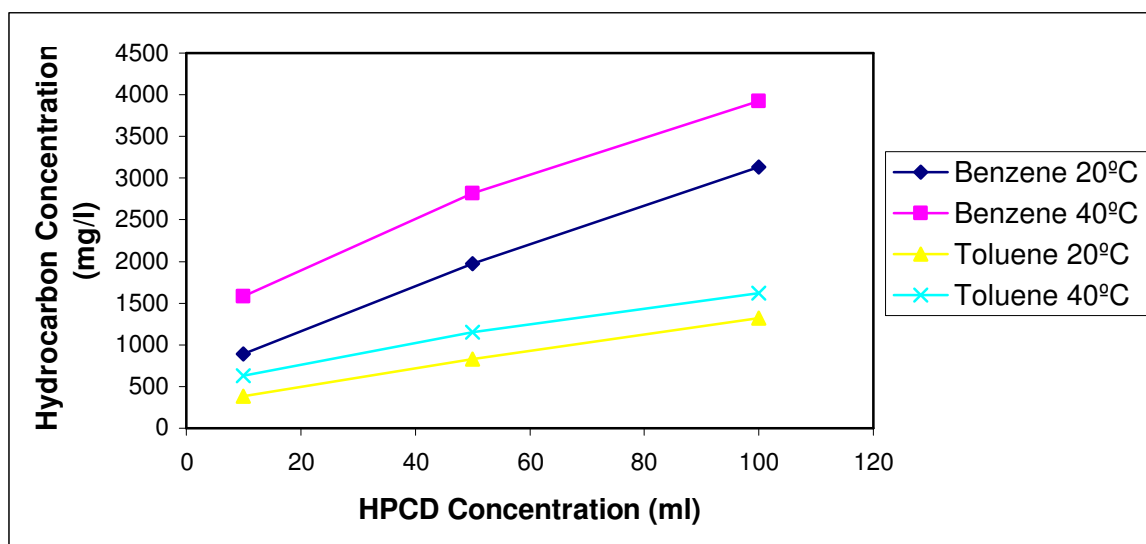


Figure 6.17. Solubility of benzene, toluene from mixture NAPL as a function of HPCD concentration at 20 and 40 $^{o}$C.

As it is observed from the graph above, there is a difference between the solubility of any HOC at different temperature. This is an indication of acceleration in the inclusion process by heat. By raising the temperature, the time needed to reach to equilibrium can be reduced. In the graph below, the concentration of toluene from mixture NAPL at different HPCD concentrations and different temperature depicted. The equilibrium solubility of toluene at 20ºC was also included for comparison.
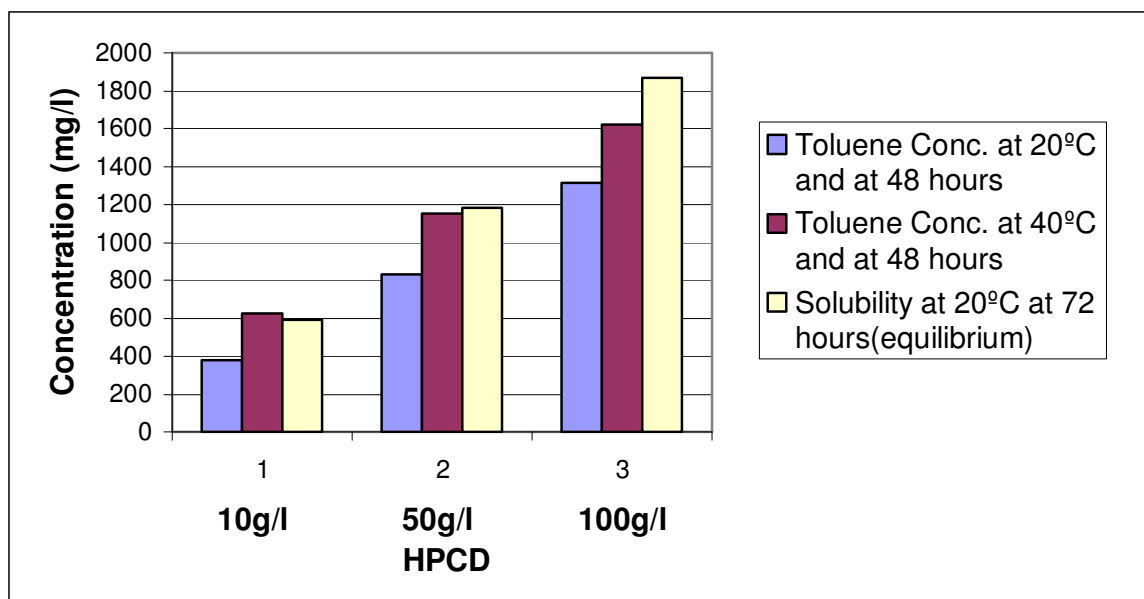
Figure 6.18. Concentration of toluene at different times and at different temperatures with respect to HPCD concentration.

With low concentration HPCD, the effect of heat on the inclusion velocity is more significant. In 48 hours and at 40ºC the equilibrium solubility of HOC was almost achieved in 50g/l HPCD solution, however with 100 g/l HPCD in 48 hours, the equilibrium solubility of HOC could not be attained.

The effect of heat on the dissolution is better pronounced in the graph below. All of the curves are of 100 g/l HPCD solution. At the end of 72 hours regardless the temperature, the concentrations become equal at the solubility level. However at 48th hour, the samples with higher temperature resulted in greater concentrations meaning that the dissolution process of organic contaminants in HPCD solution was faster for heated samples.
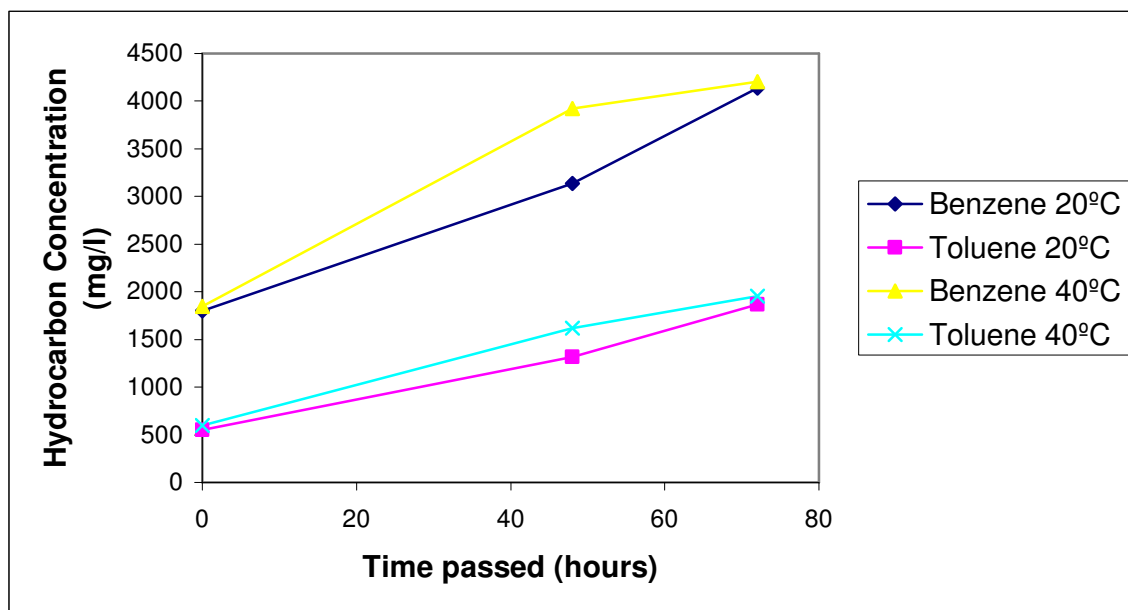
Figure 6.19. Concentration of toluene and benzene in HPCD solution with respect .to time.

## 6.2.2. Flushing Experiments

This section presents the results of the four flushing experiments conducted to evaluate the efficiency of HPCD solution to recover benzene, toluene and mixture NAPL mass entrapped in the porous medium. The glass column was filled with sand having a porosity of 0.35. HOC was injected into the deionized water saturated column in the upward direction to have a homogenous distribution. Experiments were conducted with flushing solutions containing 50 g/l HPCD. To discard the effect of heterogeneity, the sand was compacted within every 2cm increment. The flow rate of the every experiment was kept uniform at 3.1 ml/min, corresponding to a groundwater velocity of 2.27 m/day.

The first two experiments were performed with pure NAPL (toluene, benzene) where as the third one was with a mixture of benzene and toluene at the same mass amounts. These three experiments were conducted at 20ºC .The fourth experiment was conducted with mixture NAPL at a temperature of 40ºC.

6.2.2.1. Toluene Flushing Experiment: 10 gram of toluene was introduced into sand column which had been saturated with deionized water for 1 day prior to experiment with a flow rate less than 1 ml/min. The NAPL toluene was injected from the bottom end of the

column. After the injection of toluene, the column was flushed with 50g/l HPCD solution. No migration of toluene was visually detected. The effluent vials did not contain any free phase toluene either. The GC-headspace analyses were done immediately after the flushing experiment. The column was flushed with 700 ml HPCD solution. After the depletion of the flushing solution, column was flushed with 100 ml of deionized water. Figure 6.20. shows the effluent concentration as a function of the volume of the flushing solution passed through the system.
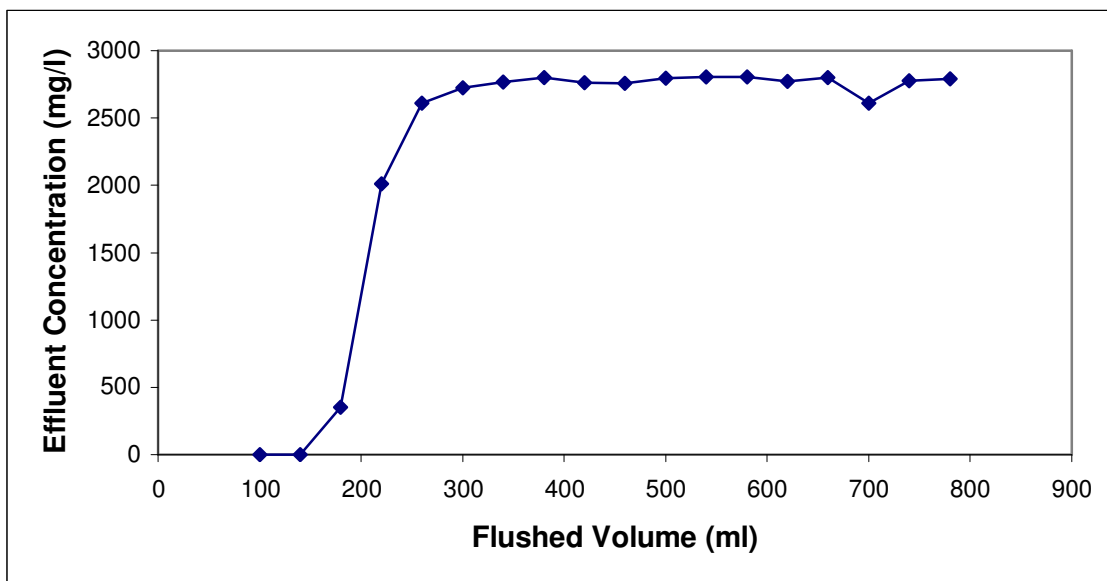


Figure 6.20. Toluene concentration as a function of flushing volume at 20ºC and for an HPCD concentration of 50 g/l.

The graph above indicates that as expected no mobilization of free phase toluene occurred. The shape of the curve corresponds to a continuous NAPL dissolution. Toluene arrival to the top end of the column at 180 ml vial is a sign of the dispersion in the column. The steady state was achieved in the middle of second pore volume. The peak concentrations in the vials, attained in the steady state were around 2700mg/l. From the solubility experiments, it is known that the equilibrium solubility of toluene in 50g/l HPCD solution was 2726 mg/l, which suggests that the equilibrium was achieved within the column at this flow rate and at this temperature.

6.2.2.2. Benzene Flushing Experiment: 10 gram of NAPL benzene was introduced into sand column which had been saturated with deionized water for 1 day prior to experiment

with a flow rate less than 1 ml/min. The NAPL benzene was injected from the bottom end of the column. After the injection of benzene, the column was flushed with 50g/l HPCD solution. No migration of Benzene was detected by naked eye. The effluent vials did not contain any free phase Benzene either. The GC-headspace analysis was done immediately after the flushing experiment. The column was flushed with 700 ml HPCD solution. After the depletion of the flushing solution, column was flushed with 100 ml of deionized water. Figure 6.21. shows the effluent concentration as a function of the volume of the flushing solution injected through the system.
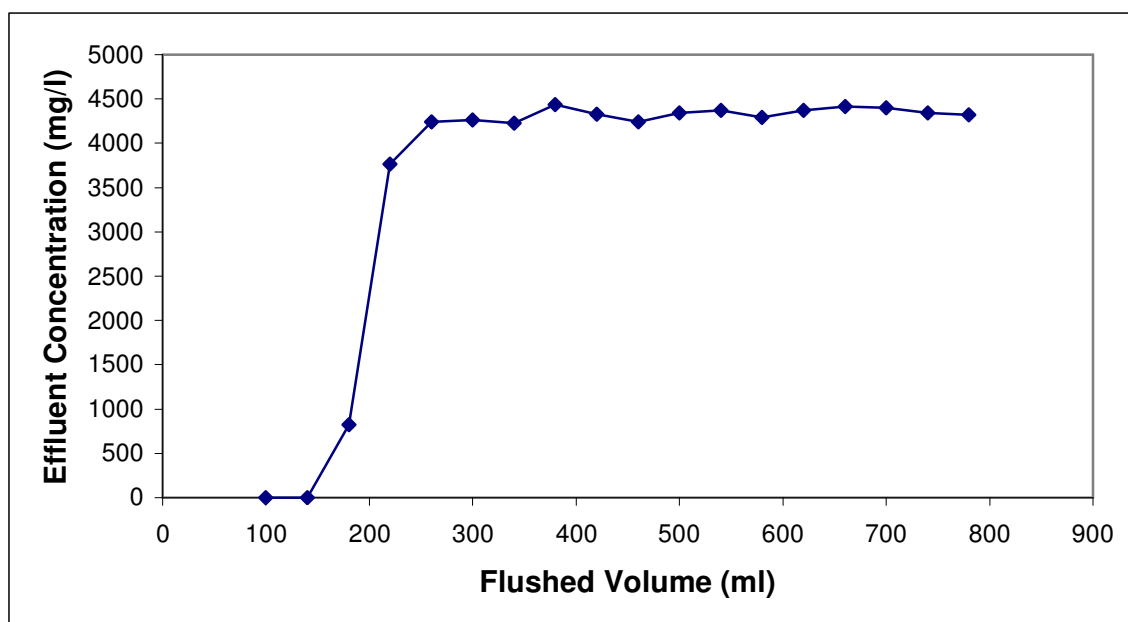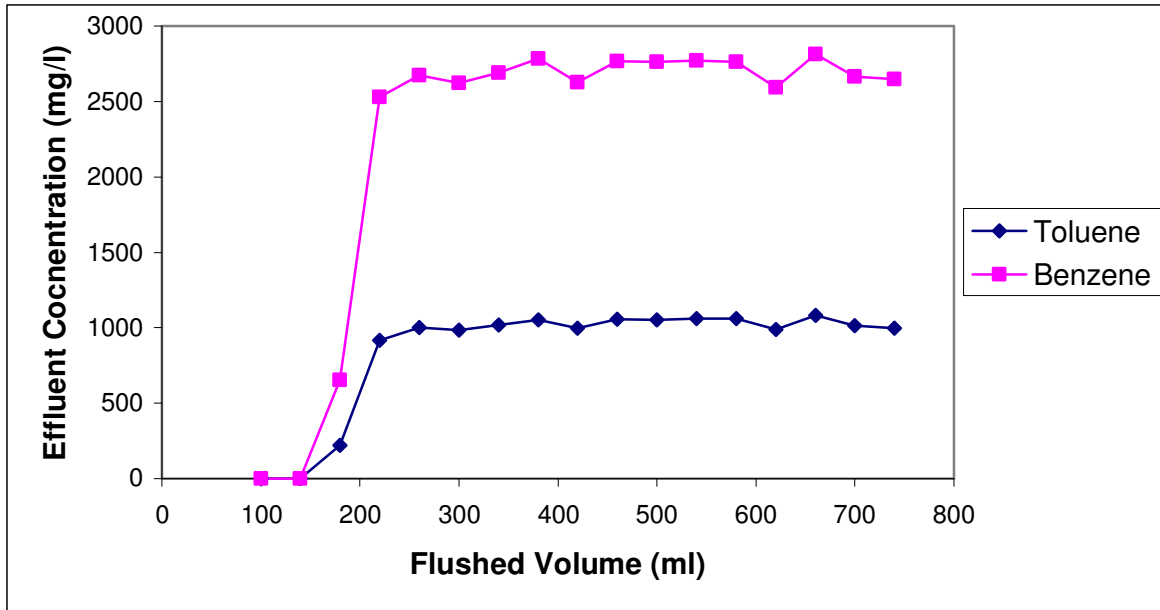


Figure 6.21. Benzene concentration as a function of flushing volume at 20ºC and for an HPCD concentration of 50 g/L.

From the graph above it is observed that there is no significant difference in the shape of the curves for the benzene and toluene flushing experiment. The shape of the curve is that of a "continuous dissolution" curve. Benzene arrived at the top end of the column at the 180 ml vial. The steady state was achieved in the middle of the second pore volume as in toluene experiment. The peak concentrations in the vials, attained in the steady state were around 4400mg/l. From the solubility experiments, it was observed that the equilibrium solubility of toluene in a 50g/l HPCD solution was 4500 mg/l, which suggests that the equilibrium was achieved within the column at this flow rate and at this temperature.

6.2.2.3. Mixture Flushing Experiment: The experiments involved mixture NAPL, were performed in 20ºC and 40ºC respectively. A NAPL mixture containing 5 grams of benzene and toluene was introduced into sand column which had been saturated with deionized water for 1 day prior to experiment with a flow rate less than 1 ml/min. The mixture NAPL was injected from the bottom end of the column. After the injection of mixture, the column was flushed with 50g/l HPCD solution. No migration of mixture NAPL was detected by naked eye. The effluent vials did not contain any free phase mixture either. The GC-headspace analysis was done immediately after the flushing experiment. The column was flushed with 700 ml HPCD solution. After the depletion of the flushing solution, column was flushed with 100 ml of deionized water. The effluent concentration at 20ºC is given in Figure 6.22.a. with respect to volume of the flushing solution passed through the column. The same graph for 40ºC experiment is presented in Figure 6.22.b.

a
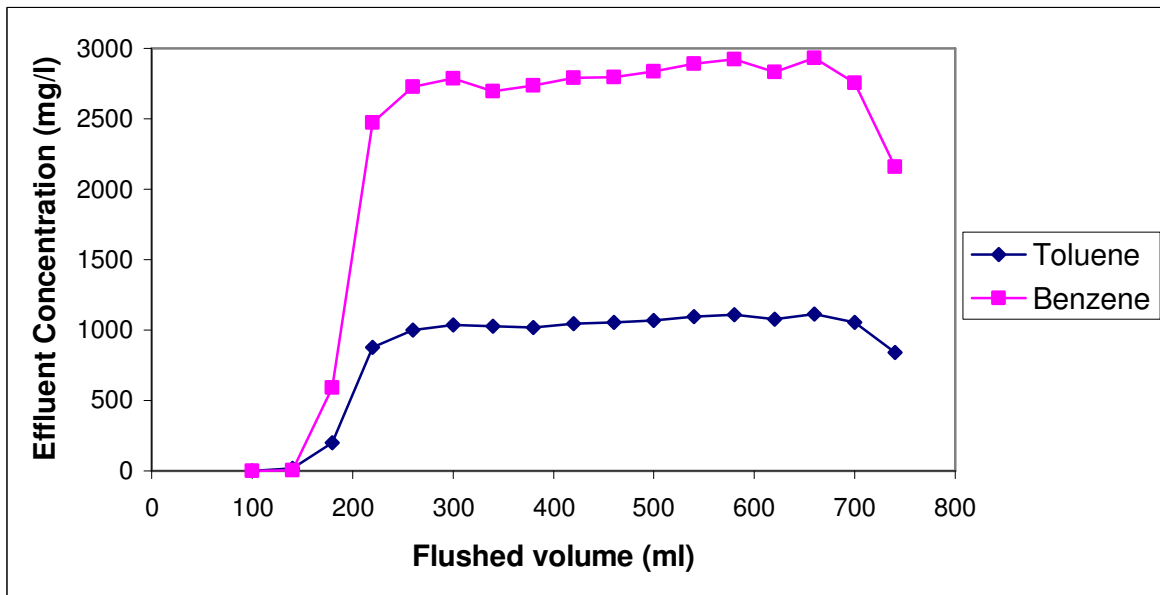


b

Figure 6.22. Toluene and benzene concentration as a function of flushing volume for an HPCD concentration of 50 mg/L at 8 a) 20ºC and (b) 40ºC

Both experiments involving mixture NAPL at 20ºC and 40ºC gave similar results to earlier experiments. The shape of the both curves obtained from 20ºC and 40ºC experiments are same as "continues dissolution" curve. The similar dispersion effect was observed at 20ºC experiment. However the concentration at 40ºC experiment started to rise earlier than other experiments and dropped at the last 50 ml. At the last 100 ml of the experiment, pure water was pumped in all experiments. This did not make any difference

in the concentration since the pore volume of the column is approximately 190 ml. However the experiment conducted at 40ºC was effected from that pure water most probably due to increased dispersion in the column by the raised temperature. The increased temperature resulted in more mixing of aquifer fluids. A part from that, the steady state concentrations were identical for both temperatures. Benzene reached a concentration around 2800mg/l at both temperatures where as toluene reached around 1100 mg/l. These concentrations are close to the effective equilibrium solubility levels of toluene and benzene as defined by Raoult's law.

# 7. FINAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

This study examines the use of two agents, ethanol and HPCD, for the enhanced remediation of groundwater contaminated with non-aqueous phase liquids. Within the scope of this work several experiments, including batch and column, were conducted to evaluate the contribution of the different transport mechanism encountered during ethanol enhanced groundwater remediation and to investigate the effect of heat on Hydroxypropyl-beta-cyclodextrin (HPCD) enhanced remediation. The main outcomes of the study are discussed below.

## 7.1. Ethanol Enhanced Remediation

This study shows that for a 50% ethanol content by volume in the flushing solution, mobility is the dominant recovery mechanism for NAPL toluene, benzene and NAPL mixtures consisting of benzene and toluene.

Results of the solubility batch experiments show that the concentration of benzene, toluene and the mixtures of both is consistent with Raoult's law which indicates that the solubility of the NAPLs is linearly related to the composition of the NAPL and consistent with the Yalkowsky cosolvency model which expresses the log of the solubility as a linear function of the ethanol content in the flushing solution.

Moreover, for NAPLs consisting of both toluene and benzene, the concentration of benzene in the effluent is higher at early times than that of toluene due to the higher solubility of benzene. With time this would lead to an increase of the toluene fraction in the NAPL which would lead to an increase in the effluent toluene concentrations at latter times.

While the mobility and dissolution processes are generally considered to be independent of each other, the flushing experiments conducted in this experiment show

that the presence of mobility increases the mixing of the NAPL with the flushing solution which in turn increases the mass transfer rate leading to enhanced NAPL solubilization in the flushing solution.

The results of this study have potential implications on the transport of fuels containing ethanol (gasoline etc.). The possible leakage of these fuels to subsurface is encountered through out the whole world. Based on the outcome of this study, it is conceived that the contamination levels of groundwater from a gasoline leakage may increase to levels of g/l from mg/l when the ethanol content of the gasoline is further increased by manufacturers.

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## 7.2. HPCD Enhanced Remediation

The second part of this research involves the use of an HPCD solution for the flushing of a benzene, toluene and NAPL mixtures from porous media. The impact of the use of heat in conjunction with the HPCD was also evaluated. A recent study showed that the effect of heat may be very influential on the alcohol (ethanol) enhanced remedial activities effecting both dissolution and mobilization mechanisms (Aydin et al., 2008). However temperature is found to be less significant for HPCD in comparison with cosolvents such as alcohols etc.

Although the results of this study indicated that a rise in the temperature of the environment does not increase the solubility of organic compounds in HPCD solutions, further analyses revealed that the inclusion process of the organic contaminants in the HPCD molecule is accelerated by application of heat. The time needed for the equilibrium is found to be less for heated environments. In other words; the solubility is attained faster when the fluids are heated. Another finding of the study was the increased dispersion, encountered in the porous media with application of heat.

When the residual NAPL is uniformly distributed in the porous media, the solubility of the organic contaminants in HPCD solution is achieved regardless of the environmental conditions (Bizzigotti et al., 1997). However due to soil heterogeneity and

as the remedial activity progresses, NAPL distribution would be spatially variable. . This non-uniformity can decrease the dissolution of the NAPL in HPCD solution due to less contact areas between the NAPL and the flushing solution. Application of heat can potentially reduce this effect and help maintain the dissolved concentration at higher levels.

## 7.3. Recommendations for Future Studies

Based on the experimental work conducted in this study, future investigations may be directed in the following issues;

- The effect of heterogeneity on the NAPL recovery: While the current study considered fairly uniform sand, NAPL movement is strongly influenced by the heterogeneity of the soil. Future studies could consider the impact of heterogeneity which would give a more accurate assessment of the conditions present in the field.

- 2-D and 3-D experiments: For a better representation of field cases including buoyancy effects, 2-D and 3-D experiments could be conducted.

- Effects of other parameters (salinity etc.) in HPCD enhanced remediation: The chemical content of the groundwater may interfere with the solubility of the NAPLs in HPCD.

- Effect of heat on other chemical agents (such as; chemical oxidants): The current study considered the effect of heat on the dissolution rate of the NAPL in the presence of HPCD. The impact of system temperature could be extended to other agents and other recovery processes.

- Modeling of enhanced remediation: Development of numerical models for enhanced recovery schemes may be helpful in the assessment of field applications prior to remediation.

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