

SOLUBILIZATION OF VOLATILE ORGANIC COMPOUNDS IN EDIBLE NONIONIC SURFACTANTS

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by

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ABSTRACT

Volatile Organic Compounds (VOCs) are major subsurface contaminants and exist as Non-Aqueous Phase Liquids (NAPLs) in the subsurface. Pump-and-treat remediation is the most common technology used to remediate contaminated groundwater. However, experience has revealed that the traditional pump-and-treat remediation is impractical for treating NAPLs in the subsurface, especially for dense NAPLs (DNAPLs). The difficult desorption of highly hydrophobic compounds and the inability to dissolve residual saturation are the major limiting factors for traditional pump-and-treat remediation. Different chemicals have been used to enhance traditional pump-and-treat remediation. Surfactant enhanced subsurface remediation is identified as a promising technology. In situ Surfactant-Enhanced Subsurface Remediation (SESR) was developed to improve removal efficiency by surfactant solubilization (formation of micelles) and mobilization (reduction in the interfacial tension between the NAPLs and groundwater). The solubilization efficiency of VOCs in an edible surfactant system is very important for the implementation of SESR. The micelle-water partition coefficient (K_m) is one of the key parameters to describe the solubilization efficiency of insoluble or sparingly soluble organic compounds in the micelles.

A headspace auto-sampler and gas chromatography system was used to test the solubilization of benzene, toluene and TCE in edible nonionic surfactants (Tween 20 and Tween 80 which are mono-fatty acid esters of polyoxyethylene sorbitan) by a modification of the EPICS (Equilibrium Partitioning In Closed Systems) method.

Benzene and toluene were used to represent light NAPLS (LNAPLs) and TCE was chosen to represent DNAPL. Preliminary tests were conducted to determine the equilibration time required for the partitioning of selected VOCs among the aqueous, micellar, and gaseous phases. Different surfactant concentrations (Tween 20 at concentrations of 330mg/L, 3300mg/L, and 13200mg/L, and Tween 80 at concentrations of 749mg/L and 3210mg/L) were used to investigate the solubilization. The fraction of VOCs partitioned into micelle, f_m , was proportional to the surfactant concentration. The micelle-water partition coefficient, K_m , for benzene was 1823.4 ± 8.5 in Tween 20 solutions and 2650.4 ± 36.6 in Tween 80 solutions. K_m for toluene was 5755.4 ± 21.8 in Tween 20 solutions and 8780.4 ± 14.1 in Tween 80 solutions. K_m for TCE was 4710.5 ± 6.7 in Tween 20 solutions and 6634.0 ± 33.0 in Tween 80 solutions. Experimental results show that Tween 80 micelles have more solubilizing capacity than Tween 20 micelles for benzene, toluene and TCE. Results also show that K_m increased as the hydrophobicity of the contaminant increased (benzene, TCE, toluene).

The effect of temperature on solubilization was studied for these three typical VOCs in 13200mg/L Tween 20 solution and 3210mg/L Tween 80 solution. 5°C, 10°C, 15°C, and 20°C were chosen to represent the subsurface temperature range. Experimental results show that more VOCs partitioned into the headspace from the aqueous phase with an increase of temperature. It is also shown that there is little change of f_m and only a slight increase of K_m with temperature. It is likely this is because the selected temperature range was much lower than the cloud point (the temperature at

which micellar solution appears turbid), and therefore the enlargement of micelle size caused by an increase in temperature was not apparent.

The effect of ionic strength on the solubilization of benzene, toluene and TCE in 13200mg/L Tween 20 solution and 3210mg/L Tween 80 solution was studied in 0.1M, 0.3M, 0.5M and 0.64M of NaCl solutions. A concentration of 0.64M of NaCl was chosen to simulate seawater. The temperature for the ionic strength effect tests was controlled at 20°C. Experimental results show that more VOCs partitioned into the headspace and micellar phase from the aqueous phase with the increase of ionic strength. It is also shown that f_m and K_m increased with ionic strength. It is likely this is because the addition of electrolytes to nonionic surfactant solutions (Tween 20 and Tween 80) causes an increase in the aggregation number of the micelles.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Volatile organic compounds (VOCs) have a tendency to migrate or diffuse from water (aqueous phase) into air (gaseous phase) until equilibrium under normal environmental conditions (Ram et al., 1990). VOCs are major surface and subsurface (including soil, sediment and groundwater) contaminants. They have caused pervasive pollution problems around the world since an immense quantity of synthetic organic compounds has been used in industrial and household applications over the last several decades. Because subsurface elements (such as soil, sediment and groundwater) are hidden from view and hard to access, and the behavior of contaminants introduced to the subsurface is complicated and not clear, remediation of the subsurface environment is a formidable challenge. This challenge has evoked intensive studies of the mobility and the fate of these contaminants in subsurface environments and of their remediation potential.

Pump-and-treat remediation is the most common technology used to cleanup contaminated groundwater. But the immiscibility with water of most organic contaminants, especially chlorinated hydrocarbons and highly hydrophobic compounds (e.g., PCBs, PAHs), results in their occurrence in the subsurface as residual (trapped) Non-Aqueous Phase Liquids (NAPLs). Remediation of residual saturation (a portion retained within the soil pores as immobile globules/ganglia) of a Dense Non-Aqueous

Phase Liquid (DNAPL) using conventional pump-and-treat method can require hundreds to thousands of pore volumes of water or more (depending on the DNAPL) to be pumped. Keeley (1989) discussed factors limiting pump-and-treat remediation, including the desorption of contaminants from media surfaces and the dissolution of trapped immiscible phases. Haley et al. (1991) summarized 19 systems for effective groundwater remediation, and also listed the sorption of organics and the presence of residual NAPL saturation as major limiting factors in remediation. Experience has shown that the desorption of highly hydrophobic compounds and the dissolution of residual saturation are the major limiting factors for the conventional pump-and-treat approach.

Palmer and Fish (1992) used different chemicals to enhance conventional pump-and-treat remediation. These included complexing agents, cosolvents, surfactant enhanced solubilization and mobilization (microemulsification), oxidation-reduction agents, precipitation-dissolution reagents, and ionization reagents. U.S.EPA (1992) enumerated the benefits and limitations of various technologies for remediation of subsurface DNAPL contamination and identified surfactant enhanced subsurface remediation as a promising technology.

Surfactant Enhanced Subsurface Remediation (SESR) focuses on increasing the efficiency of conventional pump-and-treat remediation. The pseudo-hydrophobic sink provided by surfactant micelles (colloidal aggregates) can significantly increase the solubility of insoluble or sparingly water-soluble contaminants and overcome the mass transfer limitations of conventional pump-and-treat remediation. Solubilization can

enhance the desorption of highly hydrophobic contaminants and the dissolution of residual saturation. Mobilization (microemulsification) can enhance the extraction of residual saturation because the interfacial tension becomes negligible and the solubility is increased. Thus, both solubilization and mobilization caused by surfactant micelles can significantly enhance the efficiency of contaminant extraction.

Many researchers have investigated the application and efficiency of surfactant systems. Vignon and Rubin (1989) used alkyl and alkylphenyl ethoxylated surfactants to solubilize sorbed anthracene and biphenyl. Abdul et al. (1990) observed that the recovery rate increased from 23%, by washing automatic transmission fluid in sand with water alone, to 80% by washing with ethoxylated alcohol surfactants. Valsaraj and Thibodeaux (1989) evaluated the partition coefficients for sodium dodecyl sulfate (an ionic surfactant) and eleven hydrophobic nonpolar organics, and observed a correlation between the hydrophobicity of the contaminant and the partition coefficient. Edwards et al. (1991, 1992) used alkyl and alkylphenyl ethoxylated surfactants (nonionic surfactants) to enhance the solubility of polycyclic aromatic hydrocarbons (PAHs) and also observed a correlation between the partition coefficient and the contaminant hydrophobicity. West (1992) utilized the same surfactants for solubilization of chlorinated organics (PCE, TCE and 1,2-DCE) and observed a similar relationship between the micellar partition coefficient and the octanol-water partition coefficient, K_{ow} , of the compounds. Abdul et al. (1992) also conducted a field scale study to evaluate surfactant enhanced remediation of PCB contamination in the unsaturated zone. Fountain (1992) evaluated surfactant-enhanced remediation of chlorinated organics at two different field sites.

General application of surfactant enhanced subsurface remediation faces two major problems. First, regulatory approval for the injection of surfactants must be obtained. Regulators must be convinced the selected surfactants do not have any adverse effects on the environment or health. Second, the economics of the process are questionable since a large volume of surfactant will be needed.

To address the first problem, the use of U.S. Food and Drug Administration direct food additives should be the best approach. These edible surfactants are common in food products and other consumer goods. They would not cause further contamination when they are used for subsurface remediation and left as a residual in the subsurface. However, data are scarce on evaluation of the efficiency of edible surfactants for subsurface remediation.

To address the second problem, the use of less expensive surfactants and minimizing surfactant losses due to precipitation, adsorption, coacervate formation, or partitioning into residual phases should be considered (Scamehorn and Harwell, 1987; 1989). The technologies used to recover and reuse surfactant should also be studied and improved.

The solubilization efficiency of VOCs in a system with edible surfactants is very important for the implementation of a surfactant enhanced subsurface remediation program. However, little research has been done for edible surfactants. Therefore, the development of a practical and reliable method to determine solubilization efficiency,

i.e., the micelle-water partition coefficient, K_m , is required. An investigation of solubilization efficiency for different environment conditions, such as temperature, ionic strength, pH, competition with other compounds, is also necessary. In this research, only temperature effect and ionic strength effect will be investigated.

1.2 Research Objectives

The micelle-water partition coefficient, K_m , is an effective and common indicator of solubilization efficiency. The development of a practical and reliable method, using a headspace autosampler and gas chromatography system, to determine K_m of volatile organic contaminants in different surfactant systems is required. The effect of different environmental conditions on solubilization should also be studied.

The objectives of this research are listed as follows:

- (1) To develop a reliable analytical method, based on the headspace auto-sampler and gas chromatography system, to measure the micelle-water partition coefficient K_m of a volatile organic contaminant and surfactant system.

A mathematical model will be developed to predict the dynamic equilibrium of VOCs among gas, aqueous solution and micelles using mass balance, Henry's law and the micelle-water partition coefficient K_m . The equilibrium partition of VOCs between gaseous and aqueous phases, as well as among gaseous, aqueous and micellar phases is investigated in standard headspace sample vials. A headspace auto-sampler and gas chromatography system is used to measure the headspace

concentration of VOCs. An equilibration test is performed to determine the minimum time required for the full partitioning of VOCs between micellar and aqueous phases, and the partitioning between gaseous and aqueous phases to reach a steady-state condition. The solubilization of VOCs in different surfactant solutions is investigated.

- (2) To investigate the effect of environmental conditions such as temperature and ionic strength on solubilization of selected volatile organic contaminants in different surfactant systems.

CHAPTER TWO

LITERATURE REVIEW

2.1 Subsurface Contamination and Remediation

Groundwater is an important source of fresh water. It supports 50% of all USA citizens and 97% of the USA rural population as a drinking water source. In addition, it provides 40% of water used for irrigation and a small portion of the self-supplied industrial water in USA (U.S.EPA, 1987). It supplies 7.9 million people, or 26% of the population as a domestic water source in Canada (Environment Canada, 2001).

2.1.1 Groundwater Contamination

Groundwater is frequently clean enough to be used directly. However, with the development of industry, local and regional groundwater contamination problems have arisen. Approximately 15 to 28% of all groundwater suppliers in the USA contain synthetic organic chemicals (Dyksen and Hess, 1982; Robeck and Love, 1983; Westrick et al, 1984). In 1984, the Office of Technology Assessment (OTA, 1984) listed 175 organic chemicals, more than 50 inorganic chemicals, and a variety of biological organisms and radionuclides that have been found in groundwater through out the U.S.A. VOCs have been or have the potential to be found in a good proportion of the sources of groundwater contamination (OTA, 1984).

Most volatile organic compounds are hydrophobic, and their liquid forms have limited aqueous solubility. Therefore, they are immiscible with respect to the aqueous

phase and can exist in the subsurface as a separate liquid phase, referred to as Non-Aqueous Phase Liquids (NAPLs). According to density, NAPLs are divided as LNAPLs (those are lighter than water) and DNAPLs (those are heavier than water). Most natural and refined hydrocarbons like gasoline, jet fuel, and heating oils are LNAPLs, while most chlorinated organics, and high molar weight hydrocarbons, like PCB oils, creosote, and coal tar, are DNAPLs.

NAPLs enter the unsaturated zone as discrete liquid phases (Gillham and Rao, 1990). NAPLs are transported downward by gravitational forces overcoming capillary forces until they reach a low-permeability barrier. If the quantity of NAPLs is sufficient to overcome the capillary forces in the low-permeability barrier allowing them reach the water table, then the DNAPL compounds will tend to migrate vertically through the saturated zone. In contrast, the LNAPL compounds will tend to spread laterally along the water table, forming free product. However, fluctuations in the water table can cause vertical movement and redistribution of LNAPL free product within the saturated and unsaturated zones. As the NAPL is transported through the subsurface, a portion will be retained within the soil pores as immobile globules/ganglia due to interfacial forces. This entrapped NAPL is known as residual (trapped) saturation and can occupy 5 to 40% of the pore volume (Schwille, 1984). Excess NAPLs may also accumulate as bulk free phase organic liquid at interfaces. Both the residual saturation and the bulk free phase are long-term sources of subsurface contamination.

The movement of NAPLs in the subsurface is illustrated in Figure 2-1.

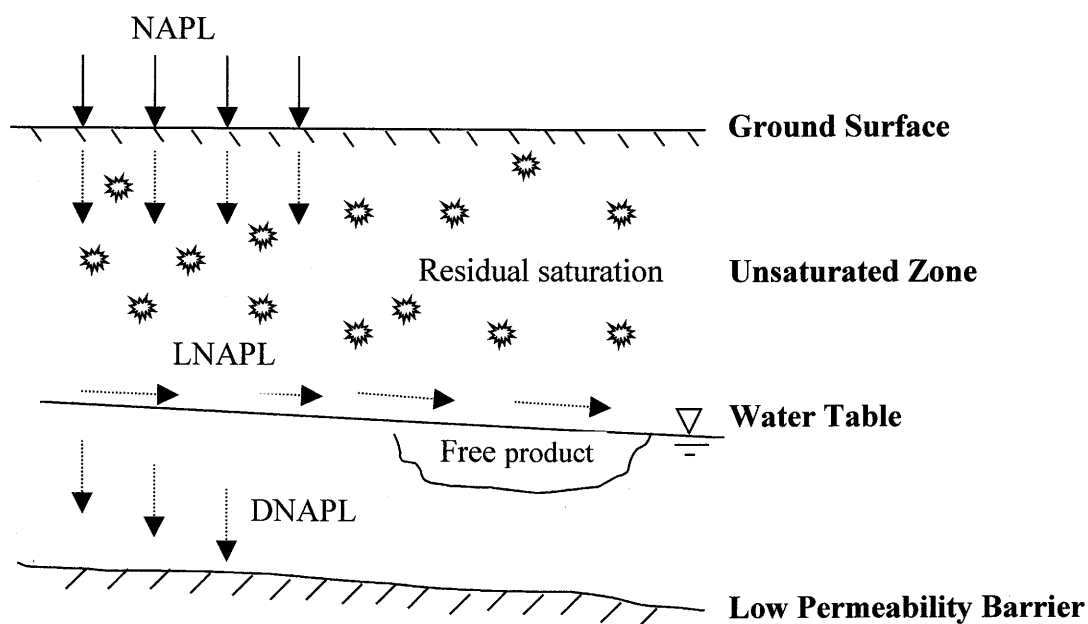


Figure 2-1 Movement of NAPL in Subsurface

The U.S.EPA established drinking water standards for eight volatile synthetic organic chemicals in the “1987 Amendments of the Safe Drinking Water Act” (see Table 2-1) (Ram et al., 1990). Within the eight VOCs, five chemicals (benzene, vinyl chloride, carbon tetrachloride, 1,2-dichloroethane and trichloroethylene) were regulated as known or probable human carcinogens; two chemicals (*para*-dichlorobenzene and 1,1-dichloroethylene) were regulated as having equivocal evidence of carcinogenicity, and one (1,1,1-trichloroethane) was regulated as noncarcinogenic. Another 12 VOCs’ standards were promulgated in 1990 and 3 more in 1991 (see Table 2-1).

Table 2-1 U.S.EPA Drinking Water Standards for VOCs (Ram et al., 1990)

VOC	Promulgation Date	MCLG (mg/L)	MCL (mg/L)
Benzene	7/87	0	0.005
Carbon tetrachloride	7/87	0	0.005
1,2-Dichloroethane	7/87	0	0.005
1,1-Dichloroethylene	7/87	0.007	0.007
<i>para</i> -Dichlorobenzene	7/87	0.075	0.075
1,1,1-Trichloroethane	7/87	0.20	0.20
Trichloroethylene	7/87	0	0.005
Vinyl chloride	7/87	0	0.002
Dibromochloropropane	12/90	0	0.0002
<i>o</i> -Dichlorobenzene	12/90	0.6	0.6
<i>cis</i> -1,2-Dichloroethylene	12/90	0.07	0.07
<i>trans</i> -1,2-Dichloroethylene	12/90	0.1	0.1
1,2-Dichloropropane	12/90	0	0.005
Ethylbenzene	12/90	0.7	0.7
Ethylene dibromide	12/90	0	0.00005
Methylene chloride	12/91	-	-
Monochlorobenzene	12/90	0.1	0.1
Styrene	12/90	0/0.1	0.005/0.1
Tetrachloroethylene	12/90	0	0.005
Toluene	12/90	2	2
Trichlorobenzene	12/91	-	-
1,1,2-Trichloroethane	12/91	-	-
Xylene(s)	12/90	10	10

Note: MCLG --- Maximum contaminant level goal;

MCL --- Maximum contaminant level (which is achievable by best available technology).

There are also similar standards in the World Health Organization Drinking Water Guidelines (WHO, 2001). They are presented in Table 2-2.

Table 2-2 World Health Organization Guidelines for Drinking Water
(WHO, 2001)

VOC	Guideline Value (mg/L)	Remarks
Carbon tetrachloride	0.002	
Dichloromethane	0.02	
1,1-dichloroethane		NAD
1,2-dichloroethane	0.03 ^a	For excess risk of 10 ⁻⁵
1,1,1-trichloroethane	2 (P)	
Vinyl chloride	0.005 ^a	For excess risk of 10 ⁻⁵
1,1-dichloroethene	0.03	
1,2-dichloroethene	0.05	
Trichloroethene	0.07(P)	
Tetrachloroethene	0.04	
Benzene	0.01 ^a	For excess risk of 10 ⁻⁵
Toluene	0.7	ATO
Xylene(s)	0.5	ATO
Ethylbenzene	0.3	ATO
Styrene	0.02	ATO
Benzo[a]pyrene	0.0007 ^a	For excess risk of 10 ⁻⁵
Monochlorobenzene	0.3	ATO
1,2-dichlorobenzene	1	ATO
1,3-dichlorobenzene		NAD
1,4-dichlorobenzene	0.3	ATO
Trichlorobenzenes (total)	0.02	ATO

Note: NAD---No adequate data to permit recommendation of a health-based guideline value.

a---For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking-water associated with an excess lifetime cancer risk of 10⁻⁵ (one additional cancer per 100000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years).

P---Provisional guideline value.

ATO---Concentrations of the substance at or below the health-based guideline value may affect the appearance, taste, or odor of the water.

Canada drinking water standards for VOCs (Ministry of Environment (Canada), 2001) are listed in Table 2-3.

Table 2-3 Canada Drinking Water Standards for VOCs
(Ministry of Environment (Canada), 2001)

VOC	MAC (mg/L)	IMAC (mg/L)	Aesthetic Objectives (mg/L)
Benzene	0.005		
Carbon tetrachloride	0.005		
1,2-Dichlorobenzene	0.2		
1,4-Dichlorobenzene	0.005		
1,2-Dichloroethane		0.005	
1,1-Dichloroethylene	0.014		
Dichloromethane	0.05		
Ethylbenzene			0.0024
Monochlorobenzene	0.08		
Tetrachloroethylene	0.030		
Toluene			0.024
Trichloroethylene	0.05		
Trihalomethanes	0.100		
Vinyl Chloride	0.002		
Xylene(s)			0.30

Note: MAC --- Maximum Acceptable Concentration;
IMAC --- Interim Maximum Acceptable Concentration.

2.1.2 Remediation Technology for Contaminated Subsurface

Recent technologies for remediation of contaminated subsurface include the follows (U.S.EPA, 1990a):

- *Pump-and-Treat*

- Extraction of contaminated ground water with subsequent treatment at the surface followed by disposal or reinjection.
- *Soil Vacuum Extraction*
 - Enhanced volatilization of compounds by applying a vacuum to the subsurface.
- *Soil Flushing/Washing*
 - Use of extracting solvents to remove contaminants from soils.
- *Containment*
 - Placement of physical, chemical, or hydraulic barriers to isolate contaminated areas.
- *Bioremediation*
 - Enhanced biodegradation of contaminants by stimulating indigenous subsurface microbial populations.

U.S.EPA (1990b) suggested pump-and-treat systems might be the only feasible option when deep groundwater contamination exists.

Pump-and-Treat Technology

Over the past 20 years, pump-and-treat has been the most common method to remediate contaminated groundwater (Mercer et al., 1990). In the pump-and-treat system, contaminated groundwater or mobile NAPLs are captured and pumped to the surface via withdrawal wells, and treated above ground (Sabatini et al., 1995). The treated water is then returned to the subsurface by injection wells or is discharged to nearby surface water (Deitsch and Smith, 1995). Pump-and-treat remediation can be

used for cleanup of both organic and inorganic contaminants within the subsurface (Sabatini et al., 1995) but it is only effective for the dilute aqueous portion of the subsurface contamination.

NAPLs have very low solubility in water and tend to exist as pockets at subsurface locations, to which they have migrated. Therefore, they dissolve slowly leading to very low removal rates by pumping. Experience has revealed that traditional pump-and-treat systems are impractical for treating NAPLs in aquifers. In particular, traditional pump-and-treat systems have little effect on DNAPLs as residual saturation due to their low water solubility, high density, and capillary forces arising from interfacial tension between the DNAPLs and water (U.S.EPA, 1994).

Surfactant Enhanced Subsurface Remediation

NAPLs tend to exist in pockets in the subsurface and are hard to remove by pump-and-treat systems. New technologies are being developed to improve removal efficiency through mobilization or solubilization of NAPLs in these pockets (U.S.EPA, 1995).

Two other remediation alternatives (Ko et al., 1998a) are: hydrophobic organic compounds (HOC) sorbing to an immobile phase that subsequently decreases HOC mobility; and HOC partitioning into a mobile phase that results in an increase in HOC mobility and apparent solubility in water. For the first approach, organoclays (Smith et al., 1990; Wagner et al., 1994; Xu and Boyd, 1995) or organooxides (Holsen et al., 1991;

Kibbey and Hayes, 1993; Sun and Jaffe, 1996) are used to remove HOCs from water. For the second alternative, in-situ surfactant-enhanced subsurface remediation (SESR) (Kile and Chiou, 1989; Abdul et al., 1990; West and Harwell, 1992; Pennell et al., 1993; Abdul and Ang, 1994) is an economically and technically feasible remediation approach, especially for DNAPLs with very low aqueous solubility. In fact, surfactant use in subsurface systems dates back to 1963 when petroleum sulfonates were patented for widespread use in enhanced oil recovery efforts (Pope and Wade, 1995).

Actually, surfactant enhanced subsurface remediation (SESR) is a modification of pump-and-treat technology. As in traditional pump-and-treat systems, contaminated groundwater is pumped to the surface and treated to remove the contaminants. Then the surfactant is added to the treated water and the solution is reinjected in separate injection wells. The contaminated subsurface is treated by flow of surfactant solution from the injection wells to the extraction wells. The surfactant solution can be reused after being treated to remove NAPLs.

There are two mechanisms (West and Harwell, 1992; Pennell et al., 1993; Shiau et al., 1994) by which surfactants can enhance the removal of NAPLs from the saturated zone.

- *Solubilization*
 - which is mediated by the formation of micelles.
- *Mobilization*

- which is caused by reducing the interfacial tension (IFT) between the DNAPLs and groundwater.

Increased DNAPL solubility will increase the mass removed per volume of water, or the rate of DNAPL removal for the same volume of water pumped out of the subsurface for treatment, thus reducing remediation times.

Surfactant Recovery and Reuse

The application of surfactant for remediation of contaminated subsurface requires the recovery and reuse of the surfactant. Surfactant separation and potential reuse is imperative for the economical and thus successful implementation of this technology. Potential operations to separate VOCs from the surfactant solutions (Krebs-Yuill et al. 1995) include: air stripping; steam stripping; vacuum-steam stripping; vacuum stripping; and pervaporation. For removing nonvolatile organic compounds, solvent extraction is the main option (Clarke et al., 1992).

In the last decade, pervaporation has been evaluated for removing VOCs from aqueous industrial process streams, wastewater, and groundwater (Blume et al., 1990). Pervaporation, "permeation + evaporation", is a membrane process for the separation of liquid mixtures (usually water and organic compounds) (Fleming, 1992). When a liquid feed is pumped through the upstream side of a nonporous polymeric membrane, the components of the liquid will sorb into the membrane, permeate through the membrane and evaporate into a vapor phase on the downstream side. The permeate leaving the

downstream side of the membrane is then condensed by cooling and or pressurization (see Figure 2-2). Jiang et al (1997) evaluated the feasibility of removing VOCs from surfactant solutions by pervaporation in order to treat and reuse the surfactant solution.

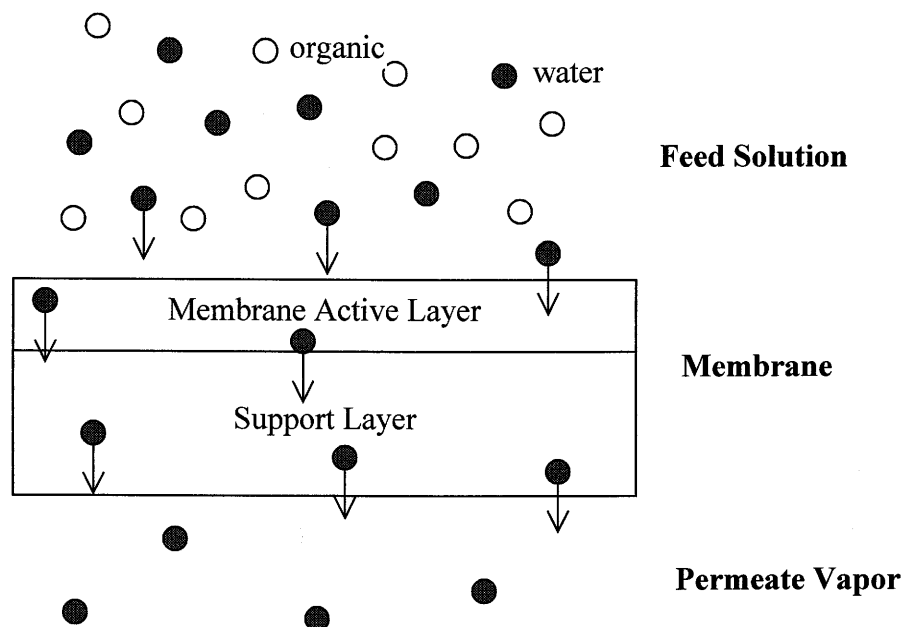


Figure 2-2 Pervaporation
(Adapted from Artisan Industries Inc., 2001)

Ultrafiltration (UF) is a pressure driven membrane technique that uses porous membranes for the separation of material in the 1nm~10 μ m size range or compounds with molecular weights in excess of 5000. Colloidal particles, macromolecules and micelles are examples of items that can be fractionated. Ultrafiltration can be used to concentrate micellar aggregates and their associated solutes and then liberate clean water in the permeate. When combined with other treatment technologies, such as steam stripping to remove volatile organics, UF treatment also can be used for micelle recovery (Lin et al., 1997). Two field-pilot tests (Ang and Abdul, 1994) conducted showed that more than 70 percent of the surfactant could be separated from the waste streams.

2.2 Surfactant

Surfactant, surface active agent, is a substance that at low concentrations adsorbs at some or all of the interfaces in a system and significantly changes the amount of work required to expand those interfaces (Rosen, 1989). An interface is a boundary between any two immiscible phases. The interfacial free energy is the minimum amount of work required to create that interface. The interfacial tension between two phases is the minimum amount of work required to create a unit area of the interface or to expand it by a unit area (Rose, 1978). Usually, surfactants act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it. Because surfactants concentrate at interfacial regions, such as air-water, oil-water, solid-liquid interfaces, they are surface active.

A surfactant molecule has two distinct structural moieties, one is polar or ionic and the other is nonpolar. The polar or ionic moiety of the surfactant molecule, may carry a positive or negative charge, or may be composed of a polyoxyethylene chain, and has an affinity for water and other polar substances, i.e., it is hydrophilic. The nonpolar moiety is usually a flexible hydrocarbon chain and is hydrophobic, i.e., it is easily soluble in many nonpolar solvents but only sparingly soluble in water. The dual nature of a surfactant is typified by sodium dodecyl sulphate (NaDS),



Hydrophobic group

Hydrophilic group

Because of the amphiphilic nature (hydrophobic and hydrophilic), a surfactant molecule can dissolve in water as a monomer and adsorb at an interface, or be incorporated with other surfactant molecules as part of a micelle. This dual nature is responsible for the phenomenon of surface activity, and of micellization and solubilization (Attwood and Florence, 1983).

Depending on the nature of the hydrophilic group, surfactants are classified (Rosen, 1978, 1989) as:

- *Anionic*
 - The surface-active portion of the molecule bears a negative charge.
- *Cationic*
 - The surface-active portion bears a positive charge.
- *Zwitterionic*
 - Both positive and negative charges may be present in the surface-active portion.
- *Nonionic*
 - The surface-active portion bears no apparent ionic charge.

The examples of these four surfactant types are listed in Table 2-4.

Table 2-4 Examples of Surfactant Types		
Surfactant	Ionic Type	Molecular Formula
Potassium laurate	Anionic	$\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-\text{K}^+$
Dodecylamine hydrochloride	Cationic	$\text{CH}_3(\text{CH}_2)_{11}\text{N}^+\text{H}_3\text{Cl}^-$
Polyoxyethylene monohexadecyl ether	Nonionic	$\text{CH}_3(\text{CH}_2)_{15}(\text{OCH}_2\text{CH}_2)_{21}\text{OH}$
N-dimethyl betaine	Zwitterionic	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$

Nonionic surfactants are surfactants that do not have a charged group. Nonionic surfactants are usually prepared by the addition of ethylene oxide to compounds containing one or more active hydrogen atoms such as alkylphenols, fatty alcohols, fatty acids, fatty mercaptants, fatty amines, fatty amides, and polyols. The molecular structures of nonionic surfactants are usually one of the following: polyoxyethylenated alkylphenols, polyoxyethylenated straight chain alcohols, polyoxyethylenated polyoxypropylene glycols, polyoxyethylenated mercaptants, long chain carboxylic acid esters (glyceryl and polyglyceryl esters of natural fatty acids, propylene glycol, sorbitol, and polyoxyethylenated sorbitol esters, polyoxyethylene glycol esters) and alkanolamines (Rosen, 1989).

The most common hydrophilic groups are the hydroxyl group (R-OH) and the ether group (R-O-R'). Other groups are the oxide (amine oxide), and triple unsaturated bond (acetylenic alcohols). In general, nonionic surfactants tend to be more strongly surface active than ionic surfactants. Nonionic surfactants have the advantage over ionic surfactants in that they are compatible with all other types of surfactants and their properties can be modified considerably by changing the length of the polyoxyethylene group and they are generally little affected by pH.

Food grade (i.e., edible) surfactants are mainly the esters based on glycerol, sorbitol and propylene glycol (Rosen, 1989). Tweens are nonionic surface-active mono-fatty acid esters of polyoxyethylene sorbitan, usually containing approximately 20 moles

of ethylene oxide. Because of their high surface activity and relatively low toxicity, they have been used as solubilizers, wetting agents and emulsifiers in pharmaceuticals.

2.2.1 Micellization

In very dilute aqueous solutions (less than 10^{-4}M), surfactants usually exist as monomers, although dimers, trimers, etc., can exist. They are completely dissociated and their physical properties approach ideality at infinite dilution (Elworthy et al., 1968). There is a large interfacial energy between the hydrocarbon chain and water (Elworthy et al., 1968). When more and more surfactant is added to the solution, more and more monomers exist in water, the total free energy of this system increases. As all chemical systems tend towards a state of minimum free energy, the aggregation of monomers to micelles occurs and results in a decrease of free energy.

As the surfactant monomers aggregate into micelles, the high energy of the hydrocarbon/water interface is lost. As Hartley (1955) pointed out there is a strong adhesion between water molecules and the hydrocarbon tends to be squeezed out from close contact with them. That's the reason why micelles are formed and surfactants adsorb at an interface with the hydrocarbon chain oriented away from the water. Meanwhile, transfer of monomers into the micelles also means that the structuring of water around the hydrocarbon part of the monomer is lost. Therefore, an ordered state has become a disordered one with regard to the water, meaning that there is a positive entropy change and a decrease in free energy (Elworthy et al., 1968).

The loss of hydrocarbon/water interfacial energy and the loss of water structure thus provide driving forces for the formation of micelles. Since there is no electrical force to oppose micellization for nonionic surfactants, nonionic surfactants form micelles at lower concentration than ionic ones. The formation of micelles is represented in Figure 2-3.

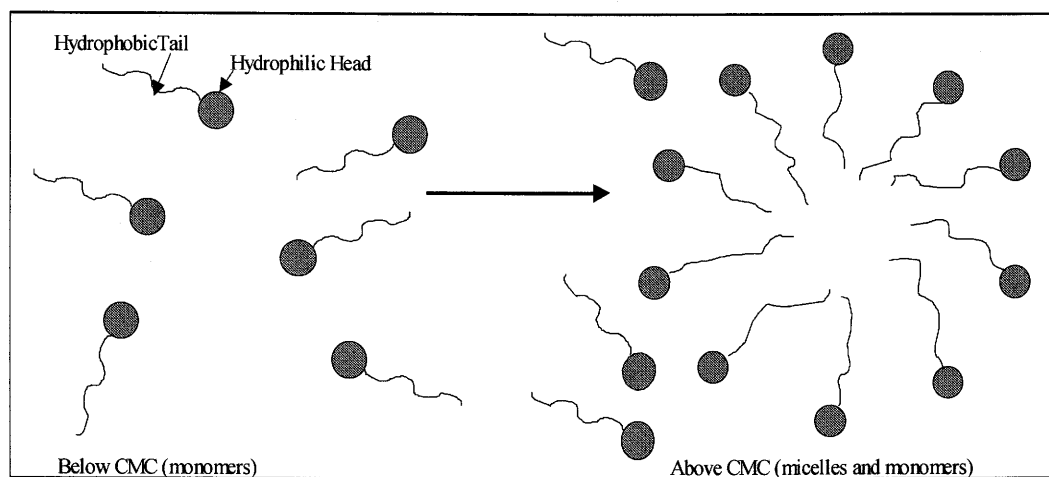


Figure 2-3 Formation of Micelle

McBain and coworkers (McBain et al., 1920; McBain, 1950) initially developed the concept of micelles. Bury and his coworkers (Grindley and Bury, 1929; Davies and Bury, 1930) and Hartley (1936) established the existence of a narrow concentration range known as the critical concentration for micelles in the early 1930's.

As the surfactant concentration is increased above the CMC (Critical Micelle Concentration, the surfactant concentration for micelle formation), more micelles are formed as a linear function of the added surfactant concentration (Martin, et al., 1969). The concentration of the nonaggregated surfactant (monomer) remains nearly constant approximately equal to the CMC (Cline Love, et al., 1984). The CMC represents the highest monomeric surfactant concentration obtainable. The more surface active the monomer is, the higher the tendency to form micelles is and the lower the CMC value is (Mukerjee and Mysels, 1971). The CMC can be determined from the inflection point of plots of some physical properties of the solution as a function of surfactant concentration (see Figure 2-4). The physical properties include: surface tension, conductivity, light scattering intensity, osmotic pressure, etc. (Attwood and Florence, 1983).

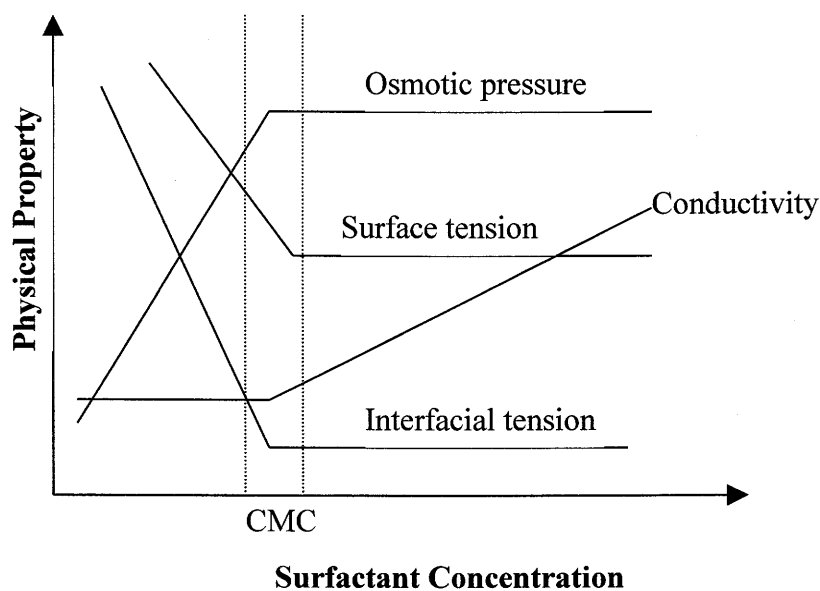


Figure 2-4 Determination of CMC
(Adapted from Attwood and Florence, 1983)

A micelle contains from 60 to 100 or more surfactant monomers. The number of monomers in a micelle is called the aggregation number. The length of the hydrocarbon tail, size of the head group and interaction of the hydrocarbon tails with one another and with the aqueous solution determine the size and shape of micelle, CMC, and aggregation number. Shapes of micelles can vary from rough spheres to prolate ellipsoids, and the diameter of micelles generally ranges from 3-6nm (Armstrong, 1985). This small diameter prevents micelles from being filtered from solution and from appreciably scattering light. Changes in temperature, concentration of surfactant, additives in the aqueous phase, and structural groups in the surfactant all may cause changes in the size, shape, and aggregation number of the micelle (Winsor, 1968).

The hydrophobic portion of each surfactant molecule in the micelle, also called the hydrophobic tail, is directed inward, toward the center of the aggregate, forming with other hydrophobic moieties a liquid core, which has a fairly smooth boundary with the outlying hydrophilic chains and polar solvent (Benedouch et al., 1983). The central region of the micelle thus forms a hydrophobic pseudophase that is distinct in its properties from the polar solvent (Hunter, 1987). The hydrophobic tail typically contains 7~21 carbons (Armstrong, 1985), and may contain single or duplicate hydrocarbon chains and multiple bonds. The hydrophobic group of the surfactant monomer prefers to reside in a hydrophobic phase such as LNAPL or DNAPL.

The hydrophilic portion of each surfactant molecule in the micelle, also called the hydrophilic head, is directed outward and close to the polar solvent surrounding. The

hydrophilic head can be a partially dissociable carboxylate, a fully ionized moiety plus counterion, or an uncharged polar species (such as polyethylene glycol). A nonionic surfactant is a hydrated, oxygen-containing chain directed outward toward the solvent (Rosen, 1989). The hydrophilic group of the surfactant monomer provides most surfactants with a high solubility in water.

2.2.2 Solubilization

When the surfactant concentration is less than a compound-specific threshold value (i.e., CMC), surfactant molecules exist predominantly in monomeric form, with some fraction being adsorbed at system interfaces. With an increase of surfactant concentrations above the CMC, the monomers assemble and form colloidal aggregates, called micelles.

Because there is a hydrophobic pseudophase in the micelle, the solubility of hydrophobic organic compounds which are insoluble or only slightly soluble in water is enhanced in surfactant solutions which have concentrations greater than the CMC. The 'apparent solubility' of these organic compounds in an aqueous surfactant solution is significantly higher than the aqueous solubility. This increase of the organic compound's solubility is referred to as 'solubilization' (see Figure 2-5). In other words, solubilization is the ability of surfactants to dissolve organic compounds which are insoluble or only slightly soluble in water.

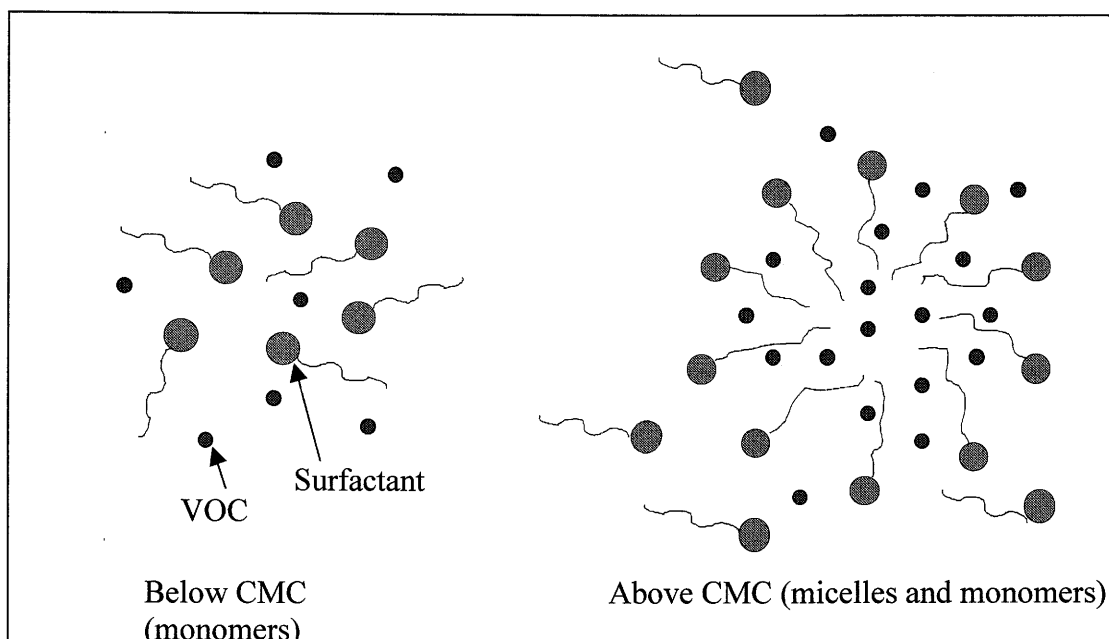


Figure 2-5 Solubilization

In a surfactant enhanced subsurface remediation system, pollutant-surfactant interactions include: specific pollutant-surfactant monomer interactions in water (Kile and Chiou, 1989), pollutant solubilization by micelles (Jafvert, 1991), pollutant solubilization by surfactant oil emulsions (Kile et al., 1990) and surfactant monolayer distribution at the hydrocarbon-water interface (Clayton et al., 1989). The solubilization of organic pollutants by micelles is the most important interaction for remediation of contaminated subsurface and it is the topic of this research.

Solubilization of hydrophobic compounds begins once the CMC is established, and is a linear function of the surfactant concentration which is greater than the CMC. Even at concentrations below the CMC, surfactants (particularly the nonionics) can affect the solubilities of sparingly soluble compounds (Pramauro and Pelizzetti, 1990). The

amount of organic compounds solubilized depends on the surfactant structure, aggregation number, micelle geometry, micelle chemistry, solubilize chemistry, solubilize size, ionic strength and temperature (Attwood and Florence, 1983; Rosen, 1989). The solubilize is the organic compound which is solubilized by the micelles.

The exact location in the micelle at which solubilization occurs varies with the nature of the material solubilized. The location is important because it reflects the type of interaction occurring between the surfactant and the solubilize.

In general, solubilization occurs at different sites in the micelle (Elworthy et al., 1968; Rosen, 1978; Attwood and Florence, 1983):

- On the surface of micelle, at the micelle-solvent interface;
- Between the hydrophilic head group (e.g., in polyoxyethylenated materials);
- In the palisade layer (the transition region between the surface of the micelle and the core of the micelle);
- More deeply in the palisade layer;
- In the inner core of the micelle.

The location or combination of locations within the micelle at which a particular contaminant will be solubilized depends primarily on the water solubility of the contaminant molecules (Harwell, 1992). Generally, non-polar solubilizes (e.g., aliphatic hydrocarbon), which have low solubility in water, are dissolved in the hydrophobic core of the micelle, where the hydrocarbon tails of aggregates serve as the solvent (Schick,

1967). Semi-polar or polar solubilizates (e.g., fatty acids and alkanols) are taken up in palisade layer of the micelle, oriented with their hydrophobic moieties towards the center of the micelle and their polar group in its surface (Elworthy et al., 1968; Rosen, 1978; Attwood and Florence, 1983).

The solubilization of an organic solute in an aqueous micellar solution has been modeled by:

- Pseudophase Separation Model (Mysels, 1955)
 - Treats the solubilization of an organic solute in micellar solutions as equilibrium of the solute between the micellar phase and the aqueous phase.
- Mass Action Model (Shinoda, 1963)
 - Treats the solubilization process as the stepwise addition of an organic solute into a micelle composed of surfactant and organic solutes. The method is based on assumed equilibrium between organic solute molecules, surfactant molecules, and micelles containing both surfactant and solubilize.
- Cell Model (Gunnarsson et al., 1980)
 - A statistical mechanics model. The micellar solution is divided into a set of identical volume elements or cells. Each cell contains a single micelle and its associated aqueous solution with the appropriate quantities of water, electrolyte, counterions, unsolubilized organic solute, etc.

The degree of solubility enhancement achieved by a surfactant can be characterized by the Molar Solubilization Ratio (MSR) or the micelle-water partition coefficient (K_m).

The molar solubilization ratio is the moles of organic compound solubilized per mole of surfactant added to solution (Attwood and Florence, 1983). It is equal to the increase of solubilize concentration per increase of micellar surfactant concentration. In the presence of the excess hydrophobic organic compound, the MSR is determined from a graph of aqueous solubilize solubility versus surfactant concentration. The MSR is the slope of the straight-line portion of the plot above the CMC (see Figure 2-6).

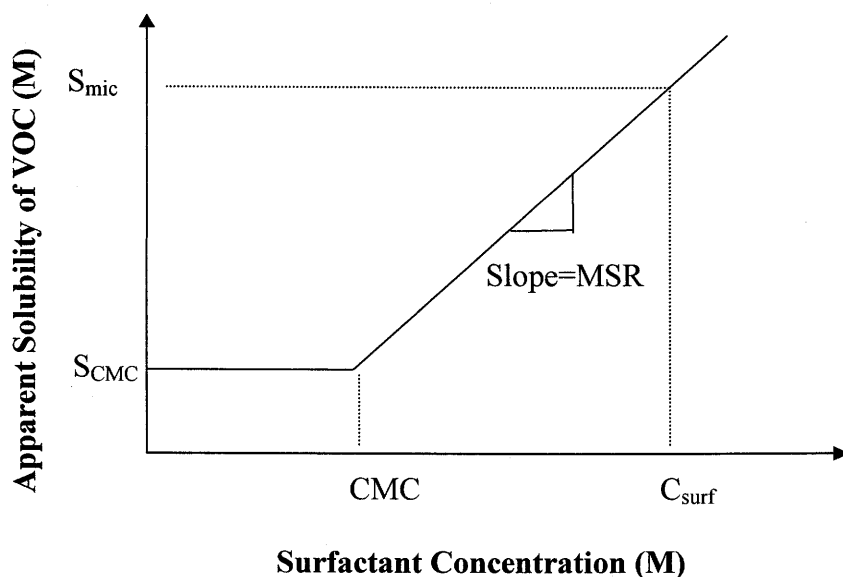


Figure 2-6 Determination of MSR

i.e.,

$$MSR = \frac{S_{mic} - S_{CMC}}{C_{surf} - CMC} \quad (2-1)$$

where, S_{CMC} --- apparent solubility of a volatile organic compound at the CMC (M);

S_{mic} --- total apparent solubility of the VOC in a particular surfactant solution

which concentration is greater than the CMC (M);

C_{surf} --- surfactant concentration at which S_{mic} is evaluated (M);

CMC --- critical micelle concentration of surfactant (M).

A higher MSR indicates greater solubilization ability for the surfactant under consideration.

The micelle-water partition coefficient (K_m) is the ratio of the mole fraction of contaminant in the micellar phase, X_m , to the mole fraction of the contaminant in the aqueous phase outside of micelles, X_a .

$$K_m = \frac{X_m}{X_a} \quad (2-2)$$

K_m can be determined from values of MSR, water solubility of the contaminant and molar concentration of water (Edward et al., 1991; Shiao et al., 1994).

$$X_m = \frac{S_{mic} - S_{CMC}}{C_{surf} - CMC + S_{mic} - S_{CMC}} \quad (2-3)$$

$$X_m = \frac{MSR}{1 + MSR} \quad (2-4)$$

$$X_a = S_{CMC} V_w \quad (2-5)$$

where, V_w --- molar volume of water, 0.01805L/mole at 25°C.

thus,

$$K_m = \frac{S_{mic} - S_{CMC}}{(C_{surf} - CMC + S_{mic} - S_{CMC})(S_{CMC}V_w)}$$
$$K_m = \frac{55.4MSR}{S_{CMC}(1 + MSR)} \quad (2-6)$$

2.2.3 Existing Techniques to Determine Solubilization Parameters

Experimental techniques used to study the solubilization of organic solutes in aqueous micellar solutions are based on specific analytical methods that can be used to determine the concentration of the organic solute in the micellar phase or in the aqueous phase.

A listing and brief description of some of these techniques are presented below:

- 1) The vapor pressure method (Smith et al., 1987; Christian, et al., 1981, 1982) and headspace gas chromatography method (Hayase and Hayano, 1977; Rytting et al., 1978; Spink and Colgan, 1983, 1984; Nguyen et al., 1988a) are used for organic solutes that have a relatively large vapor pressure in the aqueous micellar solution, especially for VOCs.

In the vapor pressure method, the highly precise values of the partial pressure of VOC can be measured by automated vapor pressure apparatus, but the partition coefficient in this method is defined as the ratio of the mole fraction of

VOC in the intracellular "solution" to the concentration of VOC in monomeric form in the bulk aqueous solution.

In the headspace gas chromatography method, vapor samples are withdrawn from the headspace after equilibrium with aqueous solution and analyzed by GC. This method is the initial EPICS (Equilibrium Partitioning In Close Systems) method.

- 2) In the maximum additive method (Shiau et al., 1994), different volumes of VOC are added to surfactant solution which has constant concentration. Solubilization limits are determined by visual inspection for remaining excess phase after equilibration with the aqueous micellar solution. However, it is difficult to separate excess pure solute from the aqueous phase.
- 3) Separation methods, including molecular sieve or gel filtration (Aboutaleb et al., 1980; Donbrow et al., 1970), micellar-enhanced ultrafiltration (Aboutaleb et al., 1977; Dougherty and Berg, 1974; Dunn et al., 1987), and semi-equilibrium dialysis (Patel and Kostenbauder, 1958; Kazmi and Mitchell, 1971; Christian et al., 1985; Bhat et al., 1987), take advantage of the differences in size between solute molecules and micelle.

In the molecular sieve or gel filtration method, dextran gel, which has a suitable degree of crosslinking, is used in a static way similar to a semipermeable

membrane in dialysis. The small molecules (the solute) are distributed between the swollen gel and the external liquid. While the surfactant is unable to penetrate the internal gel phase and remains in the external liquid.

Micellar-enhanced ultrafiltration is used to remove low molecular weight soluble organics from water. When polluted water is passed through an ultrafiltration membrane, the micelles containing the solubilized organic pollutants are blocked and the organic concentration is very small in the permeate. This method is used to recover surfactant when combined with other treatment technologies.

Semiequilibrium dialysis is similar to micellar-enhanced ultrafiltration in that it utilizes a membrane to separate a concentrated solution of solute and surfactant from a permeate solution. In this method, solutions containing surfactant and organic at known concentrations are introduced into one side of each dialysis cell and pure water is added to the other side, then the permeate solutions are analyzed by UV spectroscopy. This method is time consuming and requires preliminary work on the selection of a proper membrane for each system.

- 4) Spectroscopic methods (Quina and Toscano, 1977; Mukerjee and Cardinal, 1978; Bunton et al., 1979; Bartet et al., 1980; Hiros and Sepulveda, 1981) are based on the differences in the absorption or emission of various types of radiation

(ultraviolet, electromagnetic, fluorescence, luminescence, etc.) between organic solutes bound to the micelle and those free in the aqueous micellar solution.

- 5) Variation in the colligative properties, the Krafft point or the depression of the CMC of the ionic micelle, caused by adding organic solutes, also has been used to infer the solubility of organic solute in an aqueous micellar solution.

Nguyen et al. (1988b) discussed experimental methods which can be used to measure the solubilization isotherms (the relationship between the solubilization equilibrium constant and the intramicellar mole fraction of the organic solubilize). Nguyen et al. (1988b) defined the solubilization equilibrium constant of an organic solute in an aqueous micellar solution as the ratio of the mole fraction of organic solute in the micellar phase to the concentration of the unsolubilized monomeric organic solute in the aqueous phase.

Almgren et al (1979) also showed the micelle-water partition coefficient as the ratio of compound in the micelle to that in the water, which is not dimensionless, but has units of reciprocal concentration:

$$K_m' = \frac{C_{mic}}{C_w S_{mic}} \quad (2-7)$$

where, C_{mic} , C_w --- the concentration of compound in the micelle and water phase (M)

(both based on total aqueous phase volume);

S_{mic} --- concentration of surfactant in micellar form (M);

K_m' --- micelle-water partition coefficient (M^{-1}).

Kile and Chiou (Kile and Chiou, 1989) observed that some commercial surfactants could enhance the water solubility of DDT even at concentrations below the CMC. They thought the solubilization should be expressed in terms of the concentrations for monomers and micelles and the corresponding solute partition coefficients.

$$\frac{S_w^*}{S_w} = 1 + X_{mn} K_{mn} + X_{mc} K_{mc} \quad (2-8)$$

where, S_w^* --- apparent solute solubility at the total stoichiometric surfactant concentration of X (M);

S_w --- intrinsic solubility in "pure water" (M);

X_{mn} --- concentration of the surfactant as monomers (M);

X_{mc} --- concentration of the surfactant in micellar form (M);

K_{mn} --- partition constant of the solute between monomers and water (M^{-1});

K_{mc} --- partition constant of the solute between micelles and water (M^{-1}).

There are two reasons that cause solubilization by surfactants to occur below the CMC. First, commercial grade surfactants are mixtures and no distinct CMC value exists. Second, "partition-like" interaction with the non-polar content of the dilute surfactant is similar to the enhancement effect caused by dissolved humic materials (Kile and Chiou, 1989). Since the effectiveness of surfactant monomers enhancing organic compounds solubilities tends to be much less than that of micelles, it is often assumed to be negligible.

2.2.4 Mobilization

Surfactant-enhanced subsurface remediation can also be based on mobilization of the residual saturated NAPLs. This is the phenomenon that surfactant-enhanced oil recovery work was based on (Shah and Schechter, 1977). Mobilization has greater potential than solubilization to increase the rate of remediation, but it can be riskier because of the potential movement of free-phase liquid.

The reduction in NAPL-water interfacial tension caused by the addition of a surfactant to an aqueous solution will reduce the influence of capillary forces. Capillary forces are responsible for retention of residual NAPL and for the formation of pooled NAPL. If the interfacial tension can be lowered enough, physical mobilization of NAPL can occur. This may be desirable for LNAPL where free organic compound can be recovered in the vicinity of the water table using skimmer wells. But this may be undesirable for DNAPL where lowering interfacial tension may result in vertical mobilization of DNAPL deeper into the subsurface.

CHAPTER THREE

METHOD DEVELOPMENT

3.1 Derivation of the Micelle-Water Partition Coefficient (K_m)

The micelle-water partition coefficient (K_m) is a basic parameter that represents the solubilization power of a surfactant. It can be determined using a modification of the "Equilibrium Partitioning In Closed Systems" (EPICS) method (Valsaraj et al, 1988; Jiang et al., 1997). EPICS has been used extensively to measure Henry's law constants for VOCs (Lincoff and Gossett, 1984; Gossett, 1987; Ashworth et al., 1988). Similar methods have been used to evaluate the fraction of higher alcohols bound to the micellar phases (Hayase and Hayano, 1977; Spink and Colgan, 1983).

The method used for the research presented in this thesis consisted of equilibrating two vials containing equal volumes of aqueous solutions of VOC (see Figure 3-1). One vial contained a known amount of surfactant with a concentration greater than CMC and the other contained no surfactant. Several such pairs of vials were prepared. The concentrations of VOC were varied from one pair to another. After appropriate equilibration times, a known fixed volume of gas sample was taken from the headspace of each vial and analyzed by gas chromatography.

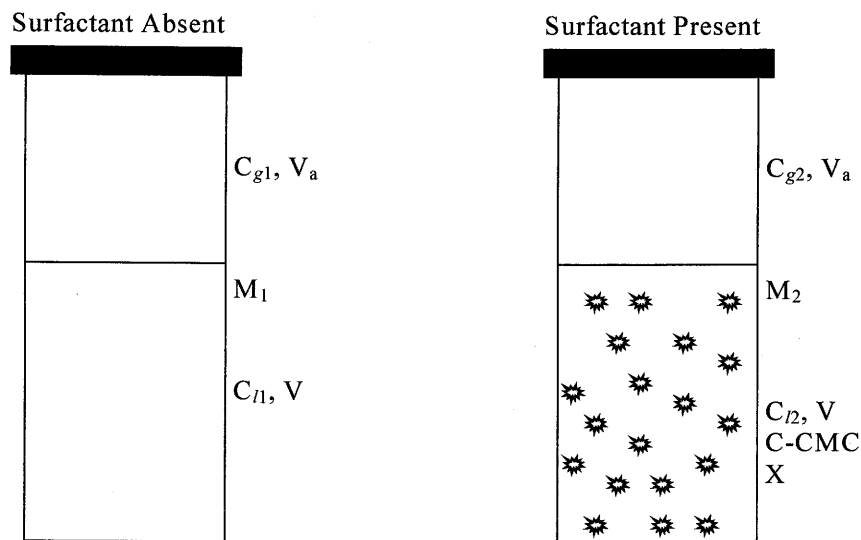


Figure 3-1 Representation of EPICS

Since there is a linear relationship between GC peak area raw data and VOC gas concentration in the headspace, the ratio of VOC gas concentrations can be replaced by the ratio of raw data (Hayase and Hayano, 1977; Lincoff and Gossett, 1984). Therefore, it is unnecessary to know the absolute gas concentration of the VOC in the headspace. That is one advantage of this method.

Assuming the volume of micellar phase is negligible, the mass balance of VOC in the vial which contains VOC solution only (i.e., surfactant absent) is

$$M_1 = C_{l1}V + C_{g1}V_a \quad (3-1)$$

where, M_1 --- mass added to the vial without surfactant (mmole);

V --- aqueous volume (L);

C_{l1} --- molar concentration of VOC in the aqueous phase when surfactant absent (mM);

C_{g1} --- molar concentration of VOC in the headspace when surfactant absent (mM);

V_a --- headspace volume (L).

The mass balance of VOC in vial which contains VOC and surfactant is

$$M_2 = C_{l2}V + C_{g2}V_a + X \quad (3-2)$$

where, M_2 --- mass added to the vial with surfactant (mmole);

C_{l2} --- molar concentration of VOC in the aqueous phase when surfactant present (mM);

C_{g2} --- molar concentration of VOC in the headspace when surfactant present (mM);

X --- mass of VOC trapped into micelles (mmole).

According to Henry's law,

$$C_g = HC_l \quad (3-3)$$

where, H --- Henry's Law constant (dimensionless).

Then, Equation (3-1) can be expressed as follows,

$$M_1 = \frac{C_{g1}}{H}V + C_{g1}V_a \quad (3-4)$$

$$M_1 = \frac{C_{g1}}{H}V(1 + H\frac{V_a}{V}) \quad (3-5)$$

Equation (3-2) can be expressed as follows,

$$M_2 = \frac{C_{g2}}{H}V + C_{g2}V_a + X \quad (3-6)$$

$$M_2 = \frac{C_{g2}}{H} V \left(1 + H \frac{V_a}{V}\right) + X \quad (3-7)$$

For two vials with the same GC responses, the headspace concentrations in the two vials would be the same ($C_{g1} = C_{g2}$), then

$$X = M_2 - M_1 \quad (3-8)$$

Assuming b is the millimolarity of VOC present in the micellar phase (mM), then

$$\frac{X}{V} = b = \frac{M_2 - M_1}{V} \quad (3-9)$$

Assuming a is the millimolarity of VOC added to the aqueous phase in the absence of surfactant (mM), according to Equation (3-5),

$$\frac{M_1}{V} = a = \frac{C_{g1}}{H} \left(1 + H \frac{V_a}{V}\right) \quad (3-10)$$

$$C_{g1} = \frac{aH}{1 + H \frac{V_a}{V}} \quad (3-11)$$

Since the headspace concentrations of the two vials are the same, Equation (3-11) can be converted to be:

$$C_{g2} = \frac{aH}{1 + H \frac{V_a}{V}} \quad (3-12)$$

$$\frac{C_{g2}}{H} = C_{l2} = \frac{a}{1 + H \frac{V_a}{V}} \quad (3-13)$$

As described in Chapter Two, the micelle-water partition coefficient (K_m) is defined as

$$K_m = \frac{X_m}{X_a} \quad (3-14)$$

where, X_m --- mole fraction of VOC in micellar phase;

X_a --- mole fraction of VOC in aqueous phase.

The mole fraction of VOC in micellar phase equals the moles of VOC in micelles over moles of all micellar components.

i.e.,

$$X_m = \frac{bV}{(C - CMC)V + bV} \quad (3-15)$$

where, C --- total molar concentration of surfactant in the aqueous phase (mM);

CMC --- critical micelle concentration of surfactant (mM);

$C - CMC$ --- molar concentration of surfactant present in the micellar phase (mM).

Therefore,

$$X_m = \frac{b}{(C - CMC) + b} \quad (3-16)$$

The mole fraction of VOC in aqueous phase equals the moles of VOC in aqueous phase over the moles of all aqueous components.

i.e.,

$$X_a = \frac{C_{l2}V}{55550V + C_{l2}V} \approx \frac{C_{l2}V}{55550V} \quad (3-17)$$

$$X_a = \frac{C_{l2}}{55550} \quad (3-18)$$

where, 55550 is the molar concentration of water in the aqueous phase (mM).

Therefore,

$$X_a = \frac{a}{55550(1 + H \frac{V_a}{V})} \quad (3-19)$$

Figure 3-2 is the plot of GC peak area against the total VOC added to the aqueous phase (mM). The upper curve in Figure 3-2 is the Henry's law curve for VOC in water. It is obtained from a series of prepared samples in the absence of surfactant. The lower curve in Figure 3-2 is the Henry's law curve for VOC in a surfactant solution. It is obtained from another series of prepared samples with added surfactant. The molar concentration of VOC present in the extramicrocellular phase, a , can be expressed as the horizontal separation between the vertical axis and the upper curve. The molar concentration of VOC present in the micellar phase, b , can be expressed as the horizontal separation between the two curves at any ordinate (see Figure 3-2).

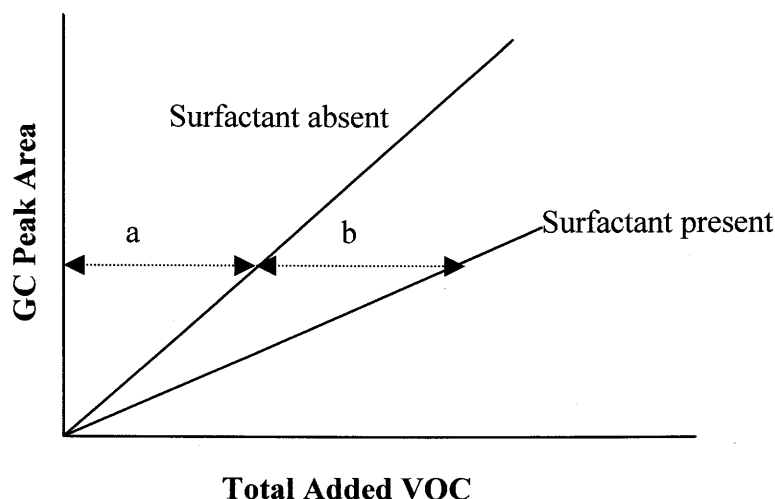


Figure 3-2 Data Analysis for Solubilization of VOC in Surfactant Solution

Parameters (a and b) can be obtained from Figure 3-2 in order to calculate X_m and X_a following Equation (3-16) and Equation (3-19). Then X_m versus X_a can be plotted to get a linear relationship, the slope of which yields the micelle-water partition coefficient, K_m (see Figure 3-3).

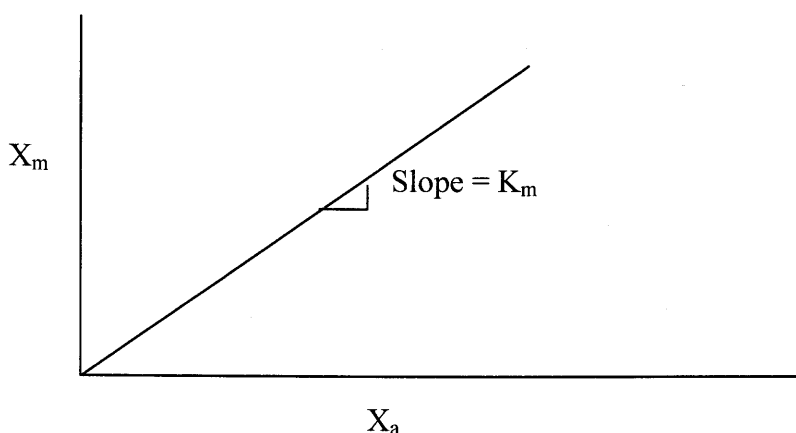


Figure 3-3 Determination of Micelle-Water Partition Coefficient, K_m

The fraction of VOC present in the micellar phase, f_m , can be determined from Figure 3-2 as follows:

$$f_m = \frac{b}{a + b} \quad (3-20)$$

where, a --- molar concentration of VOC in extramellar phase (mM);

b --- molar concentration of VOC in micellar phase (mM).

3.2 Experimental Procedure

3.2.1 Materials and Equipment

(1) Volatile Organic Compounds

Benzene, toluene and trichloroethylene (TCE) are common subsurface contaminants. Therefore, these three compounds were selected to represent typical

volatile organic compounds in this research. Benzene and toluene represent LNAPLs, and TCE represents DNAPL.

Benzene and TCE were purchased from ANNACHEMIA Ltd. Both have a purity of 99.9+%. Toluene was purchased from Omnisolv with a purity of 99.9+%. The properties of the selected VOCs are listed in Table 3-1.

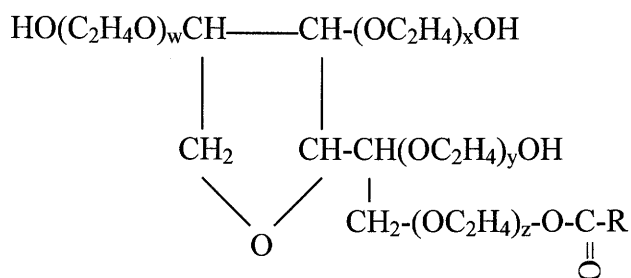
Table 3-1 The Properties of Selected VOCs			
VOC	Molecular Formula	Molecular Weight	Specific Gravity
Benzene	C ₆ H ₆	78	0.879
Toluene	C ₆ H ₅ CH ₃	92	0.87
TCE	ClCH=CH ₂	131.5	1.46

(2) Surfactants

Nonionic surfactants have specific advantages compared to ionic surfactants in the remediation of subsurface contamination because of a low CMC, low toxicity and biodegradability. In addition, they are chemically inert and stable with pH change. Since the surfactant is used to remediate subsurface contamination, further contamination by residual surfactant in the subsurface is not acceptable. Therefore, in order to facilitate regulatory approval for subsurface remediation, food-grade (edible) nonionic surfactants were chosen in this research to test the solubilization of VOCs.

Commercially available surfactants should be studied for the surfactant enhanced subsurface remediation. Tweens are polyoxyethylene sorbitan esters that are nontoxic and have high potential for biodegradation. They are commercially available and

considered edible as they are used as food and pharmaceutical emulsifiers. The molecular structures of Tweens are shown in Figure 3-4. Therefore, Tween 20 and Tween 80 were selected as the test surfactants in this research. For Tween 20, R is $-C_{11}H_{23}$; for Tween 80, R is $-(CH_2)_7CH=CH(CH_2)_7CH_3$. Tween 20 and Tween 80 are the complex mixtures and $x + y + z + w$ equals 20.



where, $x + y + z + w = 20$.

Figure 3-4 Molecular Structure of Tween Surfactants
(Adapted from Sigma-Aldrich Canada, 2001)

Tween 20 and Tween 80 were purchased from Sigma-Aldrich Canada and used as received. The properties of Tween 20 and Tween 80 are listed in Table 3-2.

Table 3-2 The Properties of Selected Surfactants

Surfactant	Trade Name	Molecular Formula	Molecular Weight	Specific Gravity	CMC (mg/L)*
Tween 20	Polyoxyethylene sorbitan monolaurate	$C_{58}H_{114}O_{26}$	1225	1.1	60
Tween 80	Polyoxyethylene sorbitan monooleate	$C_{64}H_{124}O_{26}$	1310	1.07	13

* Dawson et al. (Eds.), 1986.

(3) Sodium Chloride

Sodium chloride was used to prepare different ionic strength solutions. Sodium chloride used in this research was purchased from BDH with a minimum purity of 99%.

(4) Methanol

Methanol was used to prepare VOC stock solutions since the VOCs have small solubility. Methanol used in this research was purchased from EM Science, Gibbstown, NJ, with purity of 99.99%.

(5) Water

The lab water used in this research was distilled, deionized water (D.D. water).

(6) Equipment

The apparatus used in the sample preparation were Brinkmann Transferpettor Digital (range: 2~10mL), Hamilton Microliter (range: 0~10 μ L, 0~50 μ L), Laboratory Rotator-Model G2, and Mettler AE 163 analytical balance with a precision of 1/10000 gram.

The equilibrium partitioning of volatile organic compounds among micellar, aqueous and gaseous phases, or between aqueous and gaseous phases was established in the headspace sample vials. The vials were 22 mL glass vials equipped with an aluminum crimp cap and a Teflon-faced silicone septum. After each use, the vials were washed with detergent, rinsed with tap and D.D. water and dried in an oven at 110°C.

The headspace sample vials, aluminum crimp caps and Teflon-faced silicone septa were purchased from Chromatographic Specialties INC., Brockville, Ontario, Canada.

The prepared sample vials were placed in a Varian Genesis Headspace Auto-Sampler carousel. Sampling and VOC concentration analysis were performed by the headspace auto-sampler and gas chromatography (Varian Star 3400CX) system. Headspace auto-sampler and GC were purchased from Varian Analytical Instruments.

3.2.2 Preparation of Solutions and Sample Vials

(1) Surfactant Stock Solutions

Tween 20 stock solution was prepared as follows: 6 mL Tween 20 was transferred to a 0.5L volumetric flask and diluted to the mark with D.D. water and stirred for more than a half hour. The concentration of Tween 20 stock solution was 13200 mg/L (about 220 times CMC).

Tween 80 stock solution was prepared as follows: 3 mL Tween 80 was transferred to a 1L volumetric flask and diluted to the mark with D.D. water and stirred for more than a half hour. The concentration of Tween 80 stock solution was 3210 mg/L (about 247 times CMC).

(2) VOC Stock Solutions

Benzene stock solution --- 2 mL benzene was diluted to 10 mL with methanol.

Toluene stock solution --- 2 mL toluene was diluted to 10 mL with methanol.

TCE stock solution --- 2 mL TCE was diluted to 10 mL with methanol.

(3) Sample Vials

10 mL D.D. water or surfactant stock solution was transferred by Brinkmann Transferpettor Digital to a 22 mL headspace sample vial. Then an amount of VOC was added to the vial by a Hamilton Microliter which was inserted under the aqueous surface in order to minimize mass loss by volatilization. The vial was then sealed with a Teflon-faced silicone septum and an aluminum crimp cap immediately after injecting the VOC. Because of the low aqueous solubility of VOCs, methanol was used as a solvent in preparation of VOC stock solutions injected into the vials containing only water. The methanol effect on the partitioning of VOCs between aqueous phase and gaseous phase is discussed in Section 3.3.2. Pure VOC was injected into the vials containing surfactant solution. Each sample was prepared in duplicate. Prepared vials were put in a Laboratory Rotator-Model G2 and shaken for an appropriate time (the required shaking time is discussed in Section 3.3.1) at 300 rpm, then stabilized for 5 minutes in order to reach equilibrium.

3.2.3 The Headspace Auto-Sampler and Gas Chromatography System Set-Up

(1) Headspace Auto-Sampler

After equilibrium among phases (micellar, aqueous, gaseous) was achieved, the headspace sample vials were placed into the Genesis headspace auto-sampler which has a sample vial carousel with a maximum capacity of 50 vials. The auto-sampler takes a headspace sample from each vial and injects it into the GC automatically.

Each headspace sample vial was raised onto the sampling needle, the needle punctures the vial septum, and 1 mL of helium gas then fills the vial through the needle. A gas sample from the headspace is then drawn through the GC to the flame ionization detector (FID) by the helium carrier gas. The organic compound concentration in the headspace then can be determined by converting the GC peak area counts recorded by the detector (Wan, 1998). Headspace auto-sampling has advantages over manual injection as it provides automated injection of samples and better reproducibility (Wan, 1998). The set-up conditions for the headspace auto-sampler used in this research are listed in Table 3-3.

(2) Gas Chromatography

The basic units of the gas chromatography system are the chromatographic column and the detector. The column separates the test mixture into its components, and the detector records the concentrations of the separated components. The detector response to the separated compounds is recorded automatically. Separation in the GC column is based on difference in the distributions of the molecules of the components being separated between the mobile gas phase and the stationary phase. The stationary phase is supported as a thin coating on the inner surface of the column wall. A dynamic equilibrium is established between these phases for each component of the test mixture. At the moment of injection of the test mixture, all substances are located at the head of the column and distributed between the stationary phase and the gas phase in equilibrium. Under the action of the flow of carrier gas, the components of the mixture in the gas phase move along the chromatographic column to the detector. The components of the

mixture remaining in the stationary phase will be partitioned and redistributed between the gas phase and the stationary phase. Therefore, the readily sorbable components move along the column more slowly than sparingly sorbable components, which result in separation of the components. The rate of movement through the column for each component depends on its distribution constant between the gas and stationary phases.

Table 3-3 Headspace Auto-sampler Set-up Conditions

Item	Parameter
Platen (Platen Temperature)	25°C
Platen Equil (Platen Equilibrium Time)	0 min
Sample Equil (Sample Equilibrium Time)	0 min
Vial Size (The Size of Sample Vial)	20 mL
Mixer (Auto-Mixer)	OFF
Mix (Mixing Time)	No
Mix Power	No
Stabilize (Stabilization Time)	No
Cap Cool Down	NI min at NI
Press (The Set-up Pressure in the Sample Vial)	0.35 psi
Press Equil (Pressure Equilibrium Time)	0.25 min
Loop (Loop Fill Time)	0.50 min
Loop Equil (Loop Equilibrium Time)	0.20 min
Inject (Length of the Time for the Injection)	1.0 min
Cap Inject	NI min at NI
Valve (Temperature of Valve)	100°C
Line (Temperature of Transfer Line)	160°C
Capillary	NI
Inject per Vail (Injection Times for the Sample Vial)	1
GC Cycle Time	5 min
Parameter Optimization	OFF

The set-up conditions for the gas chromatography used in this research are listed in Table 3-4.

Table 3-4 GC Set-up Conditions

Item	Parameter
Initial Column Temp (Initial Column Temperature)	70°C
Initial Col Hold Time (Hold Time at Initial Column Temp)	4 min
Temp Program Column	No
Inject Temp (Temperature of Injector)	210°C
Detector Temp (Temperature of Detector)	250°C
Detector A or B (Detector been chosen)	A
FID Initial Atten (Initial Attenuation of FID)	8
FID Initial Range (Initial Range of FID)	11
FID A Autozero On?	Yes
Time Program FID A?	No
FID B Initial Atten (Initial Attenuation of FID)	8
FID B Initial Range (Initial Range of FID)	10
FID B Autozero On?	No
Time Program FID B?	No
Add Intergration Section?	No
Add Time Events Section?	No
Add Peak Table Section?	No
Method Complete-end Time	4 min

3.3 Preliminary Tests

3.3.1 Equilibration Time Test

In order to determine the time required for VOC equilibrium among micellar, aqueous and gaseous phases, or between aqueous and gaseous phases in the headspace sample vial, an equilibration time test is required. A set of sample vials containing VOC

solution in which surfactant was present or absent were tested by the headspace auto-sampler and gas chromatography system at different elapsed times. The GC response area counts indicated the VOC concentration in the headspace. When the response changed by less than 3%, equilibrium among micellar, aqueous and gaseous phases, or between aqueous and gaseous phases was assumed to be reached.

3.3.2 Methanol Effect Test

Since methanol was used as a solvent to prepare the VOC stock solutions (which were subsequently used to prepare the sample vials containing water only), the effect of methanol on the partitioning of VOC between aqueous phase and gaseous phase was investigated.

VOC stock solutions were 20% (v/v), and the volumes added into sample vials without surfactant were 5 to 15 μL . Therefore, the methanol concentrations in the sample vials will be 0.04% to 0.12% (v/v). The partitioning of benzene, toluene and TCE in 0%, 0.04%, 0.08%, 0.12% and 0.20% (v/v) methanol solutions were tested to determine the effect of methanol on the partitioning of VOCs between aqueous and gaseous phases.

3.4 Environmental Effects on Solubilization

3.4.1 Temperature Effect

The effect of temperature on the CMC of surfactant in aqueous medium is complicated. Temperature increase causes a decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes a

disruption of the structured water surrounding the hydrophobic group, which hinders micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range (Rosen, 1978).

Temperature has an effect on the extent of micellar solubilization. The effect is dependent on the structure of the solubilizate and of the surfactant (Attwood and Florence, 1983). In most cases, the amount of solubilization increases with temperature. This effect has been considered to be due to changes of solubilizate aqueous solubility and changes of the micelle properties (Attwood and Florence, 1983).

For ionic surfactants, an increase in temperature generally results in an increase of solubilization for both polar and nonpolar solubilizates. This may be because increased thermal agitation increases the space available for solubilization in the micelle (Rosen, 1978).

For nonionic polyoxyethylenated surfactants, the effect of temperature increase appears to depend on the nature of the solubilizate (Rosen, 1978). Nonpolar materials, (such as aliphatic hydrocarbons and alkyl halides), which are solubilized in the inner core of the micelle, appear to show increased solubility as the temperature is raised, the increase becoming very rapid as the cloud point of the surfactant is approached (Saito, 1967). The sudden onset of turbidity of a nonionic surfactant solution on raising the temperature is called the cloud point (Schick, 1967; Rosen, 1978). This rapid increase of

solubility just below the cloud point probably reflects the large increase in aggregation number of the micelles in this region (Rosen, 1978). Polar materials, which are solubilized in the palisade layer of the micelle, show a gentle or moderate increase of solubilization, caused by the increase of thermal agitation of the surfactant molecules in the micelles. Further temperature increase will cause dehydration and the polyoxyethylene chains coil tighter. This decreases the space available in the palisade layer, which results in a solubilization decrease.

Since this research is providing information for surfactant enhanced subsurface remediation, a temperature effect study was carried over the expected subsurface temperature range. Therefore, 5°C, 10°C, 15°C and 20°C were chosen to test the solubilization of benzene, toluene and TCE in Tween 20 solution (13200 mg/L) and Tween 80 solution (3210 mg/L). Sample vials were prepared in a temperature-controlled room, then placed in the Genesis Headspace Auto-Sampler's carrousel and analyzed by GC.

3.4.2 Ionic Strength Effect

In general, the effect of adding electrolytes to nonionic systems seems to result in a drop in the CMC, but the lowering of the CMC of polyoxyethylenated nonionic surfactants following the addition of electrolytes is very small (Elworthy et al., 1968).

For ionic surfactants, the addition of electrolytes appears to increase the solubilization for nonpolar solubilizates (Klevens, 1950), which are solubilized in the

inner core of the micelle. Increased solubilization occurs due to a decrease of repulsion between the similarly charged ionic surfactant head groups which causes a decrease of the CMC and an increase of the aggregation number and the volume of the micelles. The addition of electrolytes appears to decrease solubilization for polar solubilizates (Klevens, 1950), which are solubilized in the palisade layer. Decreased solubilization occurs due to the decrease of repulsion of the ionic head groups causing closer packing of the surfactant molecules in the palisade layer and a decrease in the volume available for solubilization of polar solubilizates.

For nonionic surfactants, the addition of electrolytes appears to increase solubilization only when the electrolyte addition causes an increase in the aggregation number of the micelle.

Sodium chloride was used to increase ionic strength. Sodium chloride crystal was heated at 110°C in an oven for more than 1 hour and cooled in a desiccator before use to remove hydrated water. Sodium chloride was weighed by a Mettler AE 163 analytical balance with a precision of 0.1 mg. Solutions of 0.1 M, 0.3 M, 0.5 M and 0.64 M NaCl were chosen to test the effect of ionic strength on solubilization of benzene, toluene and TCE in Tween 20 solution (13200 mg/L) and Tween 80 solution (3210 mg/L). A concentration of 0.64 M NaCl was chosen to simulate seawater.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Preliminary Tests Results

4.1.1 Linear Response Test Results

According to Wan (1998), the GC only responds linearly within a certain VOC concentrations range. The actual VOC concentrations used in the tests have to be confirmed to be within the linear range by preliminary tests. In order to examine the linear response of the GC FID detector, different pure VOC volumes were added to D.D. water and Tween 20 solution (660 mg/L) and Tween 80 solution (149.8 mg/L). The results are shown in Figure 4-1 to 4-4.

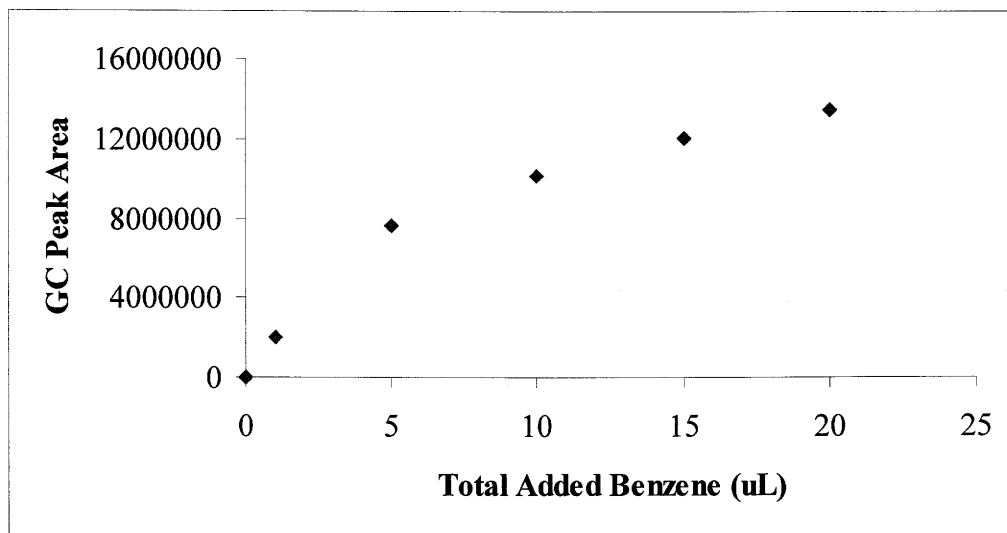


Figure 4-1 GC Response Test for Benzene in D.D. Water

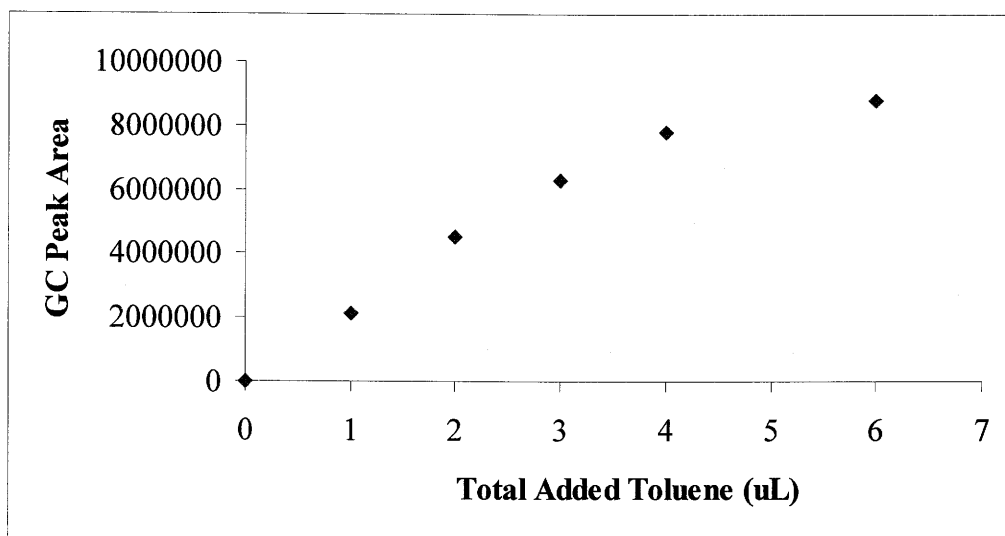


Figure 4-2 GC Response Test for Toluene in D.D. Water

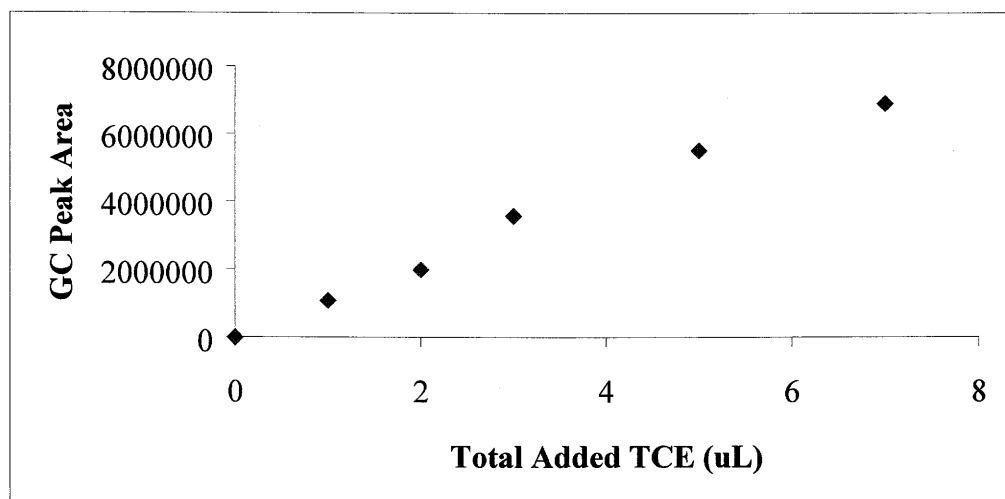


Figure 4-3 GC Response Test for TCE in D.D. Water

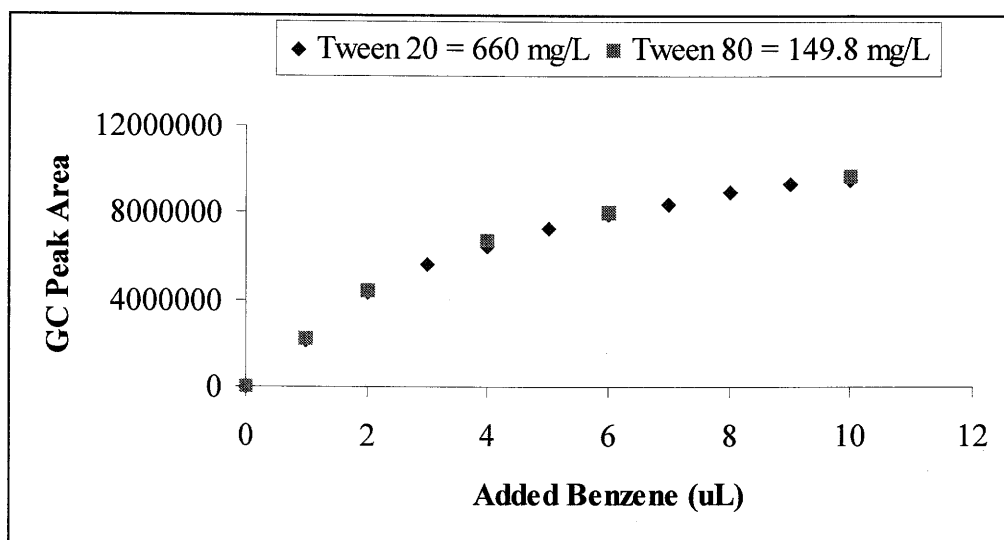


Figure 4-4 GC Response Test for Benzene in Surfactant Solutions

Figures 4-1 to 4-4 show that there is a limited linear response range of GC. To ensure linear GC response, the added ranges of selected VOCs were 0 to 2.4 μ L for benzene, 0 to 3 μ L for toluene, and 0 to 3 μ L for TCE, respectively.

4.1.2 Equilibration Time Test Results

As described in Chapter Three, the equilibrium of organic solute among micellar, aqueous and gaseous phases, or between aqueous and gaseous phases has to be reached before measuring the headspace concentration in the sample vials. The establishment of equilibrium is imperative for determining the micelle-water partition coefficient. A set of vials containing VOC solution with and without surfactant present was tested after different shaking times by the headspace auto-sampler and GC system. The results are shown in Figure 4-5 to 4-7.

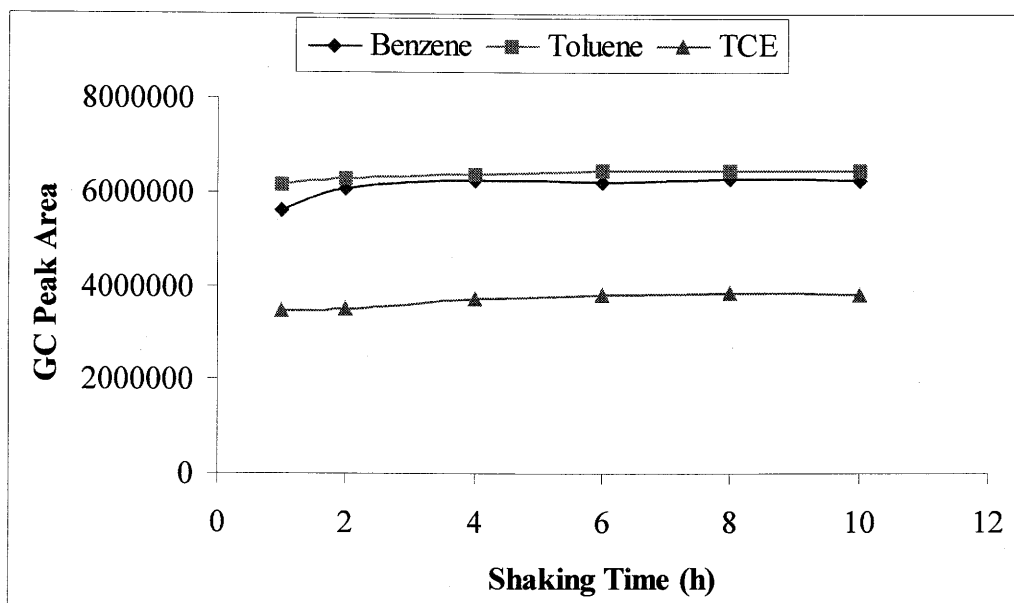


Figure 4-5 Equilibration Time Test in the Solution without Surfactant

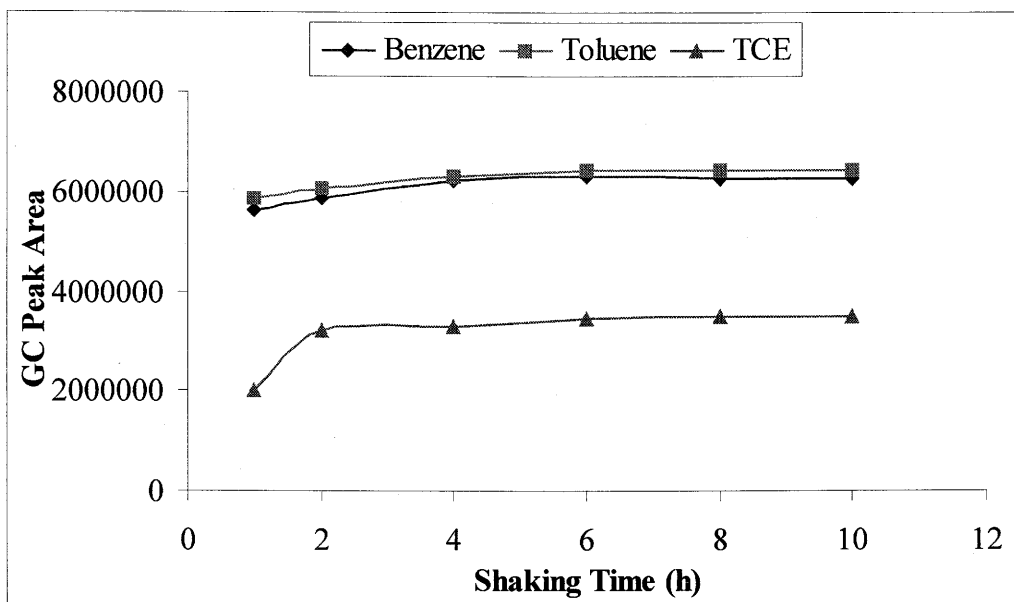


Figure 4-6 Equilibration Time Test in the Tween 80 Solution (Concentration of Tween 80 = 749 mg/L)

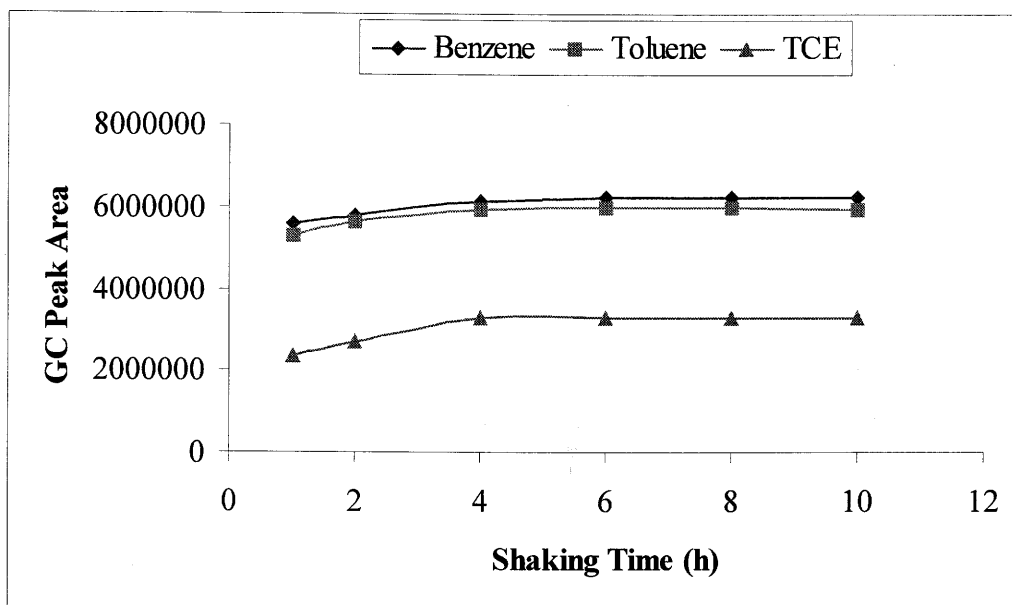


Figure 4-7 Equilibration Time Test in the Tween 20 Solution (Concentration of Tween 20 = 330 mg/L)

Figure 4-5 shows the experimental results of the equilibration time test for selected VOCs in the solution without surfactant. Figure 4-6 shows the results of the equilibration time test for selected VOCs in the Tween 80 solution. The Tween 80 concentration was 749 mg/L (about 57.6 times CMC (see Table 3-2)), which was the minimum concentration of Tween 80 used in this research. Figure 4-7 shows the experimental results for selected VOCs in the Tween 20 solution. The concentration of Tween 20 was 330 mg/L (about 5.5 times CMC(see Table 3-2)), which was the minimum concentration of Tween 20 used in this research. Table 4-1 shows that the selected VOCs GC response changed by less than 3% after 6 hours shaking with either surfactant absent or present, i.e., 6 hours shaking time was enough to reach the equilibrium for the three selected VOCs either among micellar, aqueous and gaseous phases or between aqueous and gaseous phases. To ensure that full equilibrium either among micellar, aqueous and gaseous phases or between aqueous and gaseous phases would be reached and to

facilitate experimental control, 24 hours of shaking time was chosen for all tests in this research.

Table 4-1 Relative GC Response Change at Different Shaking Times (%)

Time (Δh)	DDW			Tween 20			Tween 80		
	Benzene	Toluene	TCE	Benzene	Toluene	TCE	Benzene	Toluene	TCE
1~2	4.03	0.83	0.56	1.68	2.94	6.17	1.85	1.58	22.65
2~4	1.26	0.70	3.15	2.90	2.75	10.20	3.05	1.94	1.53
4~6	0.06	0.76	1.06	0.59	0.40	0.19	0.55	0.96	2.20
6~8	0.37	0.01	0.47	0.02	0.07	0.07	0.27	0.01	0.54
8~10	0.12	0.00	0.48	0.06	0.52	0.02	0.14	0.05	0.19

4.1.3 Methanol Effect Test Results

Benzene, toluene, and TCE in 0%, 0.04%, 0.08%, 0.12% and 0.20% (v/v) methanol solutions were tested to examine the methanol effect on the partitioning of these selected VOCs between aqueous and gaseous phases. The results are shown in Figure 4-8 and Table 4-2.

Table 4-2 Relative Deviation of GC Peak Area Counts at Different Methanol Concentrations for Selected VOCs (%)

Methanol Concentration (%)	Benzene	Toluene	TCE
0.00	0.43	0.79	0.42
0.04	0.50	0.52	0.33
0.08	0.10	0.50	0.22
0.12	0.08	0.47	0.69
0.20	1.11	0.34	0.56

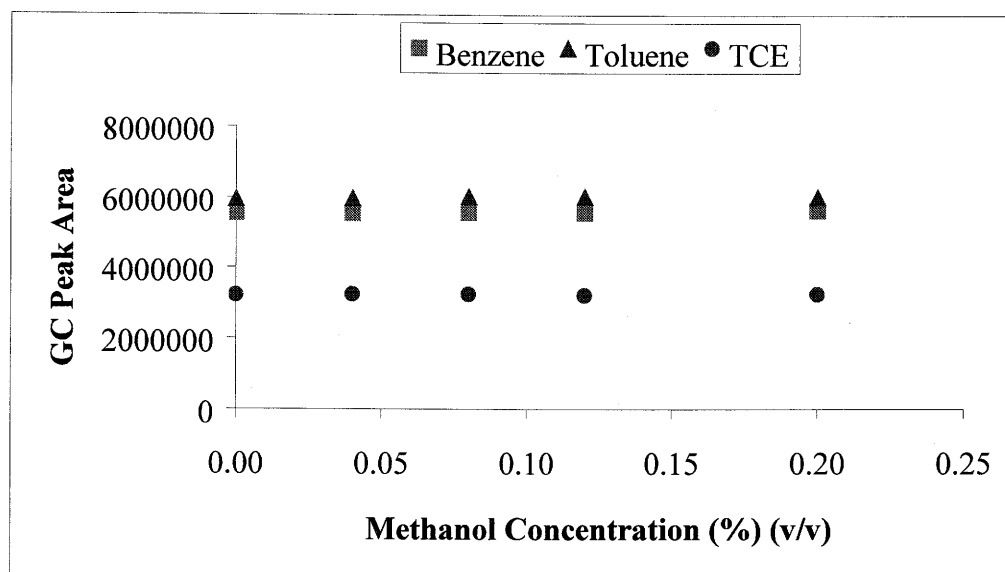


Figure 4-8 Methanol Effect on the Partitioning of Selected VOCs

As shown in Figure 4-8 and Table 4-2, the GC peak area counts had little change for benzene, toluene, and TCE in different methanol concentration solutions. All relative deviations of GC peak area counts at different methanol concentrations were less than 1% (except benzene in 0.20% (v/v) methanol solution, which is 1.11%) (see Table 4-2). It can be concluded that methanol has little effect on the partitioning of selected VOCs between aqueous and gaseous phases in this research. Gossett (1987) also observed that methanol, which was used to prepare VOC stock solutions, had negligible effect on determining Henry's Law constants.

4.2 Partitioning of VOCs among Micellar, Aqueous and Gaseous Phases

Since the Henry's law constant is a function of temperature, it is necessary to determine the Henry's law constant at the partitioning test temperature before determining the micelle-water partition coefficient, K_m .

According to Wan (1998), the relationships of selected VOC Henry's constant and temperature are given by the following:

for benzene:

$$\log_{10} H_M = 7.07 - \frac{1373}{(T + 273.2)} \quad (4-1)$$

for toluene:

$$\log_{10} H_M = 7.83 - \frac{1588}{(T + 273.2)} \quad (4-2)$$

for TCE:

$$\log_{10} H_M = 8.17 - \frac{1637}{(T + 273.2)} \quad (4-3)$$

where, H_M is Henry's constant, atm;

T is temperature, °C.

H_M can be converted to H (dimensionless) according to following formula:

$$H = \frac{H_M}{55.56R(T + 273.2)} \quad (4-4)$$

where, R is the ideal gas constant, 8.2054×10^{-5} atm·m³/mol·K.

For the partitioning tests conducted at room temperature, $21 \pm 1^\circ\text{C}$, H is 0.189 for benzene, calculated by Equation (4-1) and (4-4); H is 0.202 for toluene, calculated by Equation (4-2) and (4-4); and H is 0.301 for TCE, calculated by Equation (4-3) and (4-4).

As described in Chapter Three, parameters (a and b) can be directly determined from the plot of GC peak area against the molar concentration of total VOC added to the

aqueous phase. According to the formulae in Chapter Three, the micelle-water partition coefficient can be calculated by Equation (3-10), (3-12) and (3-14).

$$K_m = \frac{X_m}{X_a} \quad (3-10)$$

$$X_m = \frac{b}{b + (C - CMC)} \quad (3-12)$$

$$X_a = \frac{a}{55550(1 + H \frac{V_a}{V})} \quad (3-14)$$

4.2.1 Benzene

Solubilization of benzene in Tween 20 solution was investigated at different Tween 20 concentrations (330 mg/L, 3300 mg/L, and 13200 mg/L) and the results are shown in Figure 4-9, 4-10, and 4-11 according to the description in Chapter Three. The results for benzene in Tween 80 solutions (749 mg/L and 3210 mg/L) are shown in Figure 4-12 and Figure 4-13.

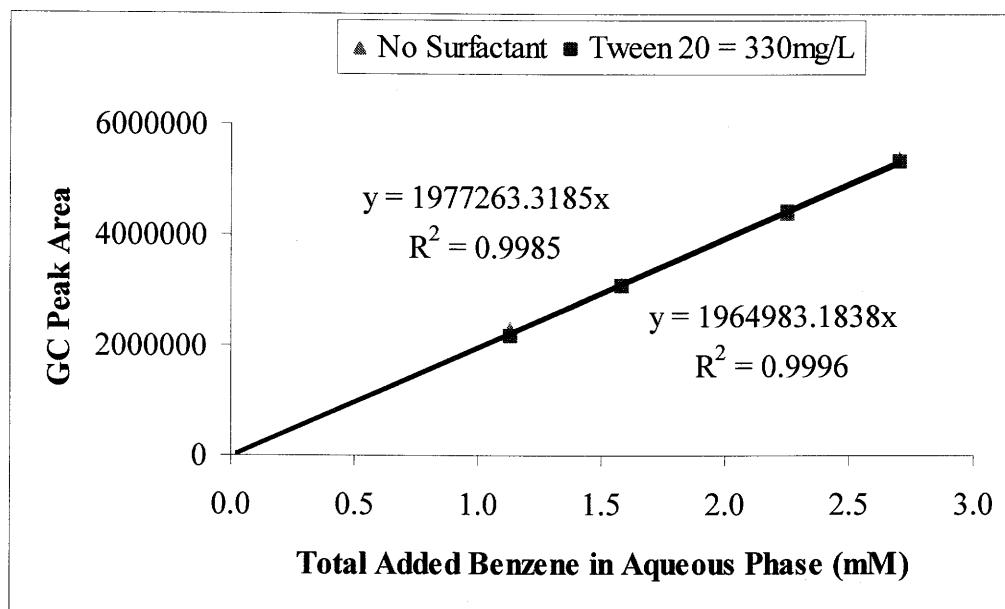


Figure 4-9 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 330 mg/L)

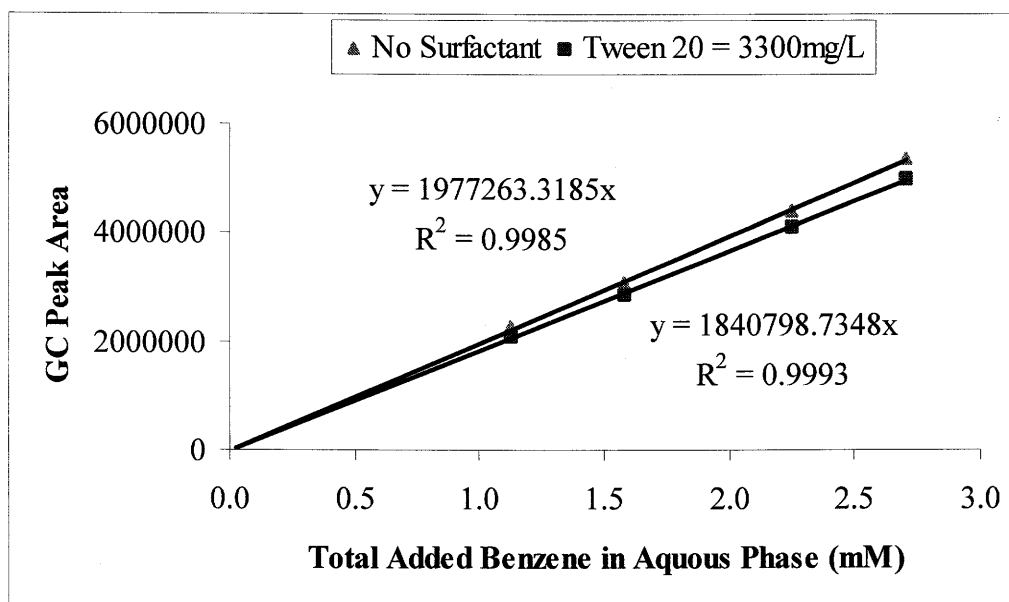


Figure 4-10 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 3300 mg/L)

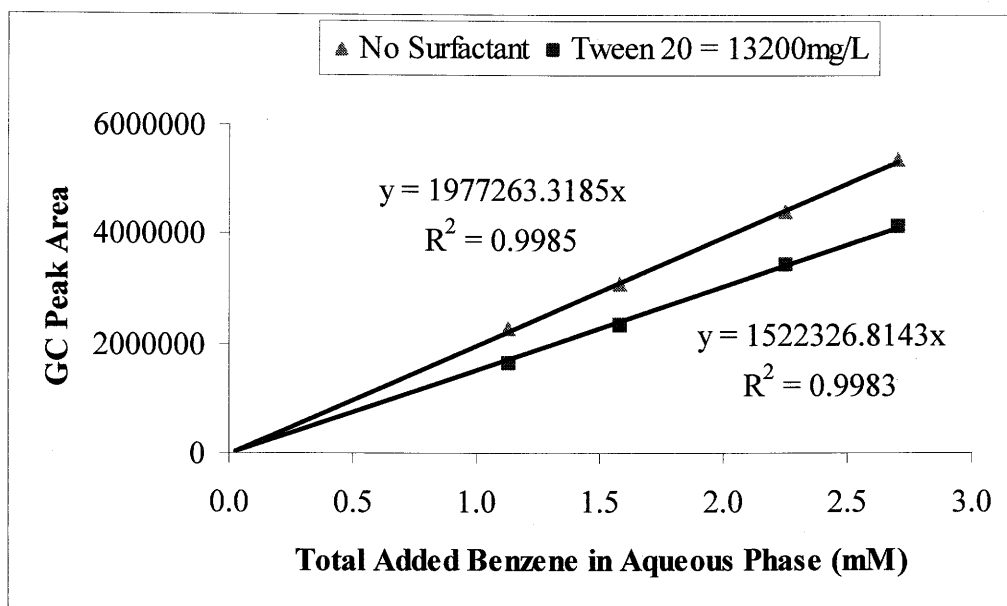


Figure 4-11 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 13200 mg/L)

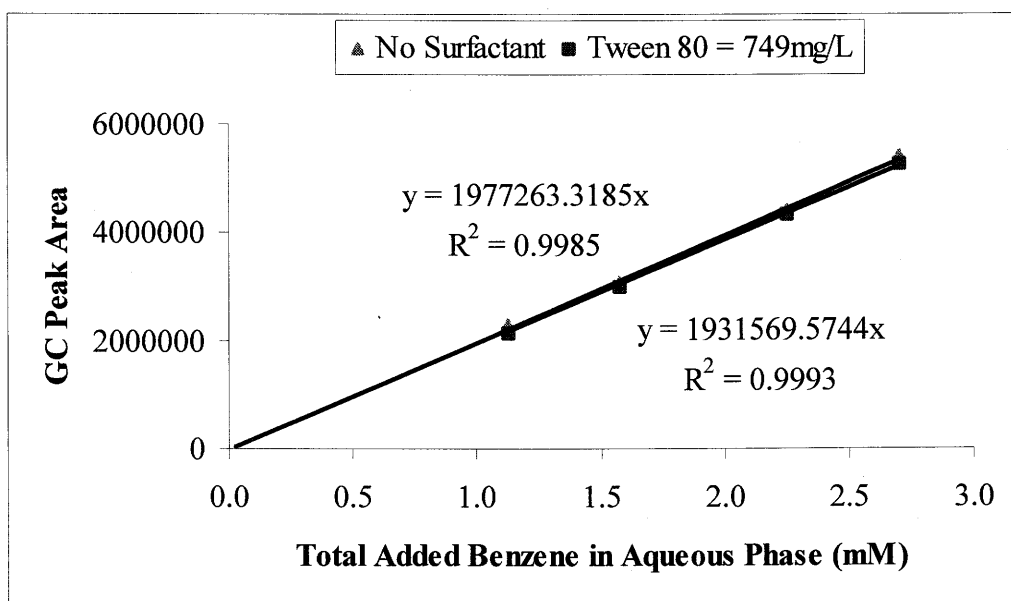


Figure 4-12 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) (Tween 80 = 749 mg/L)

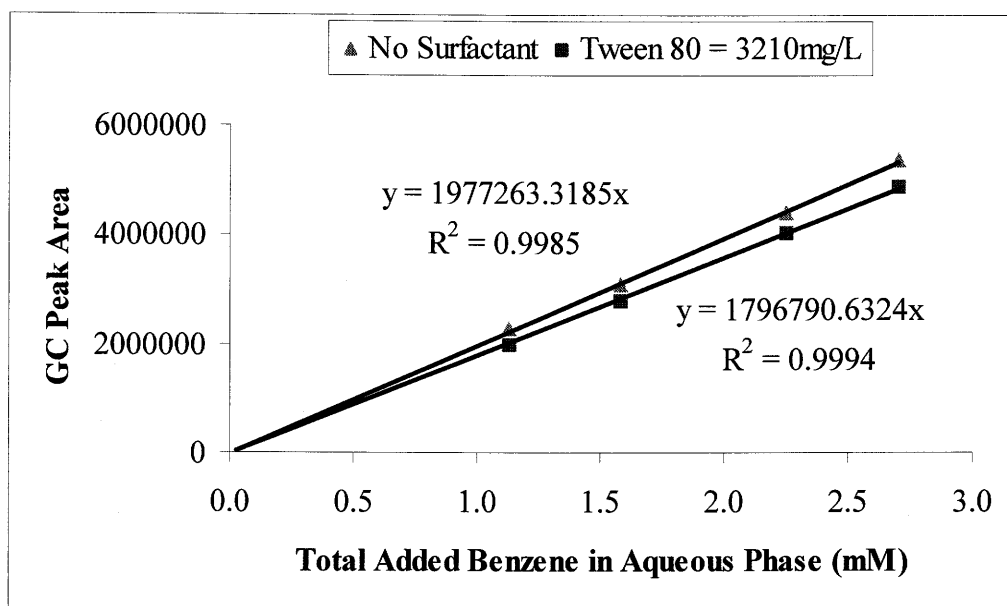


Figure 4-13 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) (Tween 80 = 3210 mg/L)

Figure 4-9, 4-10, and 4-11 show the headspace data for benzene with and without Tween 20 micelles. Figure 4-12 and 4-13 show the headspace data for benzene with and without Tween 80 micelles. For each data point, the GC peak area was the average of duplicate sample reading. It is apparent that the headspace concentrations of benzene in Tween 20 or Tween 80 solutions were lower than those in pure water. This indicates that benzene was partitioning into the micellar phase. These figures also show when the concentration of surfactant was increased, more micelles were formed, the slope of Henry's law curve for benzene in surfactant solution decreased and the horizontal distance between the two curves, b , increased, i.e., the molar concentration of benzene in the micellar phase increased.

The original GC counts for benzene solubilization test by 13200 mg/L Tween 20 are listed in Table 4-3 as a typical example of primary experimental results. Table 4-3

shows that all the relative standard deviations over the two replicates are within 3%. The small deviation values show the high reproducibility of the headspace auto-sampler and gas chromatography system results.

Table 4-3 The Original Results for Benzene Solubilization Test by 13200 mg/L Tween 20

Added Benzene (mM)	GC Counts in Water	DEV*	GC Counts in Tween 20	DEV*
1.1269	2278820	0.06%	1687657	2.64%
	2280824		1625842	
1.5777	3073187	0.60%	2350453	0.71%
	3099261		2374028	
2.2538	4443359	1.31%	3430646	0.82%
	4362019		3470823	
2.7046	5390499	0.00%	4112262	1.23%
	5390177		4184542	

* --- relative standard deviation over the two replicates

The mole fraction of benzene in the aqueous phase (X_a) and the mole fraction of benzene in the micellar phase (X_m) can be determined from the above figures.

Using Figure 4-11 as an example, the concentration of Tween 20 was 13200 mg/L and the trendline of the upper curve (Henry's law curve for benzene in water) was $Y=1977263X$. The trendline of the lower curve (Henry's law curve for benzene in Tween 20 solution, with concentration of 13200 mg/L) was $Y=1522327X$.

Assuming $a = X_1$, $b = X_2 - X_1$ (see Figure 3-2),

then,

$$1977263X_1 = 1522327X_2$$

$$1977263a = 1522327(a + b)$$

$$b = 0.2988a$$

$$H = 0.189$$

$$V_a = 12mL$$

$$V = 10mL$$

$$C = 13200mg / L$$

$$CMC = 60mg / L \text{ (see Table 3-2)}$$

$$C - CMC = 13200 - 60 = 13140mg / L = 10.7265mM$$

According to Equation (3-14),

$$X_a = \frac{a}{55550(1 + H \frac{V_a}{V})} = \frac{a}{68148.74}$$

According to Equation (3-12),

$$X_m = \frac{b}{b + (C - CMC)} = \frac{b}{b + 10.7265}$$

Determining various a , b , X_a and X_m (see Table 4-4), and plotting X_m against X_a yields a linear relationship, the slope of which yields the micelle-water partition coefficient $K_m = 1814.4$ (see Figure 4-14).

Table 4-4 Variables Used to Calculate K_m			
a	b=0.2988a	$X_a=a/68148.74$	$X_m=b/(b+10.7265)$
0.0	0.0000	0	0
0.5	0.1494	7.33689E-06	0.01373679
1.0	0.2988	1.46738E-05	0.0271013
1.5	0.4482	2.20107E-05	0.04010846
2.0	0.5976	2.93476E-05	0.05277241

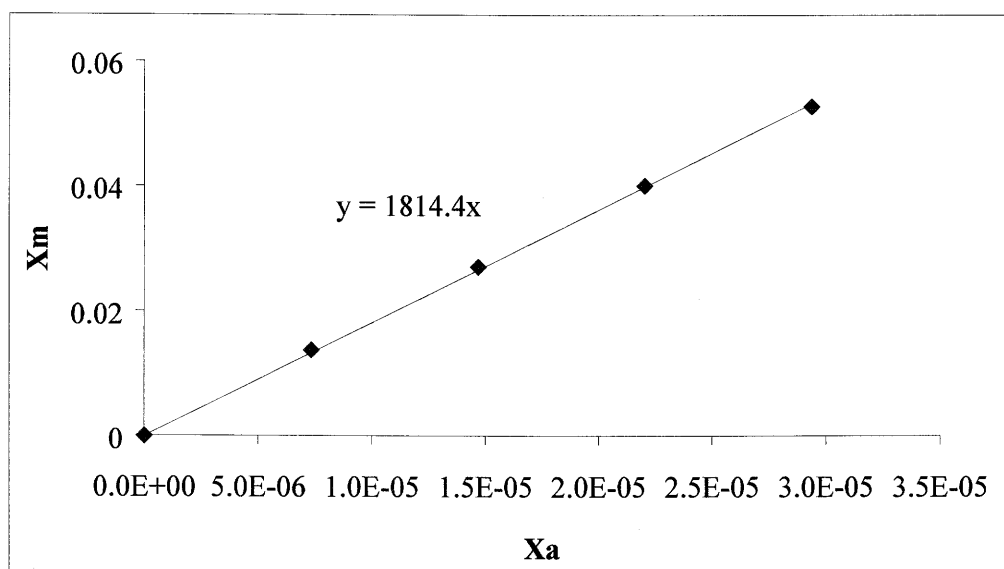


Figure 4-14 Distribution of Benzene between the Aqueous and Micellar Phases (Tween 20 = 13200 mg/L, at 21°C)

According to Figure 4-9, 4-10, 4-11, 4-12, 4-13 and Equation (3-10), (3-12), and (3-14), the average micelle-water partition coefficient, K_m , for benzene in Tween 20 solutions was 1823.4 ± 8.5 (average \pm standard deviation), and average K_m for benzene in Tween 80 solutions was 2650.4 ± 36.6 .

The fraction of VOC partitioned into micelles, f_m , can also be obtained from the Henry's law curves. The fraction, f_m , is calculated from the values of a and b as follows:

$$f_m = \frac{b}{a+b} \quad (3-15)$$

f_m for benzene in different surfactant solutions is calculated by the Equation (3-15) using Figure 4-9, 4-10, 4-11, 4-12 and 4-13. The results are listed in Table 4-5.

Table 4-5 **Summary of f_m for Benzene in Different Surfactant Solutions**

Tween 20		Tween 80	
C (mg/L)	f_m	C (mg/L)	f_m
330	0.006	749	0.023
3300	0.069	3210	0.091
13200	0.230		

Table 4-5 shows that 0.6% of the benzene added to a Tween 20 solution partitioned into the micellar phase when the Tween 20 concentration was 330 mg/L. The amount of benzene bound to Tween 20 micelles increased to 6.9% of total added when the concentration of Tween 20 increased to 3300 mg/L, and to 23% when the concentration of Tween 20 increased to 13200 mg/L. 2.3% of the benzene added to a 749 mg/L Tween 80 solution partitioned into the Tween 80 micellar phase and 9.1% of the benzene added to a 3210 mg/L Tween 80 solution was bound by Tween 80 micelles. This shows that f_m is proportional to the surfactant concentration.

The behavior of f_m versus Tween 20 and Tween 80 micellar concentration is shown in Figure 4-15. This figure shows that Tween 80 micelles solubilized more benzene than Tween 20 micelles did at the same micellar concentration, i.e., Tween 80

micelles were more effective than Tween 20 micelles for solubilizing benzene at a specific surfactant micellar concentration.

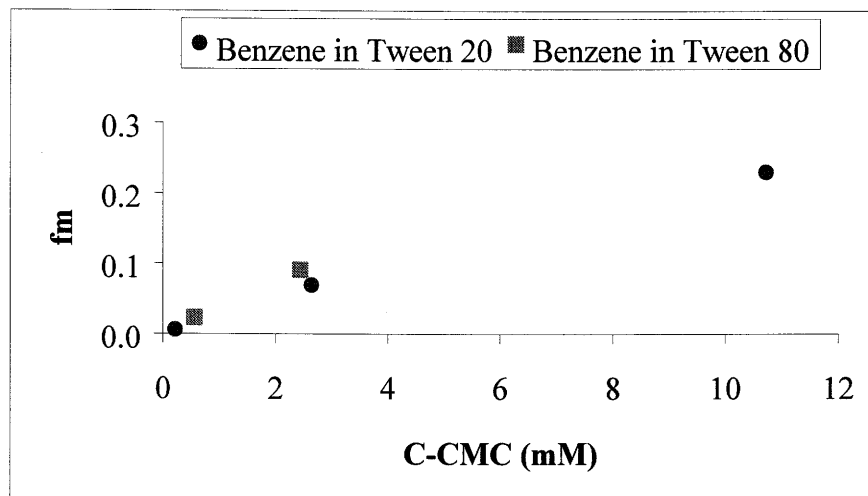


Figure 4-15 f_m vs. Surfactant Micellar Concentration for Benzene

4.2.2 Toluene

Solubilization of toluene by Tween 20 micelles was studied in different Tween 20 solutions (330 mg/L, 3300 mg/L, and 13200 mg/L) and the results are shown in Appendix A (Figure A-1, A-2, and A-3). The results for toluene in Tween 80 solutions (749 mg/L and 3210 mg/L) are shown in Appendix A (Figure A-4 and A-5).

Figure A-1 to Figure A-5 show that the headspace concentrations of toluene in Tween 20 or Tween 80 solutions were lower than those in pure water, similar to the results for benzene. This indicates that toluene was partitioning into the micellar phase. These figures also show when the concentration of surfactant increased, more micelles were formed, the slope of Henry's law curve for toluene in surfactant solution decreased

and the horizontal distance between the two curves, b , increased, i.e., molar concentration of toluene in the micellar phase increased (see Table 4-6).

Table 4-6 Slope of Henry's Law Curve for Toluene in Different Solutions

Solution		Slope of Henry's Law Curve
No Surfactant		2310825
Tween 20	330mg/L	2262439
	3300mg/L	1839807
	13200mg/L	1172365
Tween 80	749mg/L	2118976
	3210mg/L	1660116

The average micelle-water partition coefficient, K_m , for toluene in Tween 20 solution was 5755.4 ± 21.8 , calculated from Figure A-1, A-2, A-3 and Equation (3-10), (3-12), (3-14). Average K_m for toluene in Tween 80 solution was 8780.4 ± 14.1 , calculated from Figure A-4, A-5 and Equation (3-10), (3-12), (3-14).

The fraction f_m for toluene in different surfactant solutions is calculated using Equation (3-15) and Figure A-1, A-2, A-3, A-4, and A-5. The results are listed in Table 4-7.

Table 4-7 Summary of f_m for Toluene in Different Surfactant Solutions

Tween 20		Tween 80	
C (mg/L)	f_m	C (mg/L)	f_m
330	0.021	749	0.083
3300	0.204	3210	0.282
13200	0.493		

It is shown in Table 4-7 that 2.1% of toluene added to a Tween 20 solution with concentration of 330 mg/L partitioned into the micellar phase. The amount of toluene bound to Tween 20 micelles increased to 20.4% of total added when the Tween 20 concentration increased to 3300 mg/L. Further, the amount increased to 49.3% of total added when the Tween 20 concentration increased to 13200 mg/L. The amount of toluene bound to Tween 80 micelles was 8.3% of total added when the Tween 80 concentration was 749 mg/L, and increased to 28.2% when the Tween 80 concentration increased to 3210 mg/L. This shows that f_m is proportional to the surfactant concentration. These results are consistent with benzene in Tween 20 and Tween 80 solutions.

The behavior of f_m for toluene versus surfactant micellar concentration is shown in Figure 4-16. The results show that Tween 80 micelles solubilized more toluene than Tween 20 micelles did at the same micellar concentration, i.e., Tween 80 micelles have more solubilizing power for toluene than Tween 20 micelles at a specific surfactant micellar concentration.

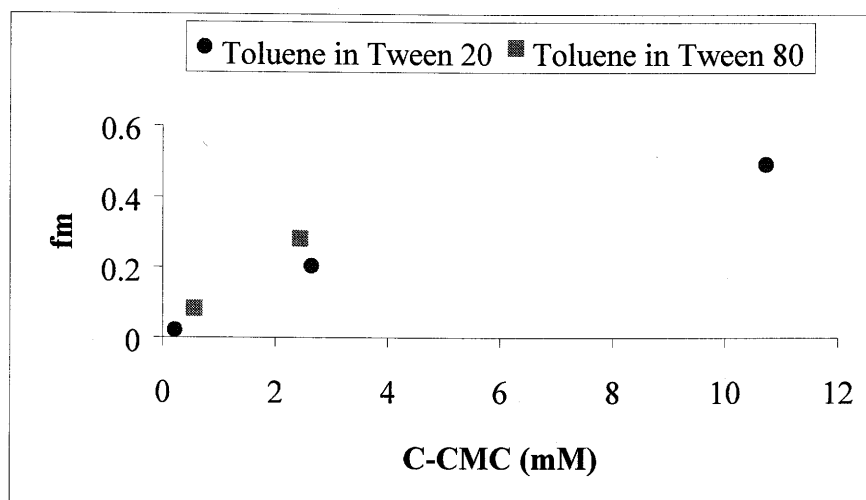


Figure 4-16 f_m vs. Surfactant Micellar Concentration for Toluene

4.2.3 TCE

Solubilization results for TCE in Tween 20 solutions (330 mg/L, 3300 mg/L, and 6600 mg/L) are shown in Appendix A (Figure A-6, A-7, and A-8). The results for TCE solubilized in Tween 80 solutions (749 mg/L and 3210 mg/L) are shown in Appendix A (Figure A-9 and A-10).

From Figures A-6 to A-10, it is apparent that the headspace concentrations of TCE in Tween 20 and Tween 80 solutions were lower than those in pure water. This shows that TCE was partitioning into the Tween 20 or Tween 80 micellar phase. These figures also show when the concentration of surfactant increased, the more micelles were formed, the slope of Henry's law curve for TCE in surfactant solution decreased, and the horizontal distance between the two curves, b , increased, i.e., more TCE was solubilized by surfactant solution (see Table 4-8).

Table 4-8 Slope of Henry's Law Curve for TCE in Different Solutions

Solution		Slope of Henry's Law Curve
No Surfactant		961335
Tween 20	330mg/L	946882
	3300mg/L	812259
	6600mg/L	700919
Tween 80	749mg/L	909174
	3210mg/L	768200

The average micelle-water partition coefficient, K_m , for TCE in Tween 20 solutions was 4710.5 ± 6.7 , calculated using Figure A-6, A-7, A-8 and Equation (3-10), (3-12), (3-14). Average K_m for TCE in Tween 80 solutions was 6634.0 ± 33.0 , calculated using Figure A-9, A-10 and Equation (3-10), (3-12), (3-14).

The fraction f_m for TCE in different surfactant solutions is calculated using Equation (3-15) and Figure A-6, A-7, A-8, A-9 and A-10. The results are listed in Table 4-9.

Table 4-9 Summary of f_m for TCE in Different Surfactant Solutions

Tween 20		Tween 80	
C (mg/L)	f_m	C (mg/L)	f_m
330	0.015	749	0.054
3300	0.155	3210	0.201
6600	0.271		

Table 4-9 shows that 1.5% of total TCE added to Tween 20 solution partitioned into the micellar phase when the Tween 20 concentration was 330 mg/L. The amount of TCE bound to Tween 20 micelles increased to 15.5% of total added when the

concentration of Tween 20 increased to 3300 mg/L, and the amount increased to 27.1% of total added when the concentration of Tween 20 increased to 6600 mg/L. 5.4% of TCE added to Tween 80 solution with a concentration of 749 mg/L partitioned into the micellar phase, while 20.1% of TCE partitioned into the micellar phase in 3210 mg/L Tween 80 solution. This shows, similar to benzene and to toluene, that f_m is proportional to the surfactant concentration.

The behavior of f_m versus surfactant micellar concentration for the two surfactants studied (Tween 20 and Tween 80) is shown in Figure 4-17. The data clearly show that Tween 80 micelles solubilized more TCE than Tween 20 micelles did at the same micellar concentration, i.e., Tween 80 micelles were more effective than Tween 20 micelles in solubilizing TCE at a specific surfactant micellar concentration.

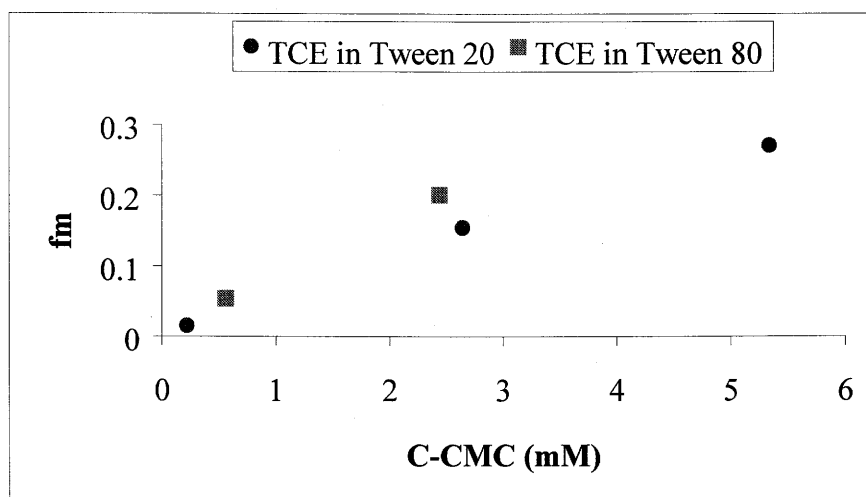


Figure 4-17 f_m vs. Surfactant Micellar Concentration for TCE

4.2.4 Summary

Table 4-5, 4-7 and 4-9 show that as surfactant concentration increased, the fraction of VOC bound to micelles also increased. This shows that f_m is proportional to the surfactant concentration. Therefore, as high a concentration of surfactant as possible should be used within economic and environmental constraints for surfactant-enhanced subsurface remediation.

These tables also show that Tween 80 micelles have more solubilizing capacity than Tween 20 micelles for the VOCs tested. This is because the decrease of interfacial free energy on micellization is greater for longer hydrocarbon chains than for short chains, and there is more water structure disruption for transfer of a long hydrocarbon chain into a micelle than a short one (Elworthy et al., 1968). Therefore, longer hydrocarbon chains cause a decrease in CMC and an increase in micelle size. Tween 80 has the same hydrophilic group as Tween 20 (see Chapter Three, Section 3.2.1 (2)). However, the hydrophobic group of Tween 80, which is $-(CH_2)_7CH=CH(CH_2)_7CH_3$, is longer than the hydrophobic group of Tween 20, which is $-C_{11}H_{23}$. As result, the CMC of Tween 80 is 13 mg/L, and the CMC of Tween 20 is 60 mg/L. This indicates that Tween 80 has a greater driving force for micellization. Thus Tween 80 micelles have more solubilization power than Tween 20 micelles.

Shinoda (1967) stated that benzene and toluene might dissolve to some extent in the hydrated polyoxyethylene core as well as in the inner hydrocarbon core. Ekwall et al. (1951) concluded that the smaller apolar solubilizates were situated in the hydrocarbon

core of the micelles. For solubilizates that are solubilized in the inner hydrocarbon core of the micelle, or deep in the palisade layer, the amount of material solubilized generally increases with the increase of micelle size. Therefore, any factor that causes an increase in either the diameter of the micelle or its aggregation number will increase the space available for solubilized materials and result in an increase of solubilization (Rosen, 1978). Since aggregation numbers increase with the increase of the "dissimilarity" degree between solvent and surfactant, an increase in the chain length of the hydrophobic portion of the surfactant generally results in the increased solubilization (Rosen, 1978). This is an additional reason why Tween 80 micelles have more solubilizing power than Tween 20 micelles.

It is shown in Table 4-10 that K_m decreased in the order of toluene, TCE, benzene for the same concentration of Tween 20 solution or Tween 80 solution. This is because toluene is more hydrophobic than benzene since toluene has a longer hydrocarbon chain than benzene. TCE is more hydrophobic than benzene, but less than toluene. It is concluded that K_m increased with the increase of solubilizate hydrophobicity. These results agree with reported trends in the literature for other compounds and micelles (Attwood and Florence, 1983; Valsaraj and Thibodeaux, 1989; Edwards et al., 1991; Shiau et al., 1994).

The solubility of compound can be used to as an indicating of the compound hydrophobicity. The lower the solubility is, the more hydrophobic the compound is. The solubility order for selected VOCs is benzene>TCE>toluene (see Table 4-10). Therefore,

the hydrophobic order for selected VOCs is toluene>TCE>benzene which agrees with the results of K_m .

The octanol-water partition coefficient K_{ow} is a parameter that represents the compound hydrophobicity. It is the ratio of the compound concentration that will dissolve in the octanol over the concentration that will dissolve in water. Usually, K_{ow} is expressed as a log value.

$$K_{ow} = \frac{C_{octanol}}{C_{water}} \quad (4-5)$$

Table 4-10 shows that $\log K_{ow}$ for toluene is greater than TCE, which is greater than benzene, i.e., the hydrophobicity order is toluene>TCE>benzene which agrees with the results of K_m .

Table 4-10 K_m for Selected VOCs in Nonionic Surfactants

VOC	Tween 20	Tween 80	Solubility ^{**}	Log K_{ow} ^{***}
Benzene	1823.4±8.5 [*]	2650.4±36.6	1780	2.13
TCE	4710.5±6.7	6634.0±33.0	1100	2.42
Toluene	5755.4±21.8	8780.4±14.1	500	2.69

*--- Average±Standard Deviation

** --- Fetter, 1993

*** --- Schwarzenbach et al., 1993

4.3 Environmental Effects on the Solubilization

Environmental effects, such as temperature and ionic strength, on the solubilization of benzene, toluene, and TCE in edible nonionic surfactant solutions were investigated. Since a high surfactant concentration was suggested for use in surfactant-enhanced subsurface remediation (see this chapter, Section 4.2.4), concentrations of

13200 mg/L and 3210 mg/L were chosen for Tween 20 solution and Tween 80 solution, respectively.

4.3.1 Temperature Effect

Temperature effect on the solubilization of benzene, toluene, and TCE in 13200 mg/L Tween 20 solution and in 3210 mg/L Tween 80 solution was studied. Measurements were conducted at 5°C, 10°C, 15°C, and 20°C.

Shimizu and Iwatsuru (1988) observed that the CMC value of Tween 20 was not affected by temperature (25°C~55°C). The concentration of Tween 20 used in the temperature effect studies was 13200 mg/L (about 220 times CMC). The concentration of Tween 80 used was 3210 mg/L (about 247 times CMC). Both of these concentrations were much greater than their CMC. Therefore, any change in CMC due to temperature change in this research would be negligible and the error introduced in the quantity C-CMC by using CMC = 60 mg/L for Tween 20 and CMC = 13 mg/L for Tween 80 would be minimal. Hence, evaluation of the specific CMC at different temperatures is unnecessary.

Henry's constants (Wan, 1998) for benzene, toluene, and TCE over a range of temperatures (5°C, 10°C, 15°C, and 20°C) are listed in Table 4-11.

Table 4-11 Henry's Constants for Selected VOCs at Different Temperatures

Temperature (°C)	Benzene	Toluene	TCE
5*	0.108	0.104	0.152
10*	0.129	0.129	0.190
15	0.154	0.163	0.241
20	0.180	0.196	0.291

* --- Calculated by Equation (4-1), (4-2), (4-3) and (4-4).

(1) Benzene

Solubilization results for benzene in Tween 80 solution (Tween 80 = 3210 mg/L) at 5°C, 10°C, 15°C, and 20°C are shown in Appendix B (Figure B-1, B-2, B-3, and B-4). Solubilization results for benzene in Tween 20 solution (Tween 20 = 13200 mg/L) at 5°C, 10°C, 15°C, and 20°C are shown in Appendix B (Figure B-5, B-6, B-7, and B-8).

Figures B-1 to B-8 show that when temperature increased, the slope of the upper curve (Henry's law curve for benzene in water) increased, and the slope of the lower curve (Henry's law curve for benzene in Tween 80 solution or Tween 20 solution) also increased (see Figure 4-18). This shows that as temperature increased, more VOCs were partitioned into the headspace from the aqueous phase. However, the difference (i.e., the horizontal distance) between the two curves, *b*, was not significantly affected by temperature increase over the range tested.

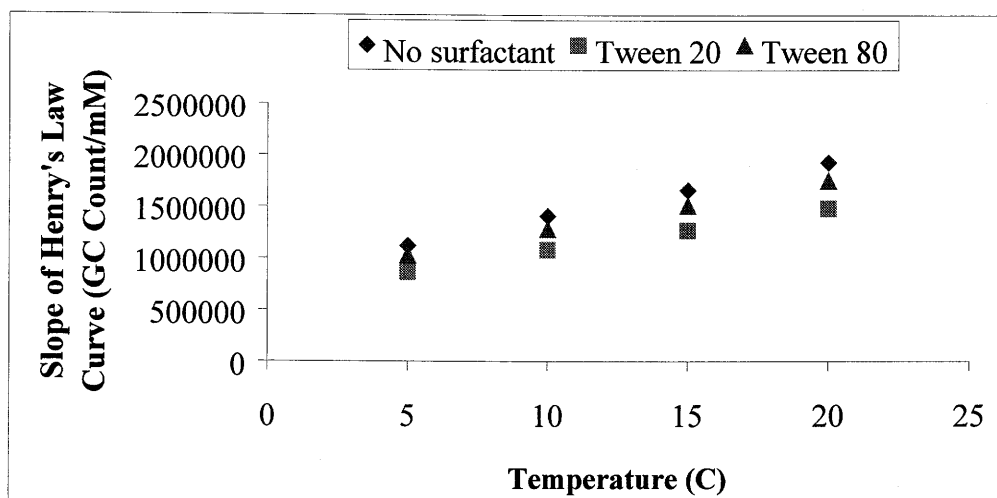


Figure 4-18 Temperature Effect on Solubilization of Benzene

The fraction of benzene partitioned into Tween 80 or Tween 20 micelles, f_m , and the micelle-water partition coefficient, K_m , for the different surfactant solutions at different temperatures are listed in Table 4-12.

Table 4-12 Summary of f_m and K_m for Benzene in Different Surfactant Solutions at Different Temperatures

T (°C)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
5	0.226	1633.2	0.083	2189.7
10	0.232	1726.4	0.092	2502.7
15	0.235	1797.0	0.091	2541.7
20	0.230	1797.2	0.091	2606.2

Table 4-12 shows the effect of temperature on the solubilizing power of Tween 20 and Tween 80 for benzene. 22.6% of total added benzene in Tween 20 solution partitioned into the Tween 20 micellar phase at 5°C. When the temperature increased to 10°C, the amount of benzene partitioned into Tween 20 micelles increased to 23.2% of

total added. At 15°C, the amount increased to 23.5% of total added, but at 20°C, the amount was 23% of total added. The absolute relative changes of f_m for benzene in Tween 20 solution over the temperature range tested were less than 1.4% (see Table 4-13). Therefore, there is little change of f_m for benzene in Tween 20 solution with the increase of temperature.

Table 4-13 Absolute Relative Change of f_m and K_m for Benzene in Different Surfactant Solutions at Different Temperatures (%)

ΔT (°C)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
5~10	1.31	2.77	5.14	6.67
10~15	0.64	2.00	0.55	0.77
15~20	1.08	0.01	0.00	1.25

Table 4-12 also shows that 8.3% of benzene added to Tween 80 solution partitioned into the micellar phase at 5°C. When the temperature increased to 10°C, the amount of benzene bound to Tween 80 micelles increased to 9.2% of total added. At 15°C and 20°C, the amount was 9.1% of total added. The absolute relative changes of f_m for benzene in Tween 80 solution over the temperature range tested were less than 5.2%, and f_m was stable at the range of 15~20°C (see Table 4-13). Therefore, the difference of f_m for benzene in Tween 80 solution at different temperature was slight.

The micelle-water partition coefficient, K_m , was 1633.2 for benzene in Tween 20 solution at 5°C, and increased to 1797.2 at 20°C (see Table 4-12). However, the increase of K_m for benzene in Tween 20 solution over the temperature range tested was less than 2.8% (see Table 4-13). Therefore, there was only a slight increase of K_m with the

increase of temperature. K_m was 2189.7 for benzene in Tween 80 solution at 5°C, and increased to 2606.2 at 20°C (see Table 4-12). However, the increase of K_m for benzene in Tween 80 solution over the temperature range tested was less than 6.7%, and K_m increased slightly over the range of 10~20°C (the increase was less than 1.3%) (see Table 4-13). Therefore, similar to Tween 20, there is only a slight increase of K_m for benzene in Tween 80 solution with an increase in temperature.

It can be concluded from the experimental results that there is only a slight increase of solubilizing capacity for benzene in Tween 20 solution and Tween 80 solution with an increase of temperature from 5°C to 20°C.

(2) Toluene

Solubilization results for toluene in Tween 80 solution (Tween 80 = 3210 mg/L) at 5°C, 10°C, 15°C, and 20°C are shown in Appendix B (Figure B-9, B-10, B-11, and B-12). Solubilization results for toluene in Tween 20 solution (Tween 20 = 13200 mg/L) at 5°C, 10°C, 15°C, and 20°C are shown in Appendix B (Figure B-13, B-14, B-15, and B-16).

Although the slopes of the upper curve (Henry's law curve for toluene in water) and the lower curve (Henry's law curve for toluene in Tween 80 solution or Tween 20 solution) increased with the increase of temperature (see Figure 4-19), the horizontal distance between the two curves, b , did not change significantly.

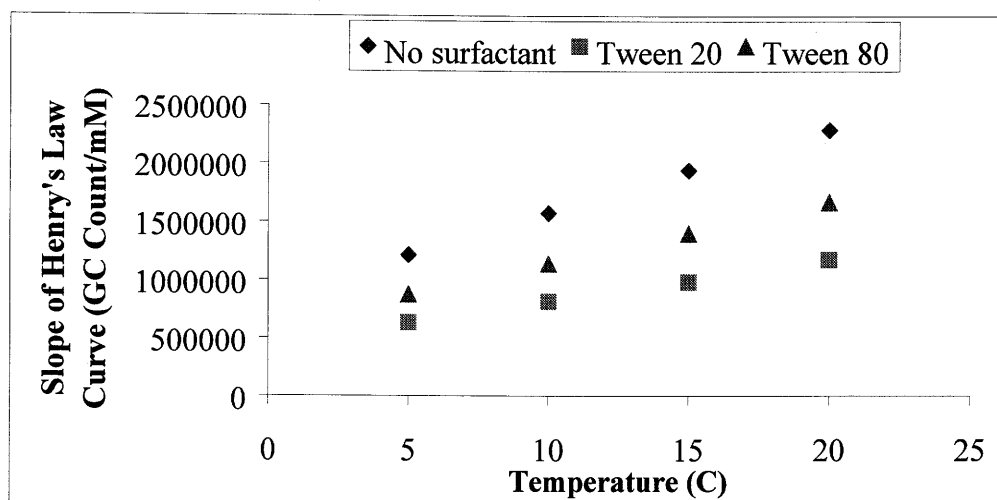


Figure 4-19 Temperature Effect on Solubilization of Toluene

The fraction of toluene partitioned into Tween 80 or Tween 20 micelles, f_m , and the micelle-water partition coefficient, K_m , for the different surfactant solutions at different temperatures are listed in Table 4-14.

Table 4-14 Summary of f_m and K_m for Toluene in Different Surfactant Solutions at Different Temperatures

T (°C)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
5	0.477	4904.0	0.282	7940.3
10	0.481	5109.0	0.276	7974.5
15	0.492	5502.0	0.279	8366.5
20	0.486	5560.6	0.273	8413.3

It is shown in Table 4-14 that 47.7% of the toluene added to a Tween 20 solution partitioned into the micellar phase at 5°C. The amount of toluene bound to Tween 20 micelles increased to 48.1% of total added when the temperature increased to 10°C, then increased to 49.2% when the temperature increased to 15°C, and decreased to 48.6%

when the temperature increased to 20°C. The absolute relative changes of f_m for toluene in Tween 20 solution over the temperature range tested were less than 1.2% (see Table 4-15). Therefore, the differences in the f_m for toluene in Tween 20 solution at different temperatures were very small.

Table 4-14 also shows that 28.2% of toluene added to Tween 80 solution partitioned into the micellar phase at 5°C. The amount decreased to 27.6% of total added when the temperature increased to 10°C. The amount for 15°C and 20°C were 27.9% and 27.3% respectively. The absolute relative changes of f_m for toluene in Tween 80 solution over the temperature range tested were less than 1.1% (see Table 4-15). Therefore, the difference in f_m for toluene in Tween 80 solution at different temperatures was relatively insignificant.

Table 4-15 Absolute Relative Change of f_m and K_m for Toluene in Different Surfactant Solutions at Different Temperatures (%)

ΔT (°C)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
5~10	0.42	2.05	1.08	0.215
10~15	1.13	3.70	0.54	2.40
15~20	0.61	0.53	1.09	0.28

The micelle-water partition coefficient, K_m , was 4904.0 for toluene in Tween 20 solution at 5°C, and increases to 5560.6 at 20°C (see Table 4-14). The increase of K_m for toluene in Tween 20 solution over the temperature range 10~15°C was about 3.7%, but the increase was only 0.53% in the range of 15~20°C (see Table 4-15). Therefore, there appears to be a relatively small increase in K_m for toluene in Tween 20 solution with the

increase of temperature. K_m was 7940.3 for toluene in Tween 80 solution at 5°C, and increases to 8413.3 at 20°C (see Table 4-14). The increase of K_m for toluene in Tween 80 solution over the temperature range tested was about 0.21~2.4% (see Table 4-15). Therefore, there is also a relatively small increase in K_m for toluene in Tween 80 solution with the increase in temperature.

(3) TCE

Solubilization results for TCE in Tween 80 solution (Tween 80 = 3210 mg/L) at 5°C, 10°C, 15°C, and 20°C are shown in Appendix B (Figure B-17, B-18, B-19 and B-20). Solubilization results for TCE in Tween 20 solution (Tween 20 = 13200 mg/L) at 5°C, 10°C, 15°C, and 20°C are shown in Appendix B (Figure B-21, B-22, B-23, and B-24).

In Figures B-17 to B-24 the slopes of the upper curve (Henry's law curve for TCE in water) and the lower curve (Henry's law curve for TCE in Tween 80 solution or Tween 20 solution) increased with the increase of temperature (see Figure 4-20). However, the horizontal distance between the two curves, b , did not change significantly.

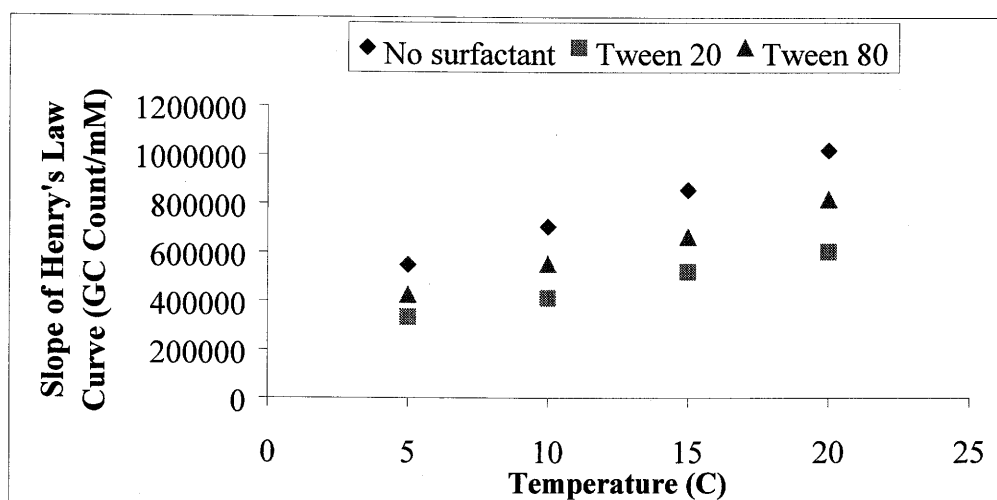


Figure 4-20 Temperature Effect on Solubilization of TCE

The fraction of TCE partitioned into Tween 20 or Tween 80 micelles, f_m , and the micelle-water partition coefficient, K_m , in different surfactant solutions at different temperatures are listed in Table 4-16.

Table 4-16 Summary of f_m and K_m for TCE in Different Surfactant Solutions at Different Temperatures

T (°C)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
5	0.393	3599.8	0.228	6624.2
10	0.416	4096.0	0.220	6607.0
15	0.392	3922.7	0.227	7187.8
20	0.408	4344.4	0.197	6467.9

Table 4-16 shows that 39.3% of total added TCE in the Tween 20 solution partitioned into the Tween 20 micellar phase at 5°C. The amount of TCE increased to 41.6% of total added at 10°C, but remained at about 40% at 15°C and 20°C. It is difficult to discern a trend of f_m for TCE in Tween 20 solution. The absolute relative changes of

f_m for TCE in Tween 20 solution over the temperature range tested were about 2~3% (see Table 4-17).

Table 4-17 Absolute Relative Change of f_m and K_m for TCE in Different Surfactant Solutions at Different Temperatures (%)

ΔT (°C)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
5~10	2.84	6.45	1.78	0.13
10~15	2.97	2.16	1.56	4.21
15~20	2.00	5.10	7.08	5.27

Table 4-16 also shows that 22.8% of total added TCE partitioned into the Tween 80 micellar phase at 5°C. The amount of TCE bound to Tween 80 micelles was 22% of total added at 10°C; and 22.7% at 15°C. Partitioned TCE was only 19.7% of total added at 20°C. Again it is difficult to discern a trend of f_m for TCE in Tween 80 solution. The absolute relative changes of f_m for TCE in Tween 80 solution over the temperature range tested were about 1.5~7.1% (see Table 4-17).

The micelle-water partition coefficient, K_m , was 3599.8 for TCE in Tween 20 solution at 5°C, 4096.0 at 10°C, 3922.7 at 15°C, and 4344.4 at 20°C (see Table 4-16). The absolute relative changes of K_m for TCE in Tween 20 solution over the temperature range tested were about 2.1~6.5% (see Table 4-17). K_m was 6624.2 for TCE in Tween 80 solution at 5°C, 6607.0 at 10°C, 7187.8 at 15°C, and 6467.9 at 20°C (see Table 4-16). The absolute relative changes of K_m for TCE in Tween 80 solution over the temperature range tested were about 0.1~5.3% (see Table 4-17). It is concluded that there is a slight

change of K_m for TCE solubilized by Tween 20 or Tween 80 with the temperature range of 5 to 20°C, but it is difficult to discern the trend within the scatter of the data.

In general, the micellar weights of nonionic surfactants increase with increasing temperature, particularly near the cloud point, the enhancement of solubilization may result mostly from the increase in micellar size (Rosen, 1978). The temperature range in this research was 5~20°C, approximating typical subsurface conditions. The cloud point for Tween 20 is 76°C and for Tween 80 is 65°C, thus, the temperature range studied is much lower than cloud point, and the enlargement of micelle size caused by increasing temperature is limited. Therefore, the solubilizing power of Tween 20 or Tween 80 for benzene, toluene, and TCE will only be enhanced slightly with increases of subsurface temperature.

4.3.2 Ionic Strength Effect

Ko et al. (1998b) found the CMC of Tween 80 was unaffected by pH and ionic strength. The concentrations of Tween 20 and Tween 80 used in this research were 13200 mg/L (about 220 times CMC) and 3210 mg/L (about 247 times CMC), respectively. These concentrations are much greater than their CMC, therefore, any change in CMC due to the presence of other dissolved species should be negligible. The error introduced in the quantity C-CMC by using CMC equals 60 mg/L for Tween 20 and CMC equals 13 mg/L for Tween 80 would be minimal. Therefore, evaluation of the specific CMC at different ionic strength is unnecessary.

Ionic strength effect on solubilization of benzene, toluene, and TCE in 13200 mg/L Tween 20 solution and in 3210 mg/L Tween 80 solution was studied for 0.1 M, 0.3M, 0.5 M, and 0.64 M concentrations of NaCl. The temperature was controlled at 20°C. Henry's constants (Wan, 1998) for selected VOCs at different ionic strengths are listed in Table 4-18.

Table 4-18 Henry's Constants for Selected VOCs at Different Ionic Strengths

Ionic Strength (M)	Benzene	Toluene	TCE
0.0	0.180	0.196	0.291
0.1	0.186	0.206	0.302
0.3	0.208	0.231	0.337
0.5	0.227	0.255	0.378
0.64	0.238	0.275	0.386

(1) Benzene

Solubilization results for benzene in Tween 80 solution (Tween 80 = 3210 mg/L) at different ionic strengths (0.1 M, 0.3 M, 0.5 M, and 0.64 M NaCl) are shown in Appendix C (Figure C-1, C-2, C-3, and C-4). The results for benzene in Tween 20 solution (Tween 20 = 13200 mg/L) at different ionic strengths (0.1 M, 0.3 M, 0.5 M, and 0.64 M NaCl) are shown in Appendix C (Figure C-5, C-6, C-7, and C-8).

It is shown in Figure C-1 to Figure C-4, and in Figure C-5 to Figure C-8 that the slopes of the upper curve (Henry's law curve for benzene in water) and the lower curve (Henry's law curve for benzene in Tween 80 solution or in Tween 20 solution) increased with the increase of ionic strength (see Figure 4-21). Hence more benzene partitioned into the headspace from the aqueous phase with an increase of ionic strength. The

horizontal distance between the two curves, b , increased approximating 24% in Tween 80 solution and 30% in Tween 20 solution with increase of ionic strength from 0.1M to 0.64M. This implies that more benzene partitioned into Tween 80 micelles or Tween 20 micelles from the aqueous phase with an increase of ionic strength.

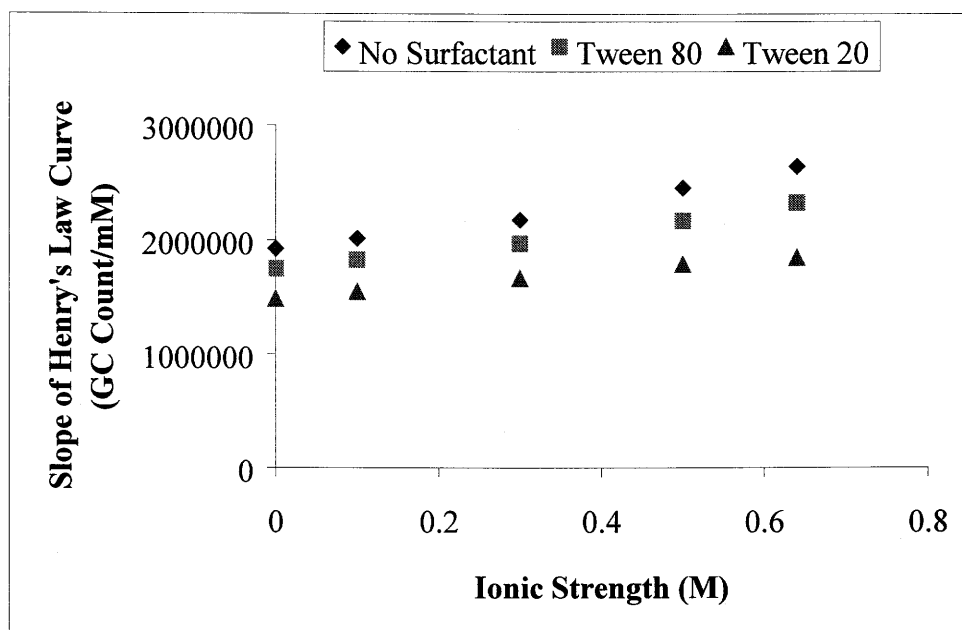


Figure 4-21 Ionic Strength Effect on Solubilization of Benzene

The fraction of benzene partitioned into Tween 20 or Tween 80 micelles, f_m , and the micelle-water partition coefficient, K_m , in different surfactant solutions at different ionic strengths are listed in Table 4-19.

Table 4-19 Summary of f_m and K_m for Benzene in Different Surfactant Solutions at Different Ionic Strengths (20°C)

Ionic Strength (M)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
0.0	0.230	1797.2	0.091	2606.2
0.1	0.232	1827.6	0.093	2675.2
0.3	0.235	1919.3	0.096	2817.3
0.5	0.272	2357.6	0.117	3582.1
0.64	0.302	2734.8	0.119	3685.4

Table 4-19 shows that f_m for benzene increased with the increase of ionic strength either in Tween 20 solution or in Tween 80 solution. K_m also increased with ionic strength. It is concluded that the solubilizing capacity of benzene by Tween 20 or by Tween 80 increases with ionic strength.

The added electrolytes affect water properties. When electrolytes are added into solution, water molecules will bond electrolytes tightly and form hydration water, which increases the polarity of the water. Therefore, hydrophobic organic compounds are more difficult to dissolve in the solution and cause a decrease of VOC solubility and an increase of Henry's law constants of VOCs (see Table 4-18). This phenomenon is called as the "salting-out effect" (Snoeyink and Jenkins, 1980; Peng and Wan, 1998). The effect of sodium chloride represented the "salting-out effect" in this research.

The micelle-water partition coefficient K_m in saline water can be represented as follows:

$$K_{ms} = \gamma K_m \quad (4-6)$$

where, K_{ms} --- micelle-water partition coefficient in salt water (dimensionless);

γ --- activity coefficient, which is a function of ionic strength;

K_m --- micelle-water partition coefficient without salt (dimensionless).

Usually, the activity coefficient γ can be estimated (Snoeyink and Jenkins, 1980)

by:

$$\log \gamma = K_s \mu \quad (4-7)$$

where, K_s --- salting-out coefficient (M^{-1});

μ --- ionic strength (M).

The ionic strength is calculated by the Lewis and Randall's equation (Snoeyink and Jenkins, 1980):

$$\mu = \frac{1}{2} \sum (C_i Z_i^2) \quad (4-8)$$

where, C_i --- mole concentration of ion i ;

Z_i --- charge of the ion i .

Therefore,

$$\log \frac{K_{ms}}{K_m} = K_s \mu = K_s \frac{1}{2} \sum (C_i Z_i^2) \quad (4-9)$$

In this research, sodium chloride was used to simulate ionic strength. Assuming the molar concentration of NaCl is C_{NaCl} , then the molar concentrations of Na^+ and Cl^- all are equal to C_{NaCl} , therefore,

$$\mu = \frac{1}{2} \{ [Na^+] \times 1^2 + [Cl^-] \times 1^2 \} = C_{NaCl} \quad (4-10)$$

i.e., the ionic strength μ can be represented by sodium chloride molar concentration,

C_{NaCl} .

The salting-out effect represented in this research is similar to Gong (1997), which expressed the salt effect on organic compound solubility as follows,

$$\log \gamma_s = \log \left(\frac{S^w}{S^s} \right) = K_s' C_s \quad (4-11)$$

where, γ_s --- activity coefficient of the hydrocarbon in the salt solution;

S^w --- solubility of the organic compound in pure water;

S^s --- solubility of the organic compound in the salt solution;

C_s --- salt molar concentration;

K_s' --- empirical Setschenow parameter.

Figure 4-22 and 4-23 show the regression analysis for benzene in Tween 20 solution and in Tween 80 solution with logarithmic activity coefficient, i.e., $\log(K_{ms}/K_m)$, which is represented as $\log(\gamma)$, against ionic strength (M). The salting-out coefficient is determined from the slope of the regression line. The values of the salting-out coefficients are listed in Table 4-20.

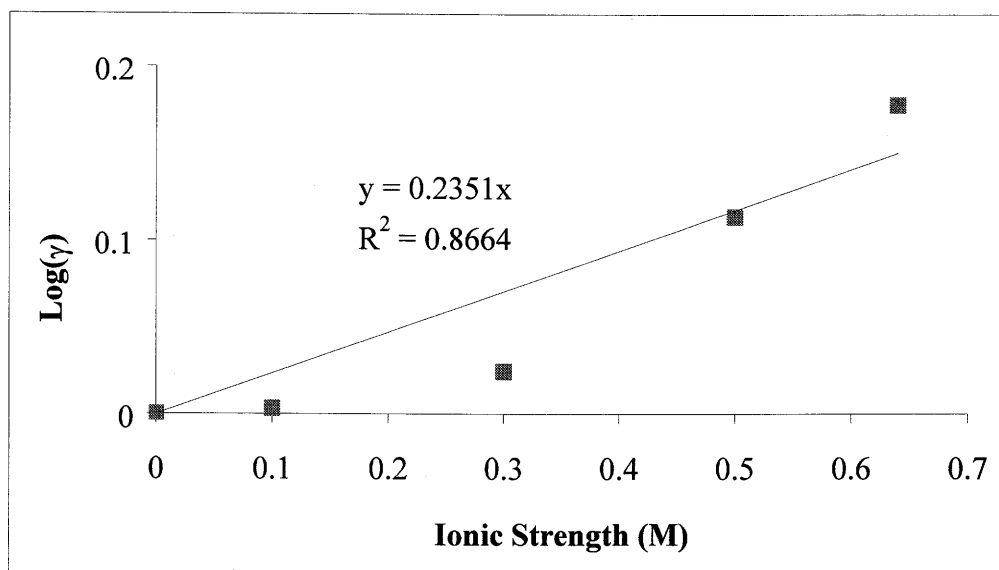


Figure 4-22 Salting-Out Coefficient for Benzene in Tween 20 Solution

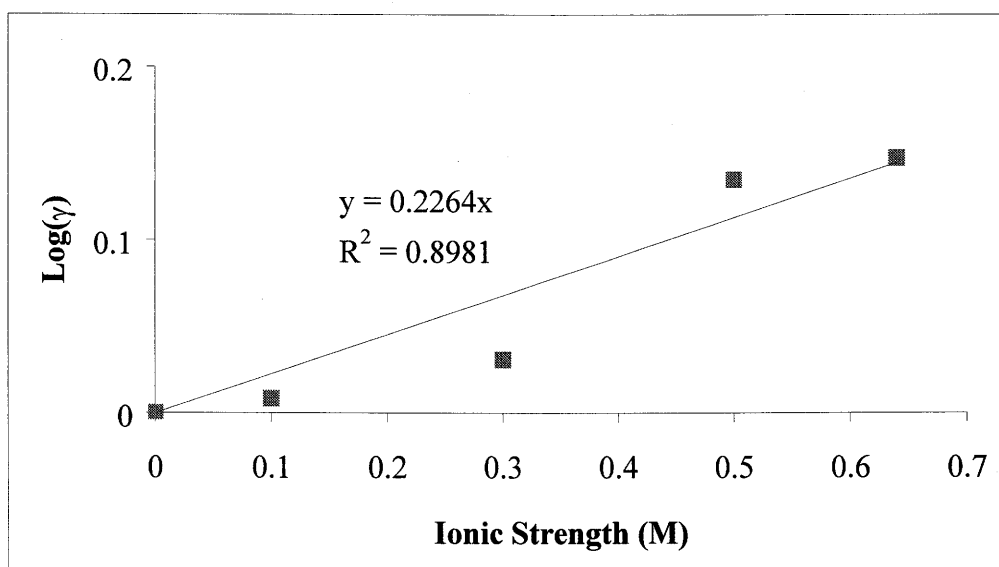


Figure 4-23 Salting-Out Coefficient for Benzene in Tween 80 Solution

Table 4-20 Salting-Out Coefficients for Selected VOCs at 20°C (M⁻¹)

VOC	Tween 20	Tween 80
Benzene	0.235	0.226
Toluene	0.150	0.149
TCE	0.198	0.308

(2) Toluene

Solubilization of toluene in Tween 80 solution (Tween 80 = 3210 mg/L) at different ionic strengths (0.1 M, 0.3 M, 0.5 M, and 0.64 M NaCl) was studied and the results are shown in Appendix C (Figure C-9, C-10, C-11, and C-12). The results of toluene in Tween 20 solution (Tween 20 = 13200 mg/L) at different ionic strengths (0.1 M, 0.3 M, 0.5 M, and 0.64 M NaCl) are shown in Appendix C (Figure C-13, C-14, C-15, and C-16).

It is shown in Figure C-9 to Figure C-12 and in Figure C-13 to Figure C-16 that the slopes of the upper curve (Henry's law curve for toluene in water) and the lower curve (Henry's law curve for toluene in Tween 80 solution or in Tween 20 solution) increased with the increase of ionic strength (see Figure 4-24). This implies that more toluene partitioned into the headspace from the aqueous phase with the increase of ionic strength. The horizontal distance between the two curves, b , also increased with ionic strength. Hence, more toluene partitioned into Tween 20 micelles or Tween 80 micelles from the aqueous phase with the increase of ionic strength.

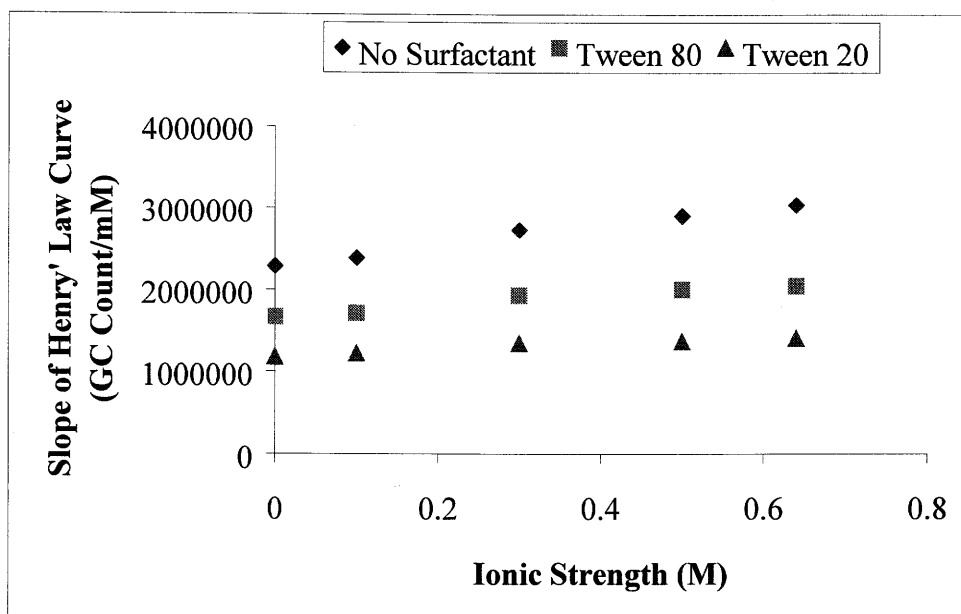


Figure 4-24 Ionic Strength Effect on Solubilization of Toluene

The fraction of toluene partitioned into Tween 20 or Tween 80 micelles, f_m , and the micelle-water partition coefficient, K_m , in different surfactant solutions at different ionic strengths are listed in Table 4-21.

Table 4-21 Summary of f_m and K_m for Toluene in Different Surfactant Solutions at Different Ionic Strengths (20°C)

Ionic Strength (M)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
0.0	0.486	5560.6	0.273	8413.3
0.1	0.489	5587.2	0.283	8866.7
0.3	0.508	6229.9	0.293	9422.1
0.5	0.530	6899.5	0.310	10360.1
0.64	0.537	7216.1	0.326	11176.4

Table 4-21 shows that f_m and K_m for toluene increased with ionic strength either in Tween 20 solution or in Tween 80 solution. It is concluded that the solubilizing capacity of toluene by Tween 20 or by Tween 80 increased with ionic strength.

Figure 4-25 and 4-26 show the regression analysis for toluene in Tween 20 solution and in Tween 80 solution with logarithmic activity coefficient. The values of the salting-out coefficients for toluene in Tween 20 solution and in Tween 80 solution are listed in Table 4-20.

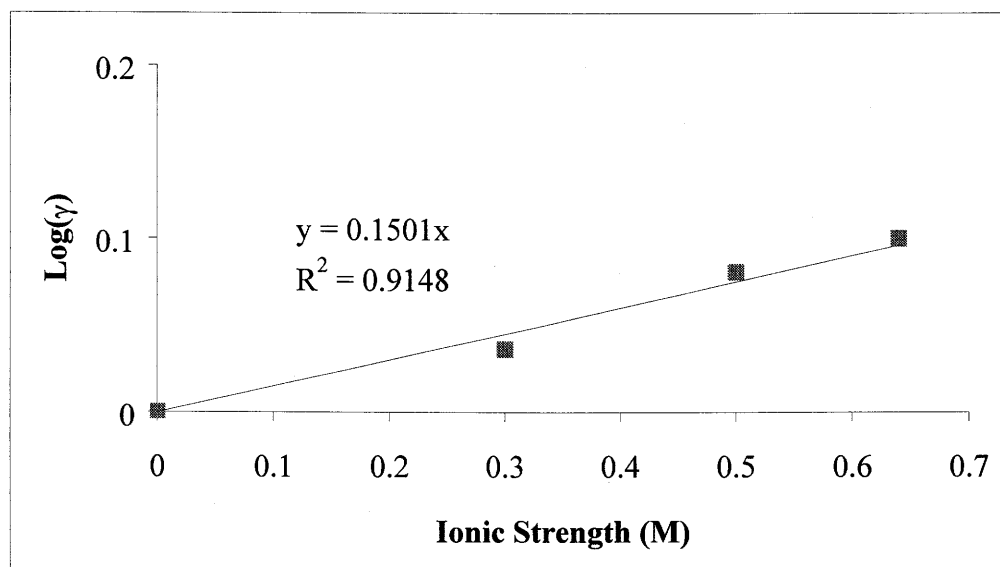


Figure 4-25 Salting-Out Coefficient for Toluene in Tween 20 Solution

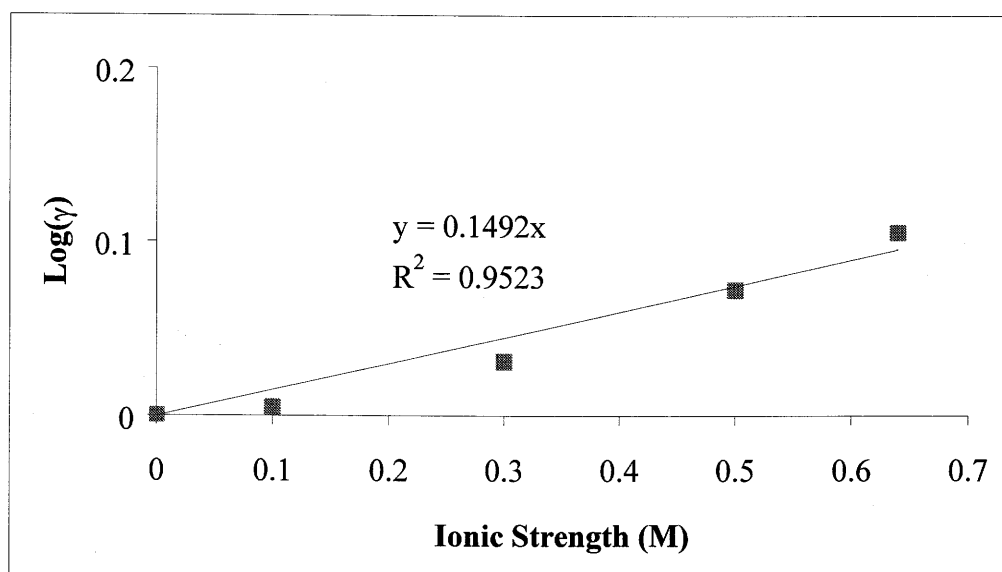


Figure 4-26 Salting-Out Coefficient for Toluene in Tween 80 Solution

(3) TCE

Solubilization of TCE in Tween 80 solution (Tween 80 = 3210 mg/L) at different ionic strengths (0.1 M, 0.3 M, 0.5 M, and 0.64 M NaCl) was studied and the results are shown in Appendix C (Figure C-17, C-18, C-19, and C-20). The results of TCE in Tween 20 solution (Tween 20 = 13200 mg/L) at different ionic strengths (0.1 M, 0.3 M, 0.5 M, and 0.64 M NaCl) are shown in Appendix C (Figure C-21, C-22, C-23, and C-24).

Figure C-17 to Figure C-20, and Figure C-21 to Figure C-24 show that the slopes of the upper curve (Henry's law curve for TCE in water) and the lower curve (Henry's law curve for TCE in Tween 80 solution or in Tween 20 solution) increased with an increase of ionic strength (see Figure 4-27). This implies that more TCE partitioned into the headspace from the aqueous phase with the increase of ionic strength. The horizontal distance between the two curves, b , also increased with the increase of ionic strength.

Hence more TCE partitioned into Tween 80 micelles or Tween 20 micelles from the aqueous phase with an increase of ionic strength.

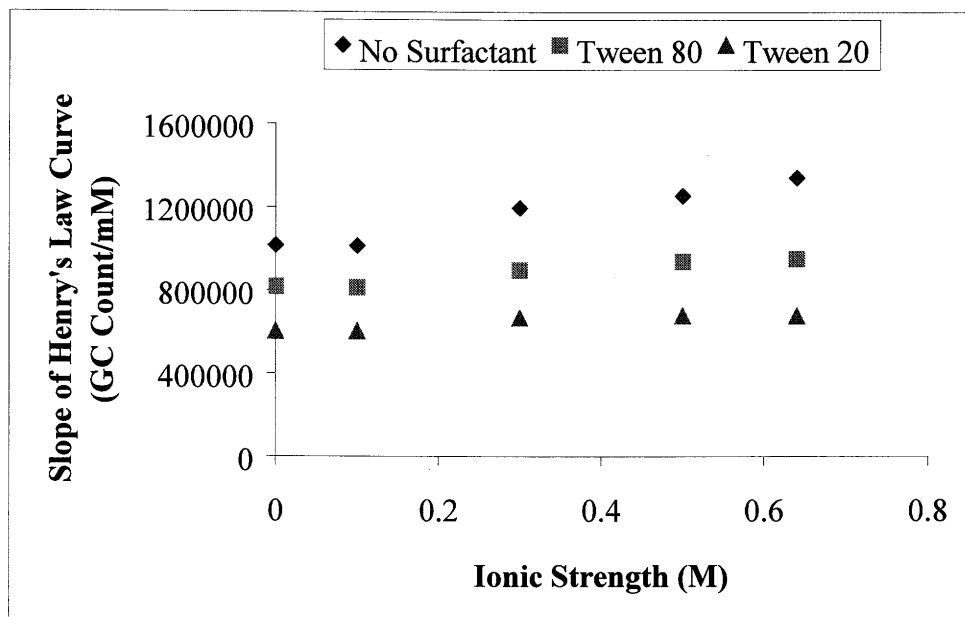


Figure 4-27 Ionic Strength Effect on Solubilization of TCE

The fraction of TCE partitioned into Tween 20 or Tween 80 micelle, f_m , and the micelle-water partition coefficient, K_m , in different surfactant solutions at different ionic strengths are listed in Table 4-22.

Table 4-22 Summary of f_m and K_m for TCE in Different Surfactant Solutions at Different Ionic Strengths (20°C)

Ionic Strength (M)	Tween 20		Tween 80	
	f_m	K_m	f_m	K_m
0.0	0.408	4344.4	0.197	6467.9
0.1	0.406	4381.4	0.198	6558.6
0.3	0.443	5199.6	0.250	8696.7
0.5	0.460	5797.4	0.251	9058.7
0.64	0.496	6660.8	0.291	10729

Table 4-22 shows that f_m and K_m increased with ionic strength for TCE both in Tween 20 solution and in Tween 80 solution. It is concluded that the solubilizing capacity of TCE by Tween 20 or by Tween 80 increases with an increase of ionic strength.

Figure 4-28 and 4-29 show the regression analysis for TCE in Tween 20 solution and in Tween 80 solution with logarithmic activity coefficient. The values of the salting-out coefficients for TCE in Tween 20 solution and in Tween 80 solution are listed in Table 4-20.

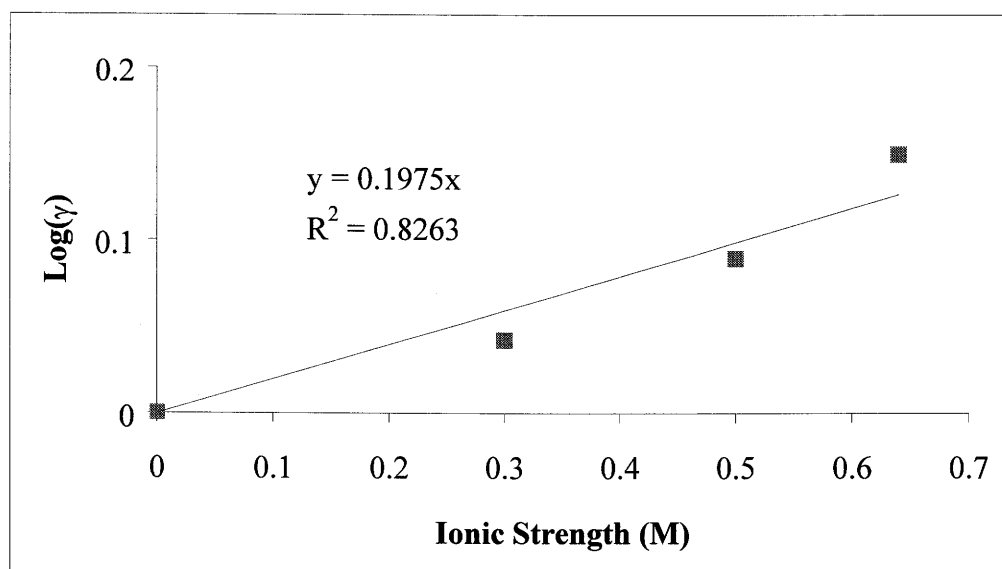


Figure 4-28 Salting-Out Coefficient for TCE in Tween 20 Solution

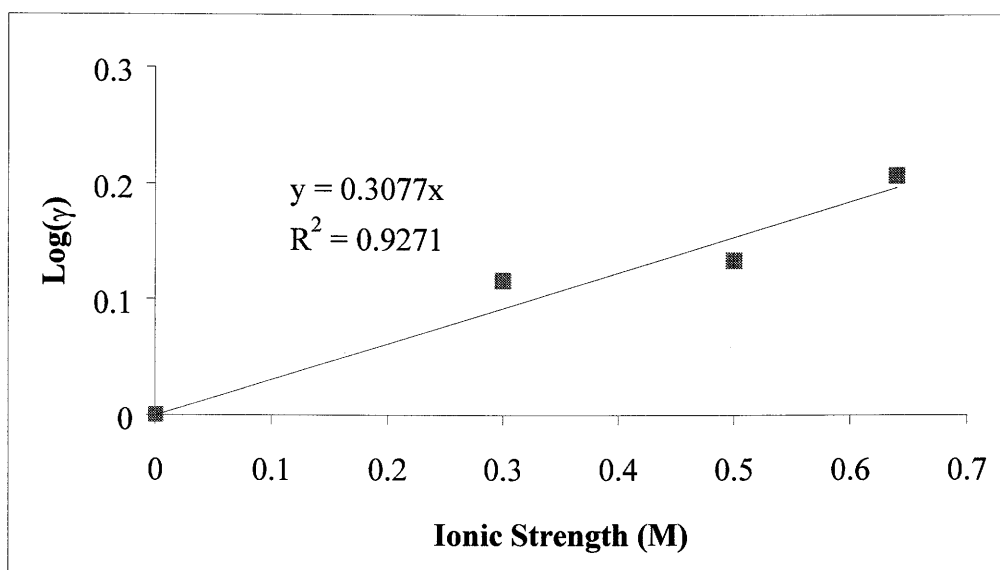


Figure 4-29 Salting-Out Coefficient for TCE in Tween 80 Solution

The addition of electrolytes to nonionic polyoxyethylenated surfactant solutions causes an increase in the aggregation number of the micelles (Saito and Shinoda, 1967). The increase in aggregation number of the micelles presumably results in an increase in the inner hydrocarbon core of Tween 20 and Tween 80 micelles. Therefore, the solubilization of Tween 20 and Tween 80 increases with an increase of ionic strength.

4.4 Engineering Considerations

The surfactant enhanced pump and treat method is a promising technology for remediation of contaminated subsurface sites. In this research the equilibrium micelle-water partition coefficient, K_m , and the fraction of VOCs partitioned into micelles, f_m , were determined under batch conditions in the laboratory. The results of this research have shown that the fraction of VOCs partitioned into micelles is proportional to the surfactant concentration. In a field application, a continuous flow system would be used rather than batch treatment. The recommended surfactant dosage to be used in the field

would depend upon the surfactant capacity to partition VOCs and the surfactant cost considering loss within the system and recycle after extraction of VOCs.

In a field remediation system, a surfactant and treated groundwater solution would be injected into the subsurface through several spatially distributed injection wells. The contaminated subsurface would be treated by contacting the flow of surfactant solution from the injection wells to a series of recovery wells. Hydrophobic organic compounds like NAPLs, which are insoluble or only slightly soluble in water, would become partitioned into micelles in the surfactant solution. NAPLs would be transferred from pools of free product and from residual saturation to the mobile aqueous phase (the surfactant solution containing micelles). Since the flow of the aqueous phase would be continuous in a field situation, equilibrium may not be established between the NAPLs and the micellar phase. The deficit of actual NAPLs held in the micellar phase and the maximum capacity of the micelles to hold NAPLs (i.e. the equilibrium condition) is the driving force for the transfer of NAPLs to the mobile aqueous phase. After the mobile aqueous phase is recovered from the subsurface, the NAPLs can be separated from the micellar phase and the surfactant solution then reinjected for reuse. The groundwater table in the vicinity of the injection and recovery wells could be cyclically raised and lowered to assist in the removal of NAPLs from the subsurface unsaturated zone.

The effects of two primary environmental conditions (temperature and ionic strength) on the solubilization of NAPLs were investigated in this research. It was shown that temperature had no significant effect on the solubilization in the range of 5°C to

20°C. Therefore, in most subsurface applications, it should not be necessary to consider temperature effect upon subsurface remediation.

Various NaCl solution concentrations were prepared to investigate ionic strength effect upon NAPLs solubilization in a surfactant solution. Ionic strength was shown to have a significant effect on the solubilization. However, in a field situation, there would be a mixture of typical major anions and cations, including sodium, magnesium, calcium, potassium, chloride, sulfate, bicarbonate, etc., in groundwater. Therefore, the potential effect of typical subsurface ionic strengths and ion mixtures should be considered before the implementation of a SESR system.

In general, the quantity of total dissolved solids (TDS) in groundwater is much larger than those in surface water. TDS can range from 25 mg/L at some locations in the Canadian Shield to 300,000 mg/L in some deep saline waters in the Interior Plains (Environmental Canada, 2001). However, most groundwater has a relatively low ionic strength. The ionic strength can be roughly estimated using the Langelier Equation (Snoeyink and Jenkins, 1980) as follows:

$$\mu = 2.5 \times 10^{-5} \times TDS \quad (4-12)$$

where TDS is expressed in mg/L, and μ is in M.

Groundwater acceptable for drinking water purposes would typically have a maximum TDS in the range of 500 to 1500 mg/L (Areco, 2001). This range expressed as ionic strength (approximately 0.013M to 0.038M) is much lower than the minimum ionic

strength tested in this research (0.1M). Therefore, in many subsurface remediation situations the ionic strength effect upon solubilization may not be significant.

An additional important consideration in the application of a SESR system is to prevent leaving residual surfactant in the groundwater. Biodegradable surfactants should be used to prevent this occurrence even if there is some surfactant loss by biodegradation during the remediation operation. This is more acceptable than leaving residual surfactant that is non-biodegradable in the subsurface. However, the biodegradability of surfactants used in the remediation of the subsurface cannot be excessive or there will be significant surfactant loss by microbial action resulting in an ineffective or uneconomical SESR system.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Solubilization of benzene, toluene, and TCE in edible nonionic surfactants (Tween 20 and Tween 80) was studied using a headspace auto-sampler and gas chromatography system. The advantages of this system include:

- The procedure in this system is carried out by a high precision instrument to ensure consistent and accurate measurements, and
- The data used to calculate K_m and f_m are determined by direct injection of a headspace sample from the closed headspace vials into the GC so that chemical loss due to volatilization is eliminated.

A modification of "Equilibrium Partitioning in Closed system" (EPICS) method was used to determine the micelle-water partition coefficient, K_m . The advantage of this method is that the absolute concentrations of the volatile organic compounds in the headspace do not have to be determined. It eliminates any error caused by converting GC peak area raw data to actual chemical concentration.

For objective (1), following conclusions are made:

- The micelle-water partition coefficient, K_m , equals:

$$K_m = \frac{X_m}{X_a}$$

The mole fraction of VOC in micellar phase, X_m , equals:

$$X_m = \frac{b}{b + (C - CMC)}$$

The mole fraction of VOC in extramellar phase, X_a , equals:

$$X_a = \frac{a}{55550(1 + H \frac{V_a}{V})}$$

a and b can be obtained directly from the plot of Henry's law curves.

- Preliminary tests showed that 6 hours of shaking time for benzene, toluene, and TCE in solution was enough to reach equilibrium among micellar, aqueous, and gaseous phases, or between aqueous and gaseous phases with or without surfactant. To ensure full equilibrium at different conditions and to facilitate experiment control, 24 hours of shaking time was used for all tests in this research.
- In the presence of surfactant (Tween 20 or Tween 80), the headspace concentration of VOCs decreased. The Henry's law curves for each solution were interpreted in terms of the fraction of VOC bound to the micellar aggregates.
- The fraction of benzene, toluene, and TCE bound to Tween 20 micelles or to Tween 80 micelles increased linearly with the increase of surfactant micellar concentration. Therefore, the higher the concentration of surfactant solution used, the more effective a surfactant-enhanced subsurface remediation will be. However, the maximum feasible surfactant dosage must be determined by evaluating economic considerations.

- Experimental results showed that Tween 80 micelles had more solubilizing capacity than Tween 20 micelles for benzene, toluene and TCE. Although Tween 80 micelles and Tween 20 micelles have the same hydrophilic group, the hydrophobic group of Tween 80 is larger than that of Tween 20. The longer hydrocarbon chain causes a decrease in CMC and an increase in micelle size. For hydrocarbons that are solubilized in the inner core of the micelle, the amount of material solubilized generally increases with the increase of micelle size. Therefore, Tween 80 has more solubilizing power than Tween 20.
- Experimental results showed K_m increased as the hydrophobicity of the contaminants (benzene, TCE, and toluene) increased. These results agree with the solubility and octanol-water partition coefficient trends of the VOCs used in the experiments.

For objective (2), following conclusions are made:

- Since high surfactant concentration (13200 mg/L for Tween 20 and 3210 mg/L for Tween 80) was used in this research, and the CMC of nonionic polyoxyethylenated surfactants are not sensitive to temperature changes or to the presence of other electrolytes, the error introduced in the quantity C-CMC by using CMC equals 60 mg/L for Tween 20 and CMC equals 13 mg/L for Tween 80 would be minimal. Therefore an evaluation of the specific CMC at different temperature or at different ionic strengths is not necessary.
- 5°C, 10°C, 15°C, and 20°C were used to study temperature effect on the solubilization of benzene, toluene, and TCE in 13200 mg/L Tween 20 solution

and 3210 mg/L Tween 80 solution. These temperatures were chosen to represent typical subsurface temperature range. With an increase of temperature, the fraction of benzene, or toluene, or TCE bound to Tween 20 micelles or to Tween 80 micelles did not vary significantly. This is because the temperatures used in this research were lower than the cloud point and the micelle properties did not change much with the change of temperature. K_m for benzene, toluene, and TCE solubilized by Tween 20 or Tween 80 increased slightly with an increase of the temperature.

- 0.1 M, 0.3 M, 0.5 M, and 0.64 M of NaCl were used to investigate ionic strength effect on the solubilization of benzene, toluene, and TCE in 13200 mg/L Tween 20 solution or in 3210 mg/L Tween 80 solution. 0.64 M of NaCl was used to simulate seawater. The temperature was controlled at 20°C for the ionic strength effect tests. Experimental results showed that the fraction of benzene, toluene, and TCE bound to Tween 20 micelles or to Tween 80 micelles increased with an increase of ionic strength. Therefore, the solubilizing capacity of Tween 20 or Tween 80 for benzene, toluene, and TCE increased with ionic strength. The addition of electrolytes to nonionic polyoxyethylenated surfactant solutions causes an increase in the aggregation number of the micelles, which results in an increase in hydrocarbon solubilization in the inner core of the micelle. The ionic strength effect on solubilization can be quantified using the salting-out coefficient.

5.2 Recommendations

For future research, the followings are suggested:

- Solubilization of a representative number of different types of VOCs (such as carbon tetrachloride, dichloromethane, ethylbenzene, monochlorobenzene, tetrachloroethylene, vinyl chloride, xylene(s), etc.) in different commercially available edible nonionic surfactant solutions (such as Span 80, etc.) should be studied using the headspace auto-sampler and gas chromatography system. The results of these studies will provide additional data (i.e., K_m and f_m) for the design of subsurface remediation systems.
- A precise method to measure the exact CMC of nonionic surfactants at different temperatures and at different ionic strengths should be developed. The surface tension method is currently the best way to measure the CMC of nonionic surfactants.
- Laboratory water should be replaced by representative groundwater in laboratory tests to investigate the effect of ion mixtures on solubilization of VOCs in surfactant solutions. Subsurface conditions (temperature, ionic strength, and light) should be simulated during these laboratory tests.
- The cosolvent effect should be investigated for different natural organic materials (NOM) and synthetic hydrophobic organic compounds (like DDT, PCB, alachor, aldicarb, aldrin+dielrin, bromoxynil, etc.) mixed with surfactant solutions.
- Surfactant loss during remediation such as adsorption by soil or partitioning into residual phases should be investigated. A proposed method to measure the surfactant loss by adsorption would consist of equilibrating two vials containing

equal volumes of aqueous surfactant solution. One vial would contain a known amount of soil and the other would contain no soil. Several such pairs of vials could be prepared. After appropriate equilibration times, a known fixed volume of aqueous sample could be taken from the aqueous phase of each vial and the surfactant concentration measured. The surfactant concentration difference of the two vials would be the surfactant loss by soil adsorption.

- Biodegradation of surfactant should be investigated. The microbial biodegradation of surfactant could be investigated in the laboratory. Temperature, ionic strength and light should simulate field conditions. The method would consist of equilibrating two vials containing equal volumes of aqueous surfactant solutions. One vial would contain microbes taken from the subsurface and the other would contain no microbes. Several such pairs of vials would be prepared. After appropriate elapsed times, a known fixed volume of aqueous sample would be taken from the aqueous phase of each set of vials and the surfactant concentration measured. The surfactant concentration difference between the sets of two vials over time would allow the determination of the surfactant biodegradation rate.
- The fraction of VOCs partitioned into micelles determined in this research was investigated using batch reactors. For the implementation of SESR, a continuous flow and partitioning model should be developed to predict the partitioning of NAPLs between free product or residual saturation, and the mobile aqueous phase containing surfactant micelles.

The implementation of surfactant enhanced subsurface remediation should be investigated at a field site.

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Appendix A

Experimental Results for Toluene and TCE Partitioning Tests at Room Temperature

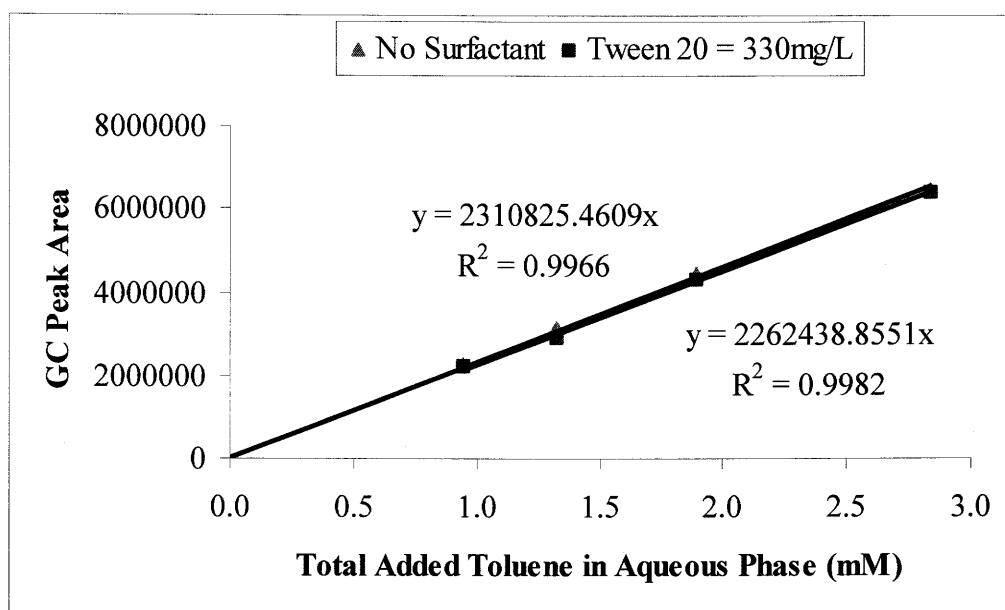


Figure A-1 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 330 mg/L)

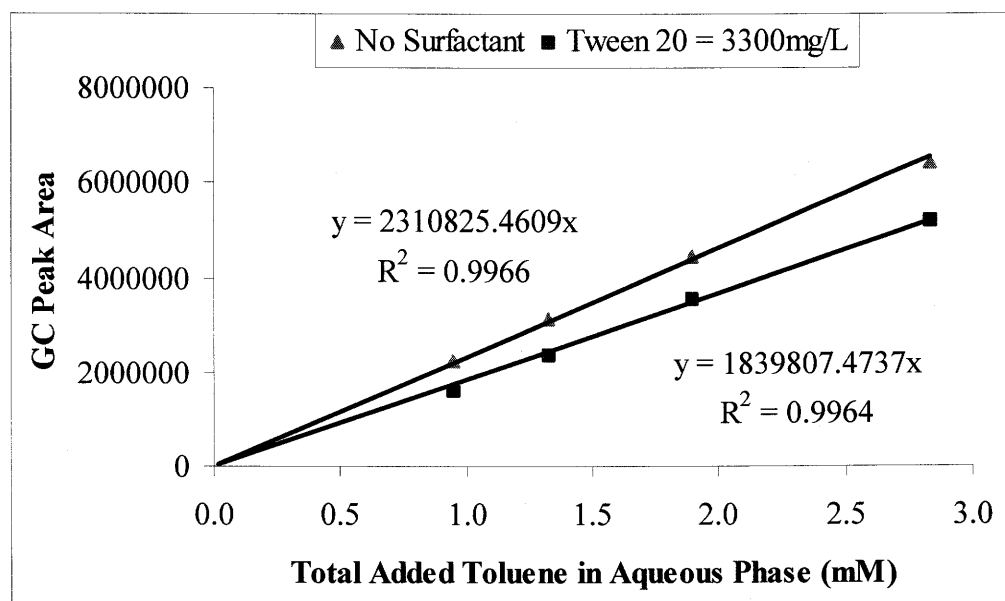


Figure A-2 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 3300 mg/L)

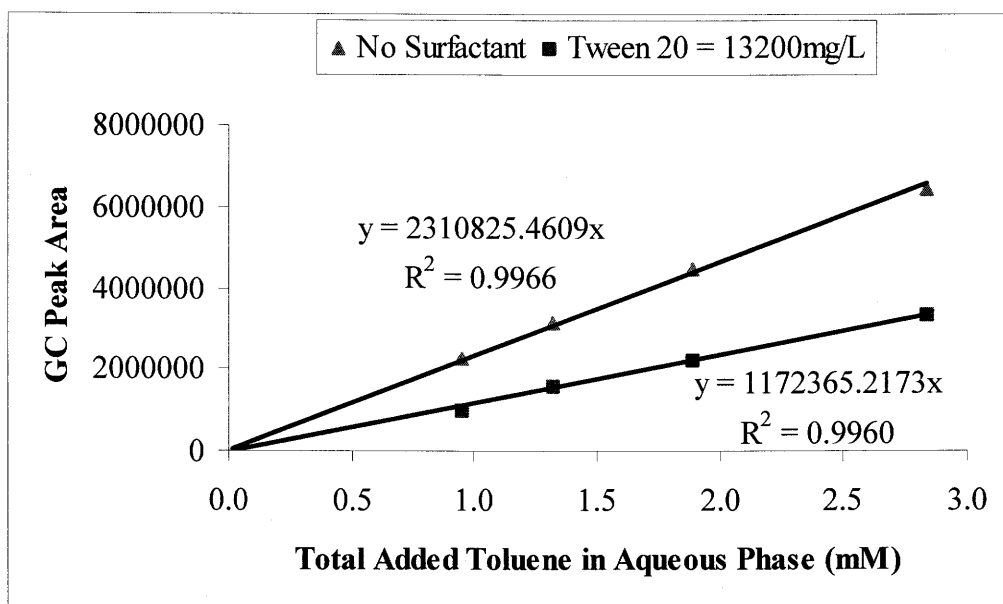


Figure A-3 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 13200 mg/L)

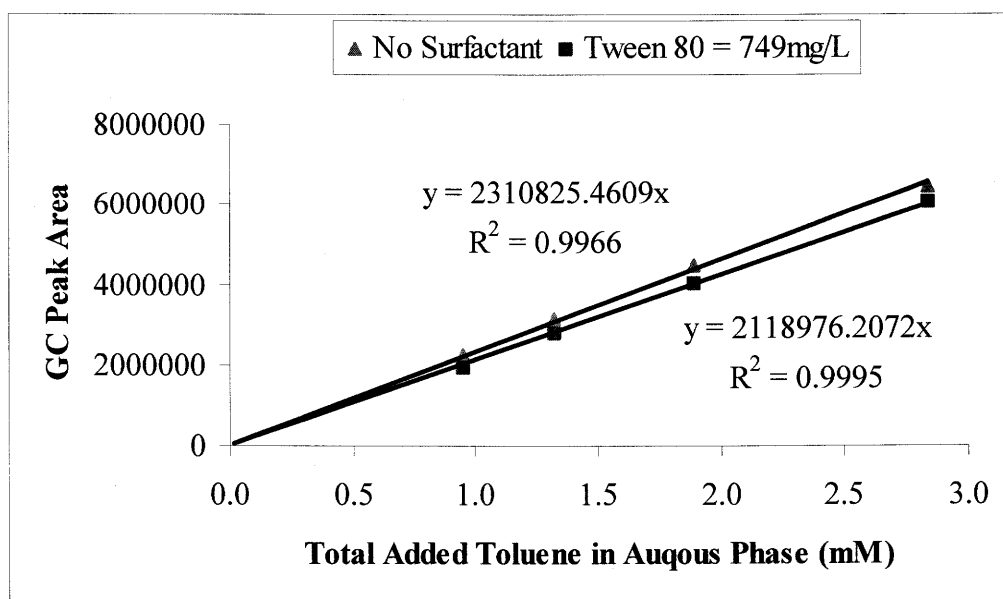


Figure A-4 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) (Tween 80 = 749 mg/L)

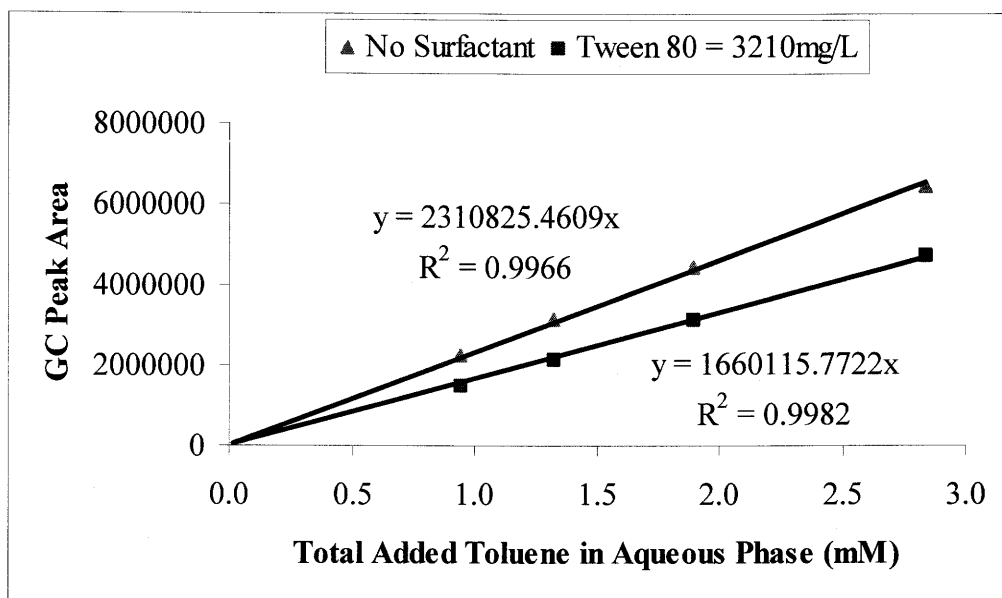


Figure A-5 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) (Tween 80 = 3210 mg/L)

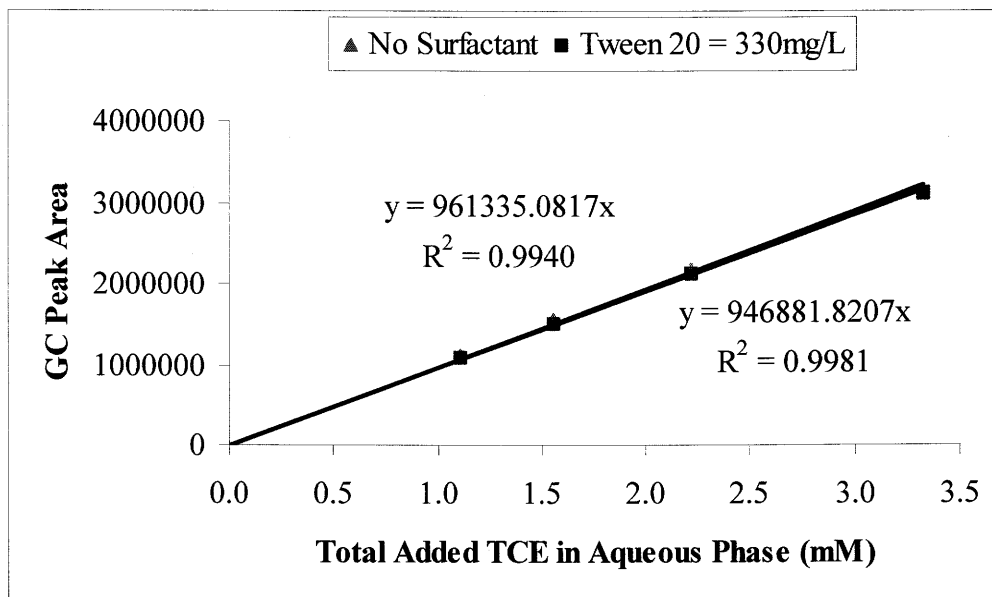


Figure A-6 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 330 mg/L)

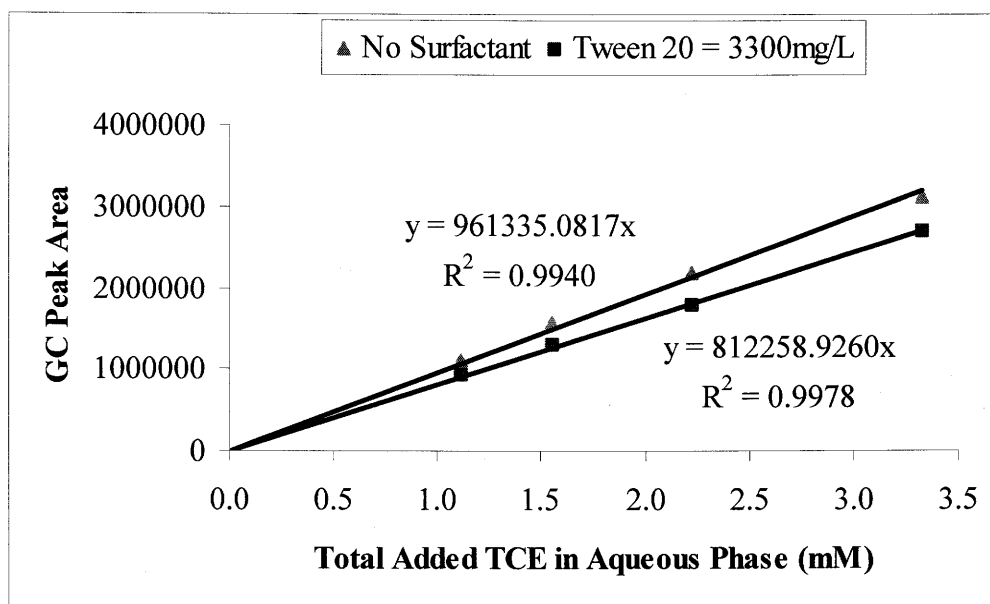


Figure A-7 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 3300 mg/L)

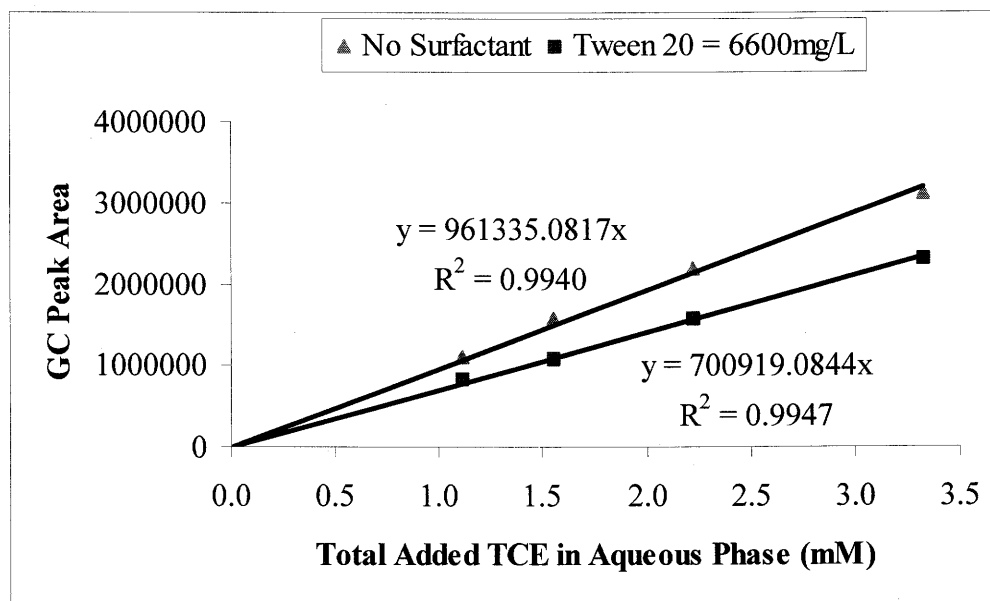


Figure A-8 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) (Tween 20 = 6600 mg/L)

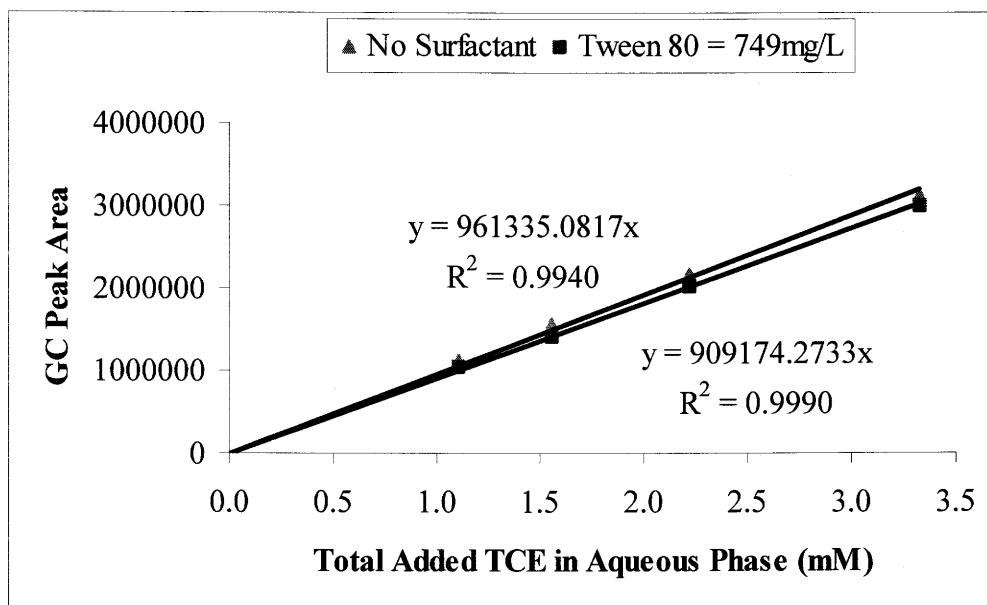


Figure A-9 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) (Tween 80 = 749 mg/L)

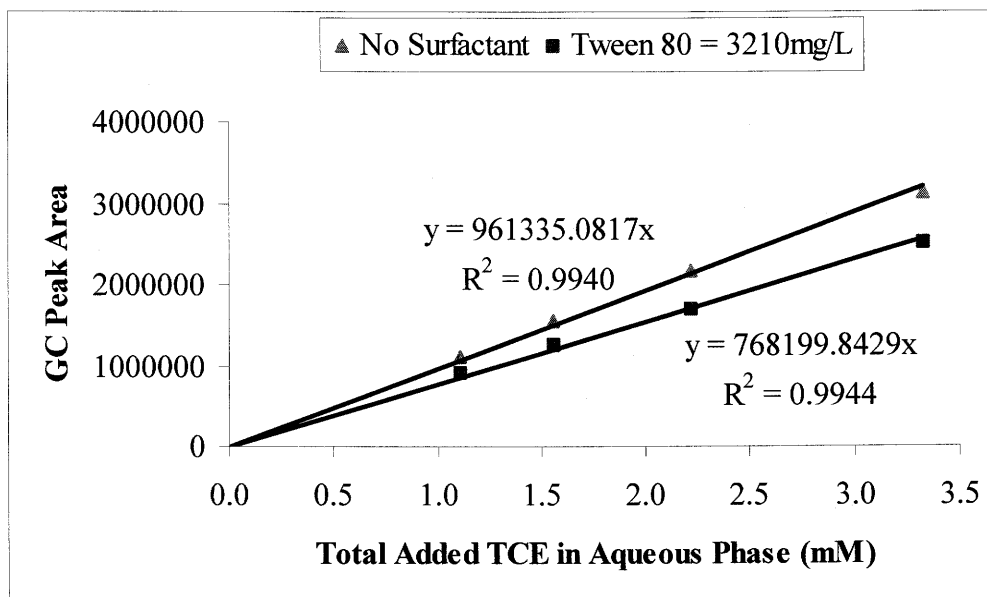


Figure A-10 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) (Tween 80 = 3210 mg/L)

Appendix B

Experimental Results for Temperature Effect Tests

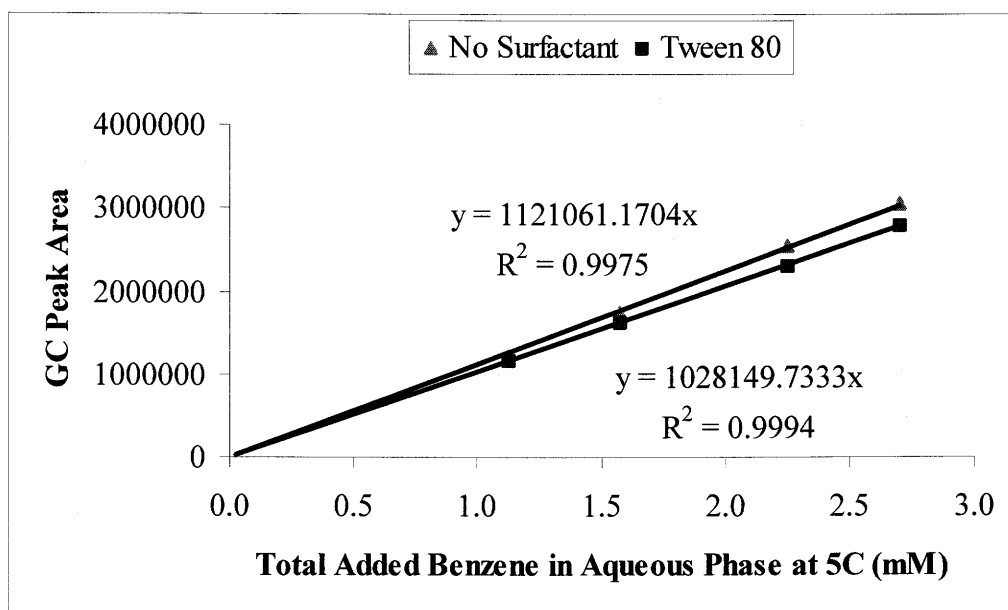


Figure B-1 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 5°C (Tween 80 = 3210 mg/L)

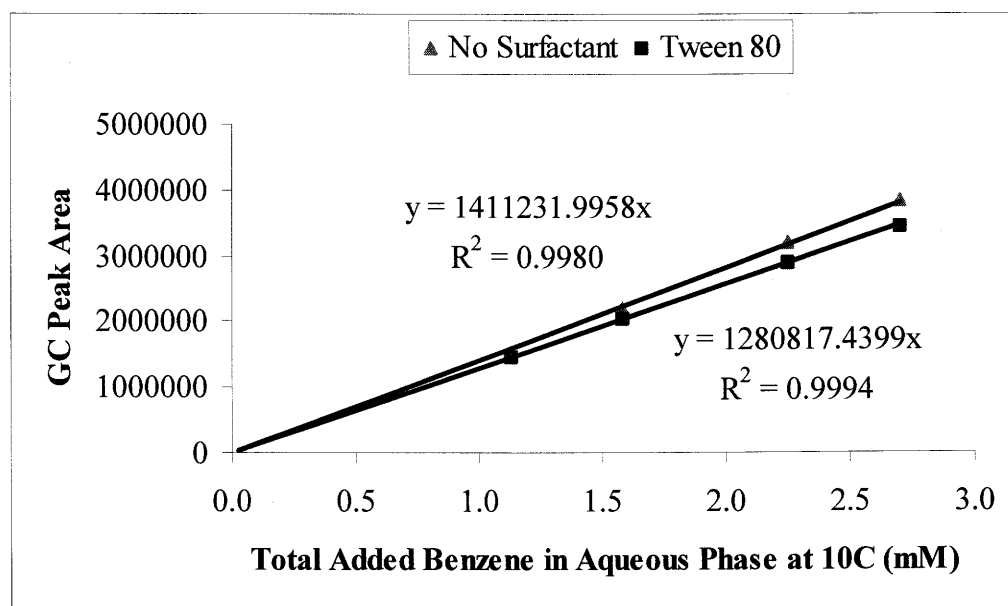


Figure B-2 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 10°C (Tween 80 = 3210 mg/L)

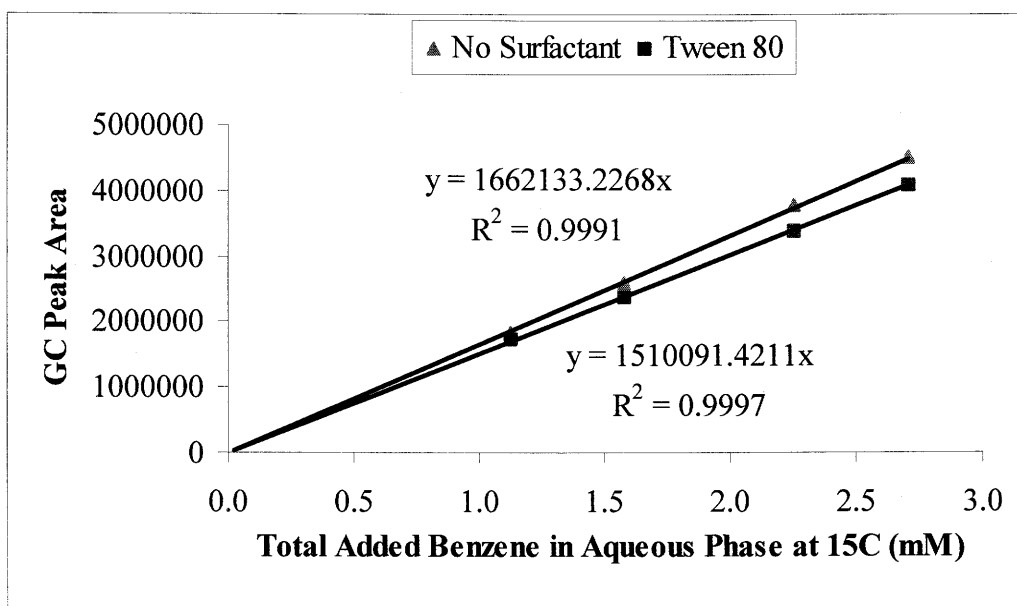


Figure B-3 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 15°C (Tween 80 = 3210 mg/L)

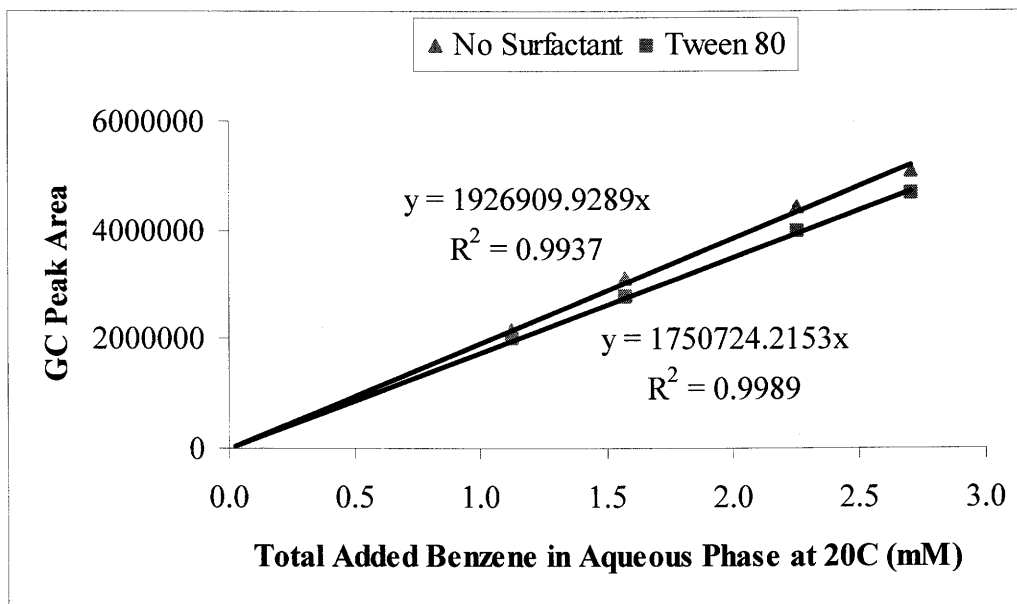


Figure B-4 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 20°C (Tween 80 = 3210 mg/L)

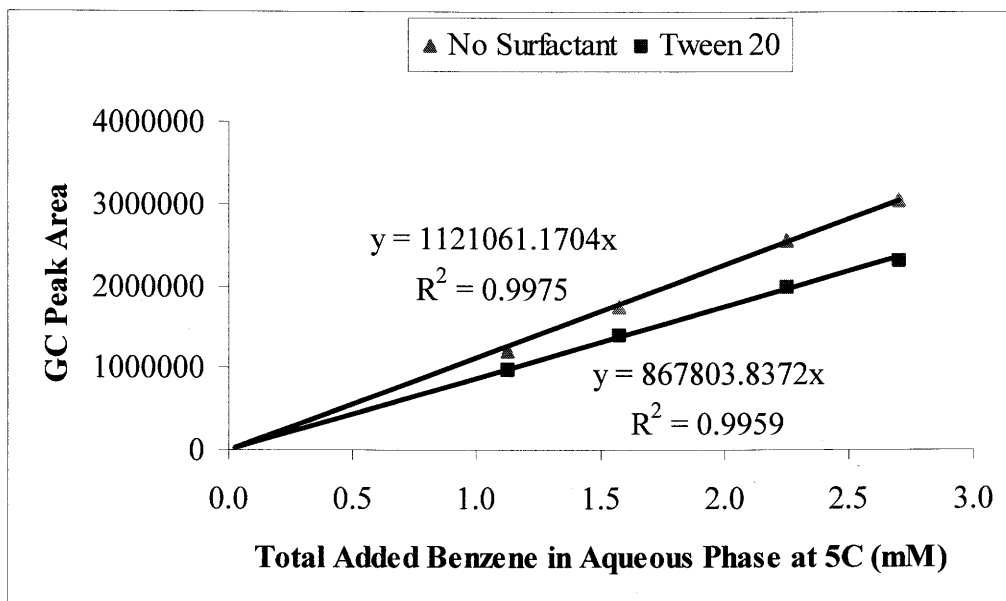


Figure B-5 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 5°C (Tween 20 = 13200 mg/L)

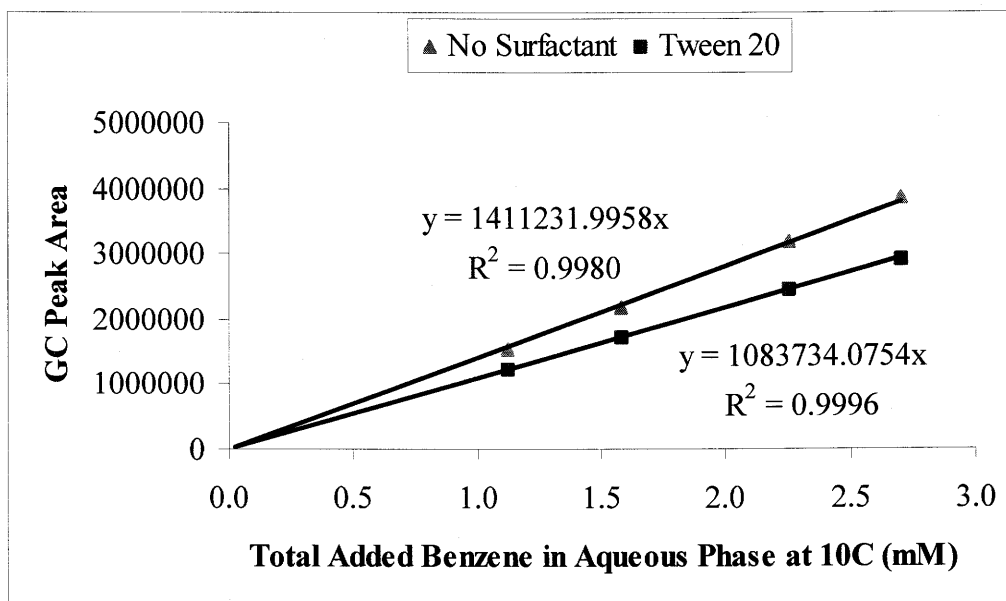


Figure B-6 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 10°C (Tween 20 = 13200 mg/L)

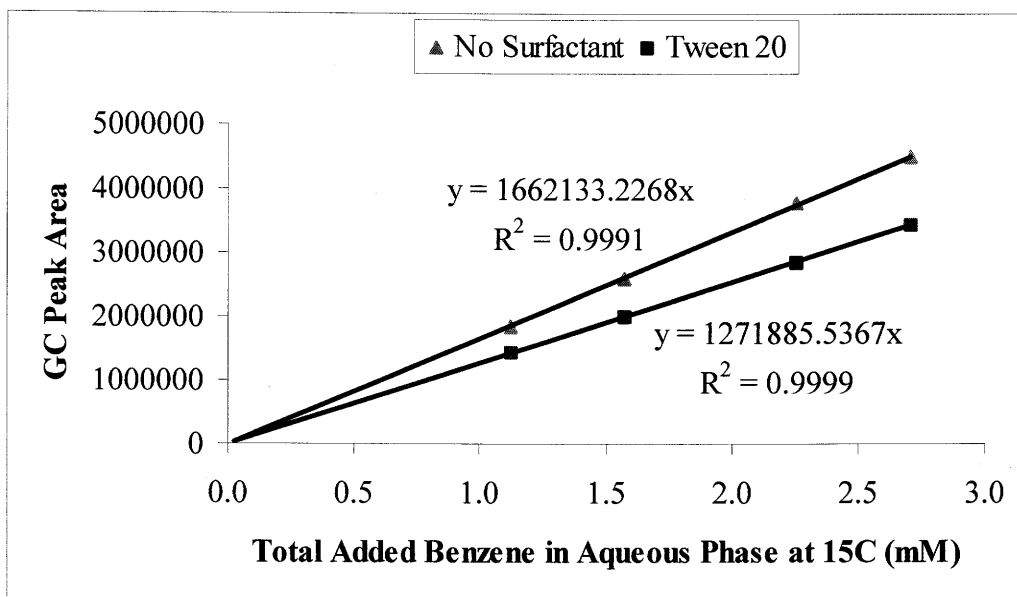


Figure B-7 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 15°C (Tween 20 = 13200 mg/L)

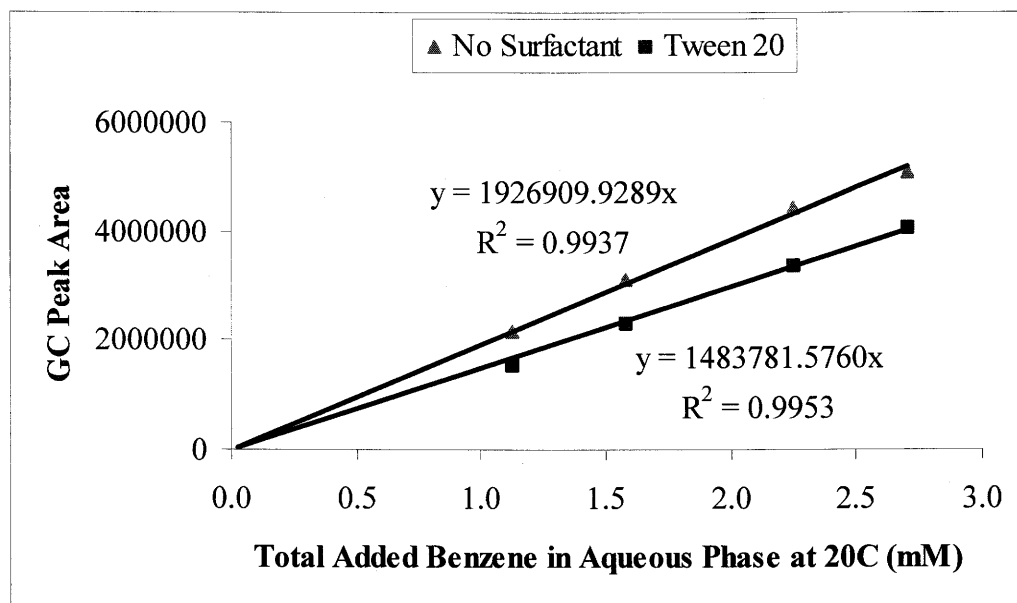


Figure B-8 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 20°C (Tween 20 = 13200 mg/L)

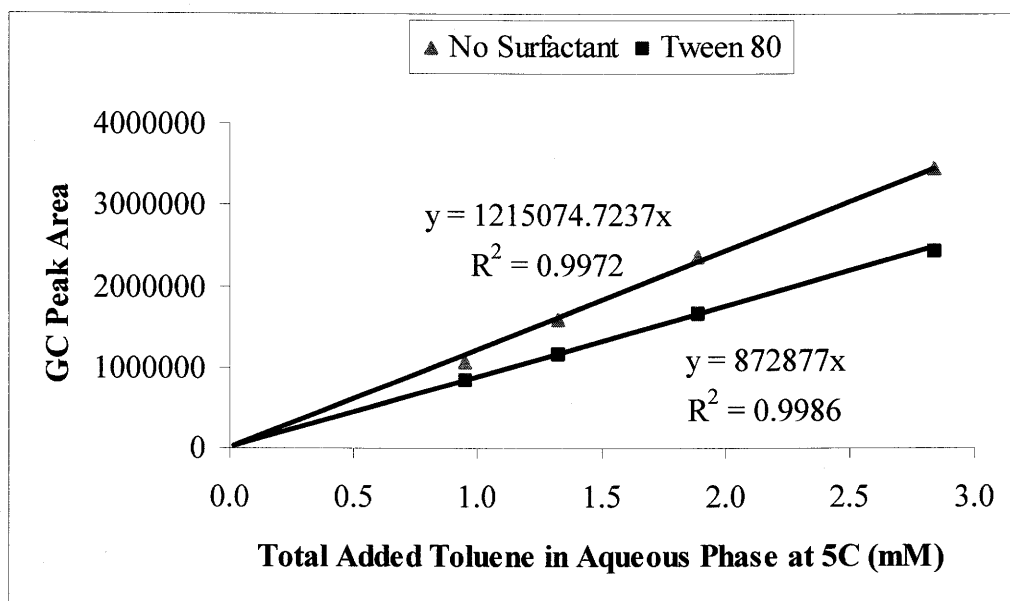


Figure B-9 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 5°C (Tween 80 = 3210 mg/L)

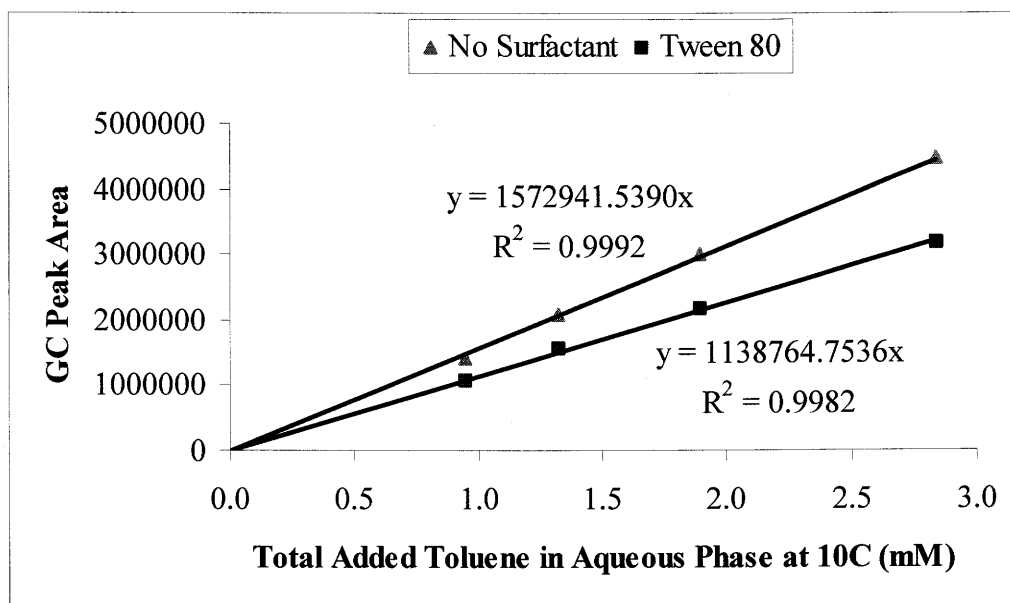


Figure B-10 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 10°C (Tween 80 = 3210 mg/L)

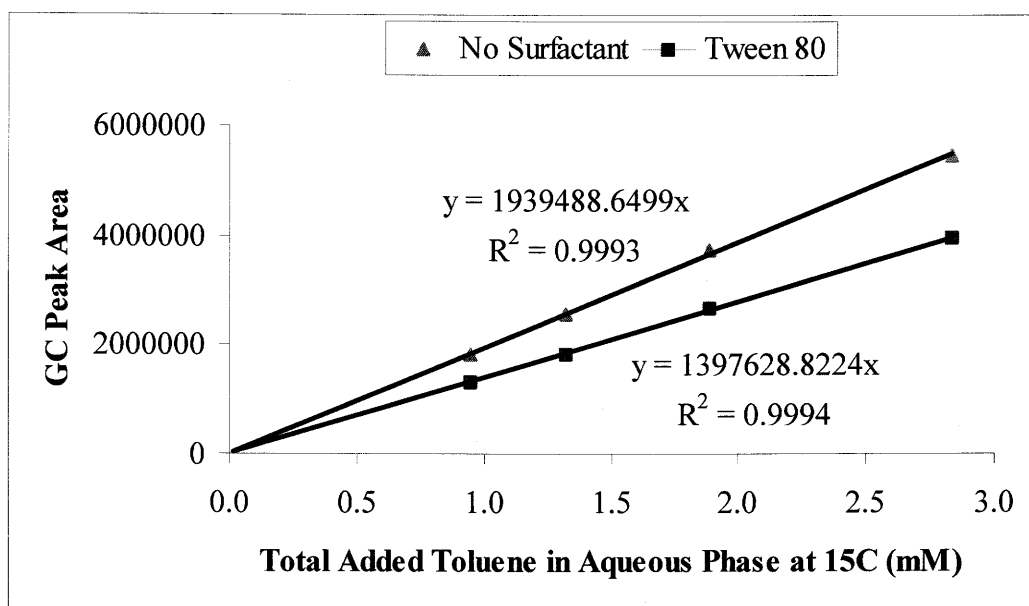


Figure B-11 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 15°C (Tween 80 = 3210 mg/L)

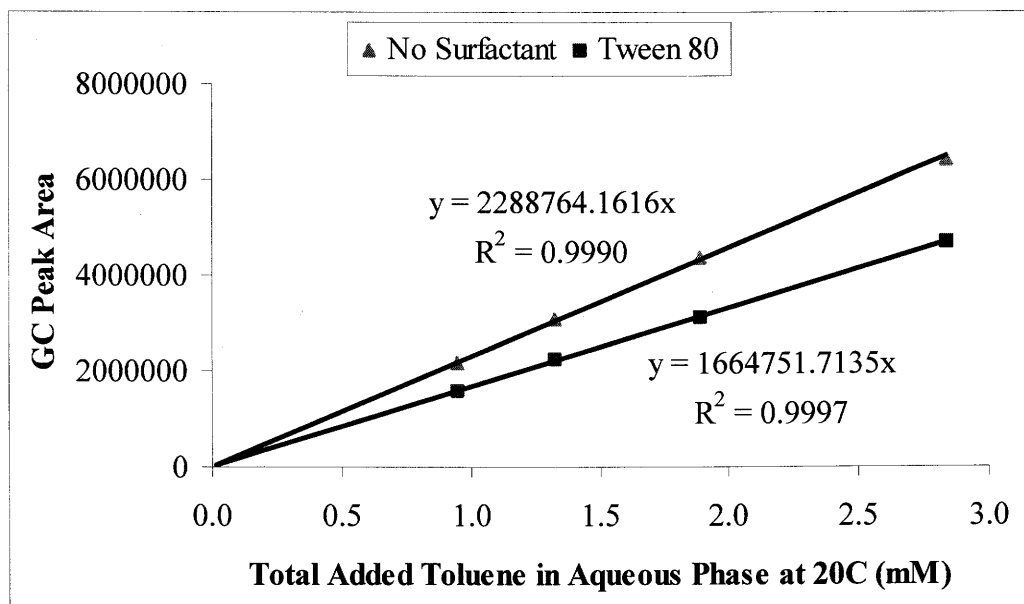


Figure B-12 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 20°C (Tween 80 = 3210 mg/L)

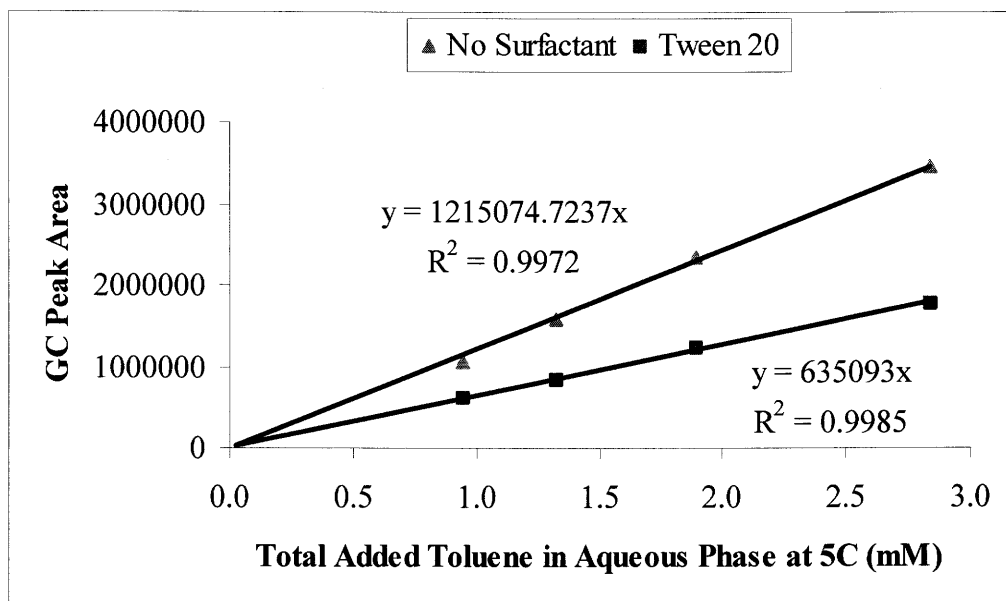


Figure B-13 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 5°C (Tween 20 = 13200 mg/L)

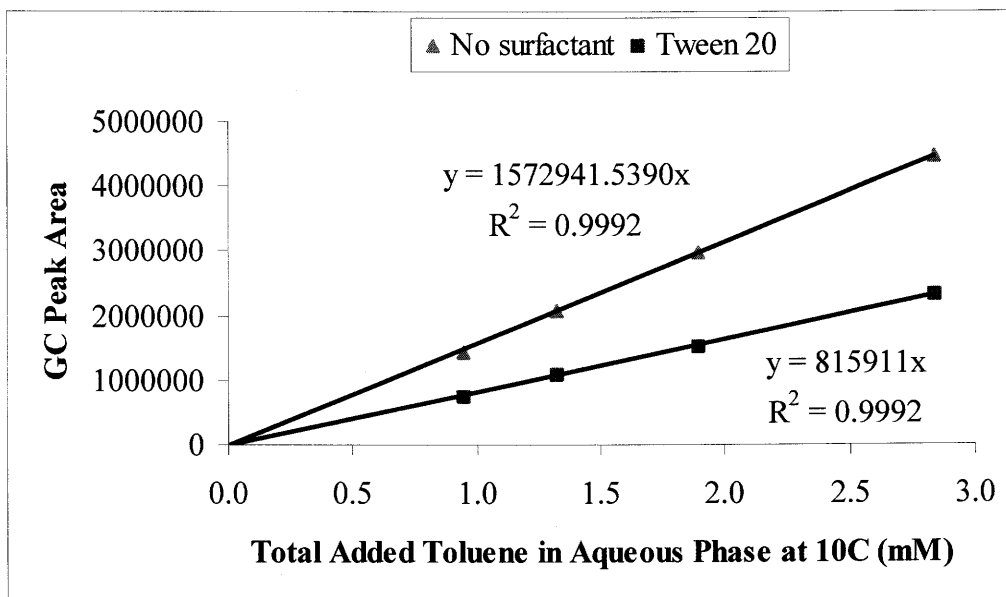


Figure B-14 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 10°C (Tween 20 = 13200 mg/L)

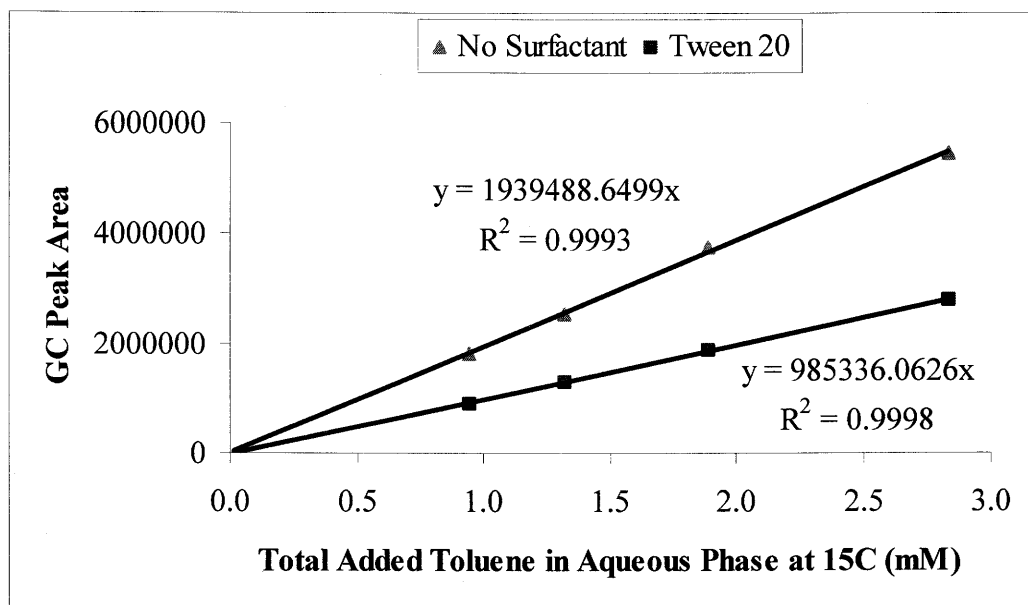


Figure B-15 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 15°C (Tween 20 = 13200 mg/L)

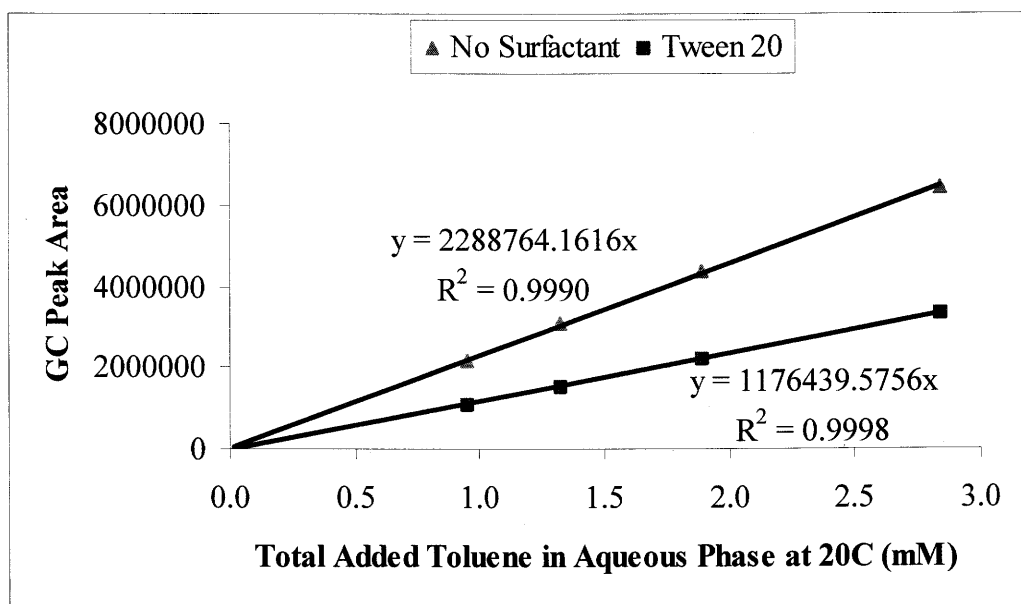


Figure B-16 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 20°C (Tween 20 = 13200 mg/L)

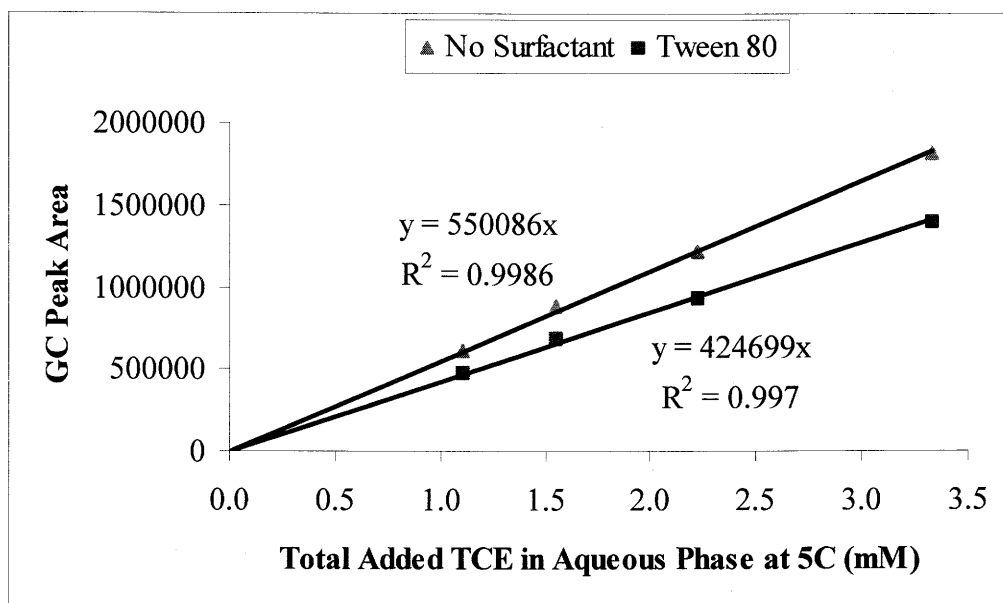


Figure B-17 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 5°C (Tween 80 = 3210 mg/L)

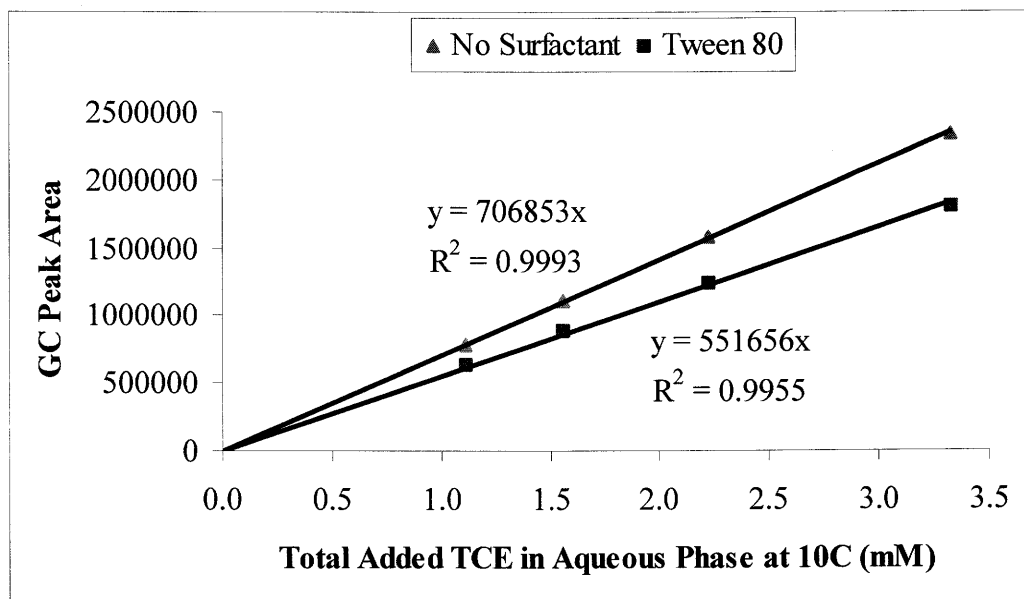


Figure B-18 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 10°C (Tween 80 = 3210 mg/L)

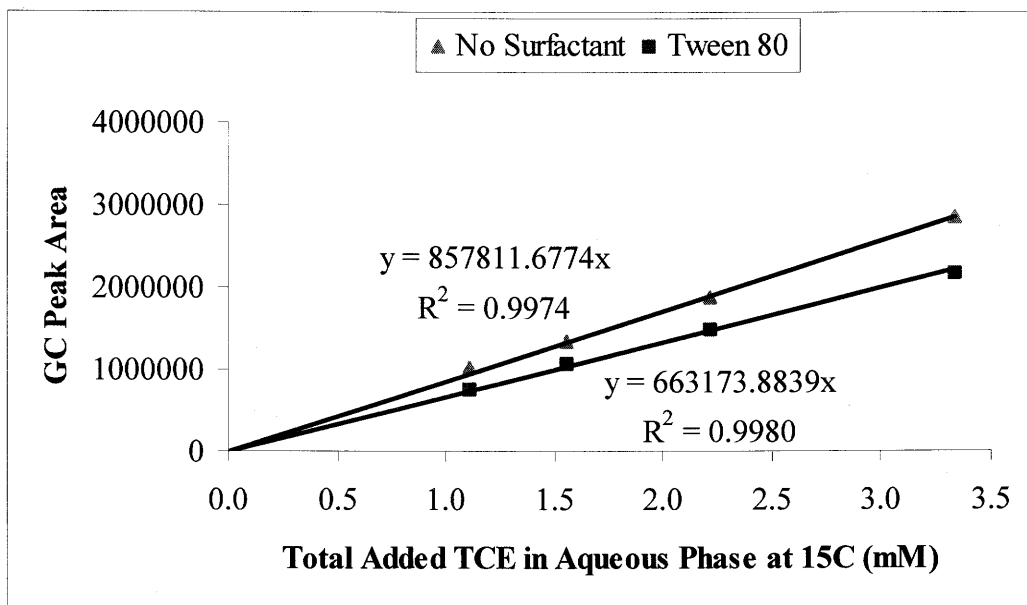


Figure B-19 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 15°C (Tween 80 = 3210 mg/L)

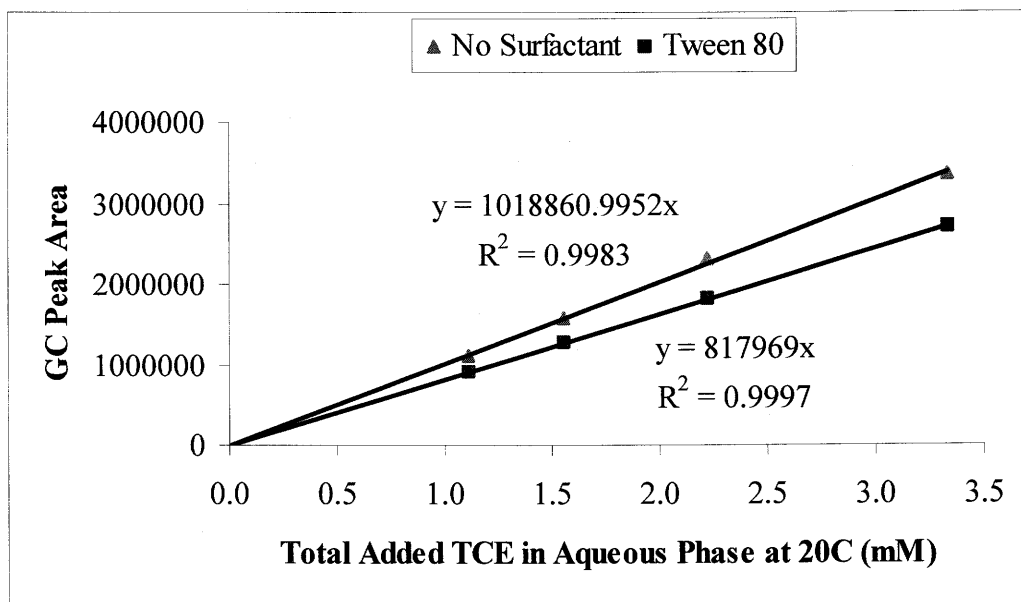


Figure B-20 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 20°C (Tween 80 = 3210 mg/L)

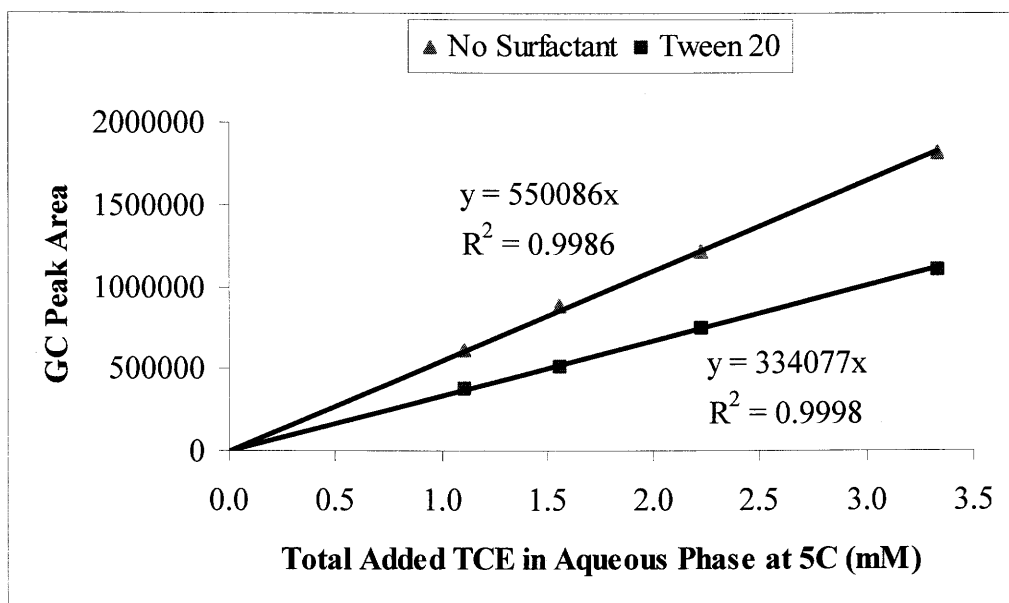


Figure B-21 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 5°C (Tween 20 = 13200 mg/L)

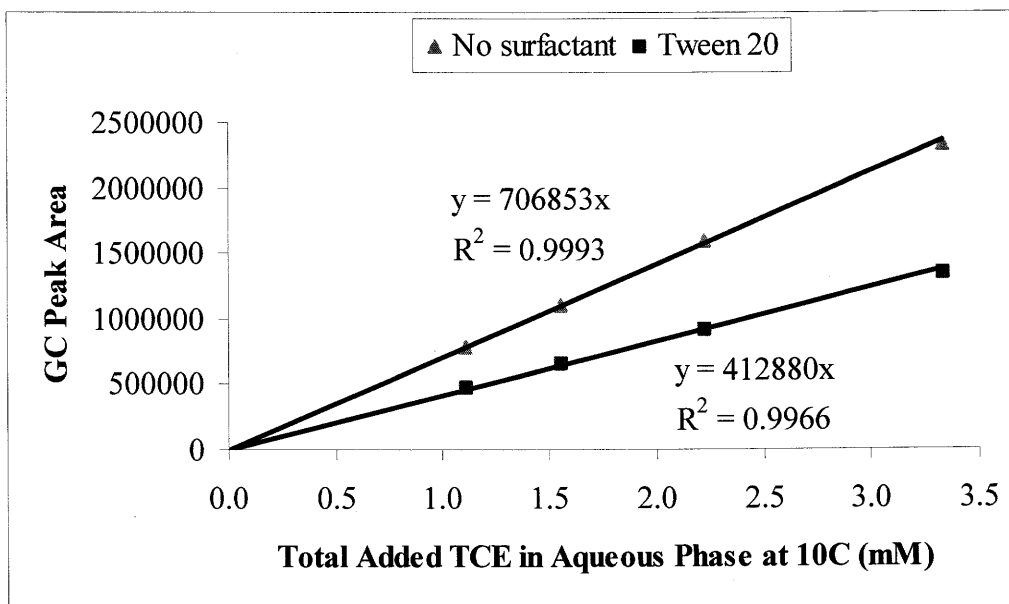


Figure B-22 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 10°C (Tween 20 = 13200 mg/L)

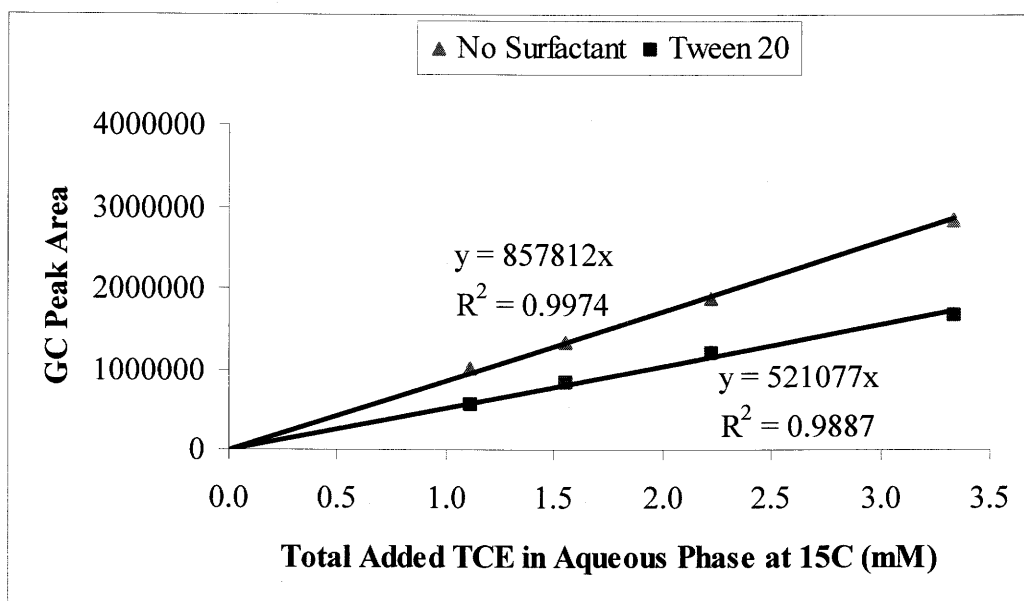


Figure B-23 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 15°C (Tween 20 = 13200 mg/L)

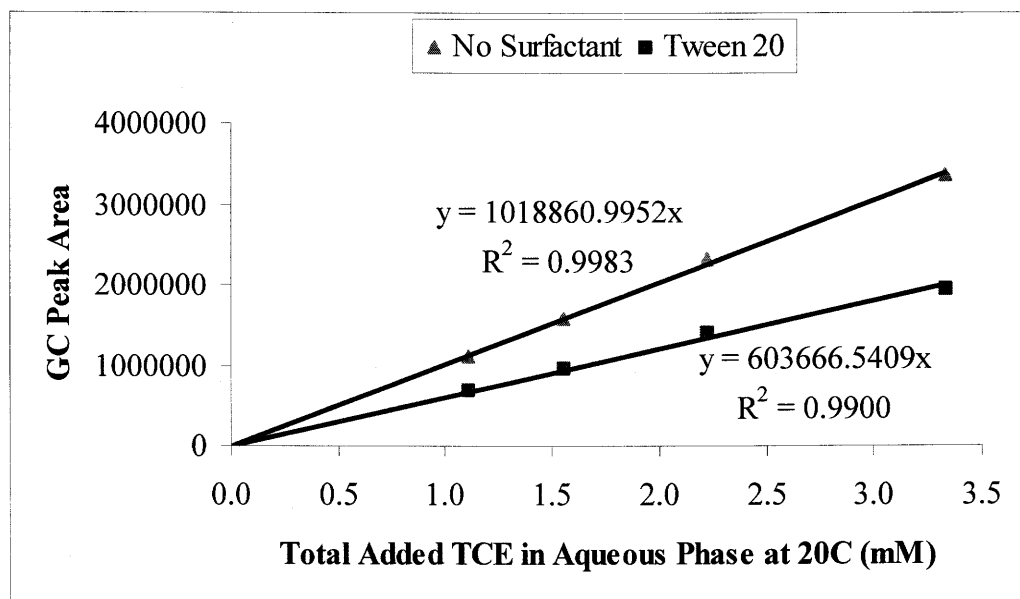


Figure B-24 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 20°C (Tween 20 = 13200 mg/L)

Appendix C

Experimental Results for Toluene and Ionic Strength Tests

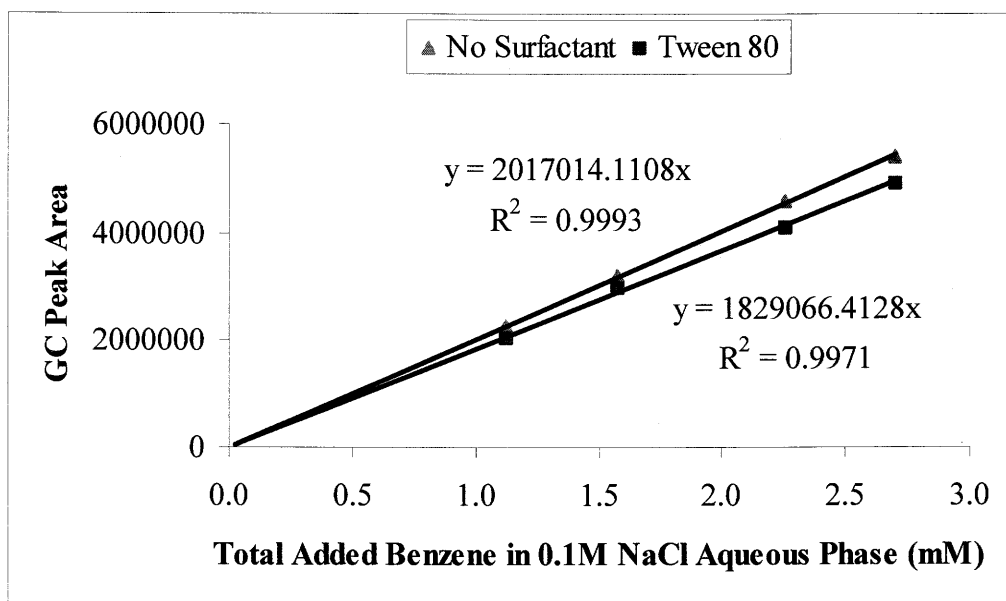


Figure C-1 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 0.1 M NaCl (Tween 80 = 3210 mg/L)

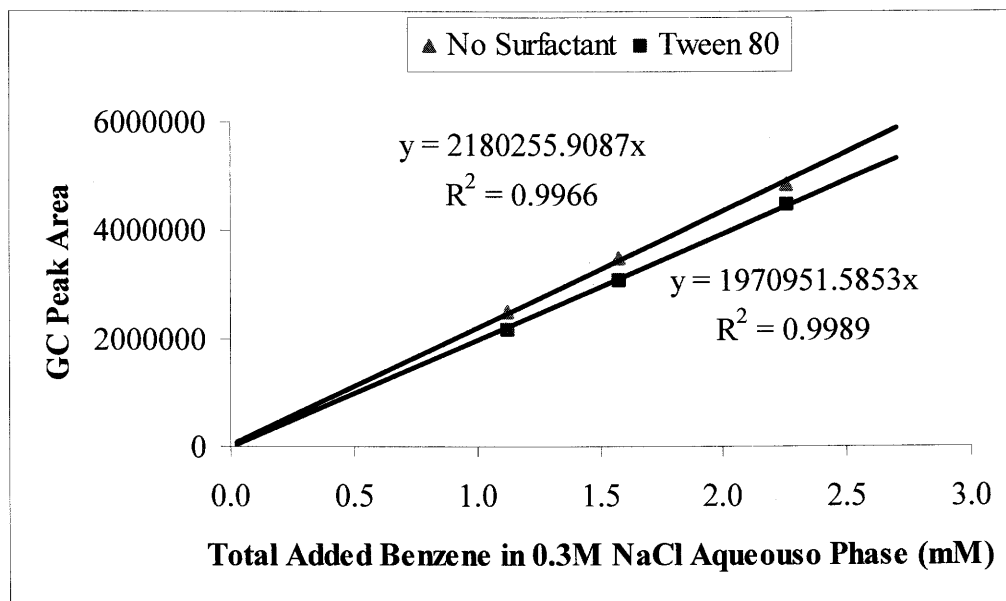


Figure C-2 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 0.3 M NaCl (Tween 80 = 3210 mg/L)

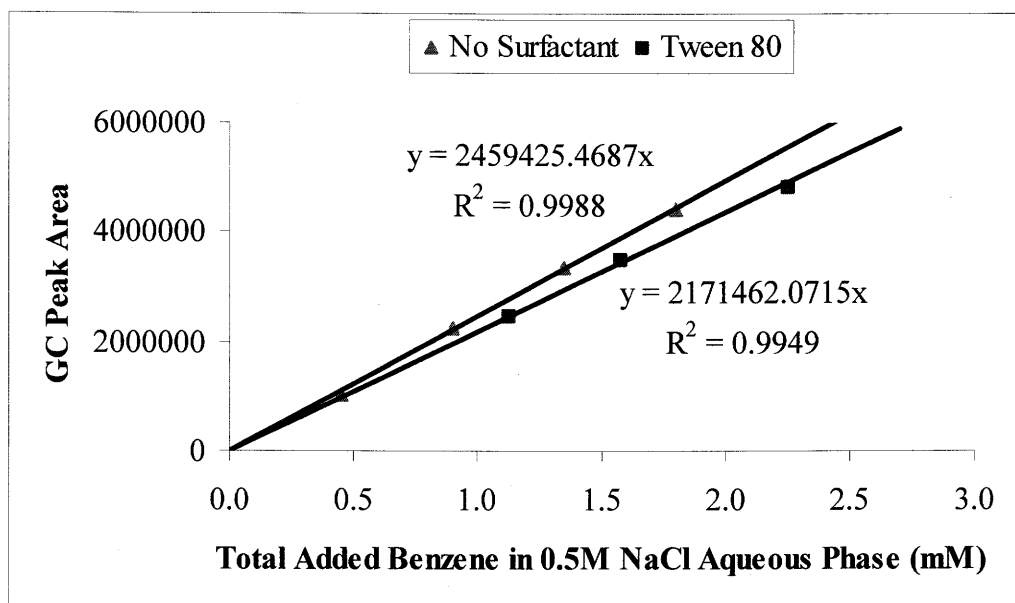


Figure C-3 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 0.5 M NaCl (Tween 80 = 3210 mg/L)

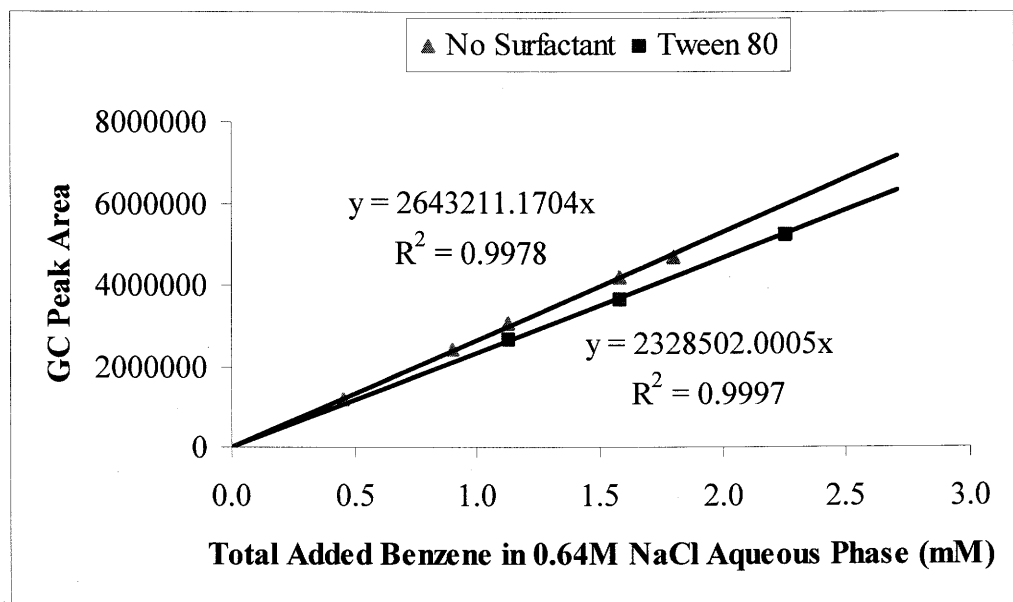


Figure C-4 Henry's Law Curve for Benzene in Water (upper) and Tween 80 Solution (lower) at 0.64 M NaCl (Tween 80 = 3210 mg/L)

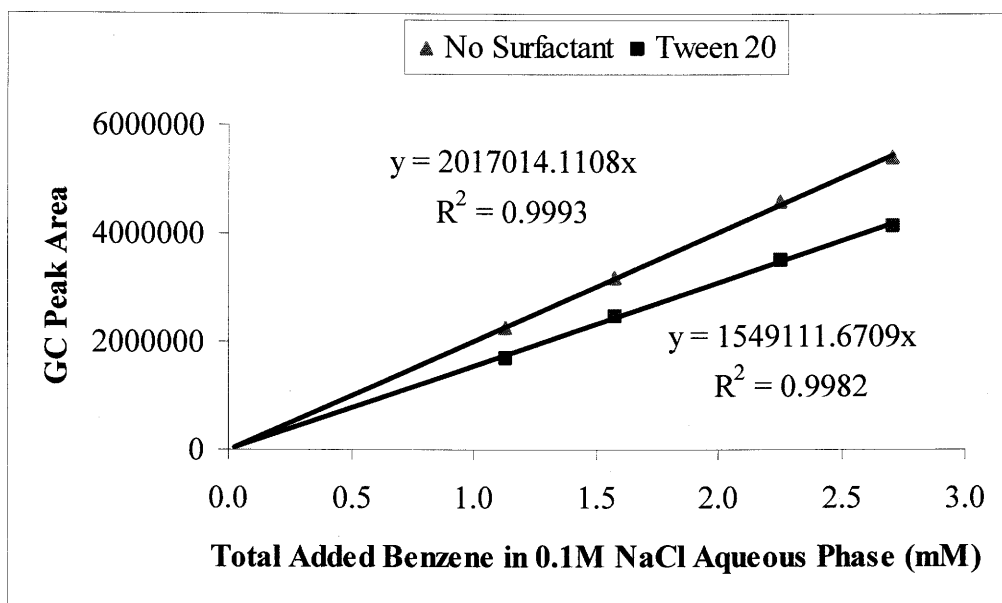


Figure C-5 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 0.1 M NaCl (Tween 20 = 13200 mg/L)

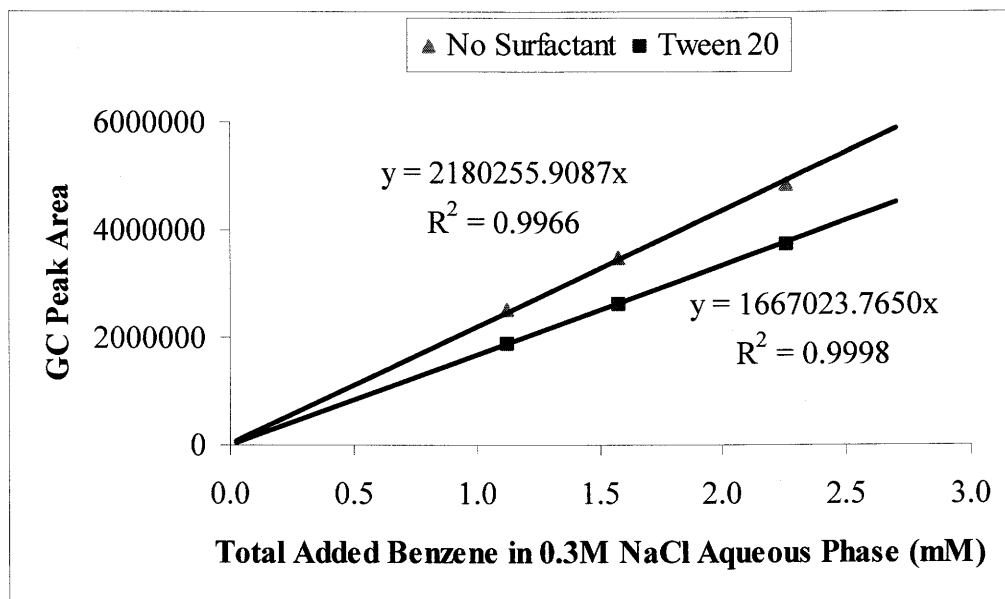


Figure C-6 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 0.3 M NaCl (Tween 20 = 13200 mg/L)

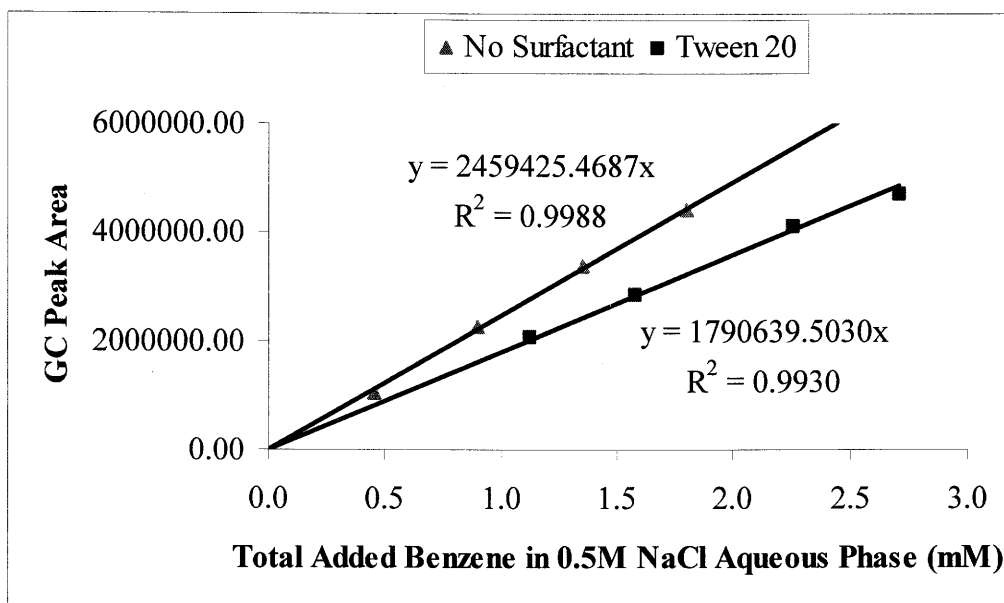


Figure C-7 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 0.5 M NaCl (Tween 20 = 13200 mg/L)

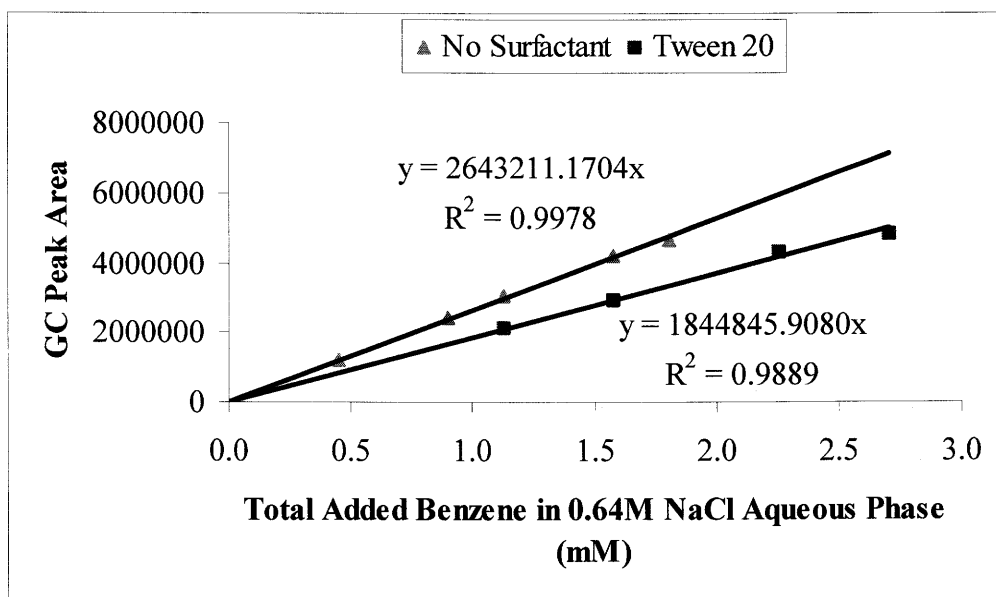


Figure C-8 Henry's Law Curve for Benzene in Water (upper) and Tween 20 Solution (lower) at 0.64 M NaCl (Tween 20 = 13200 mg/L)

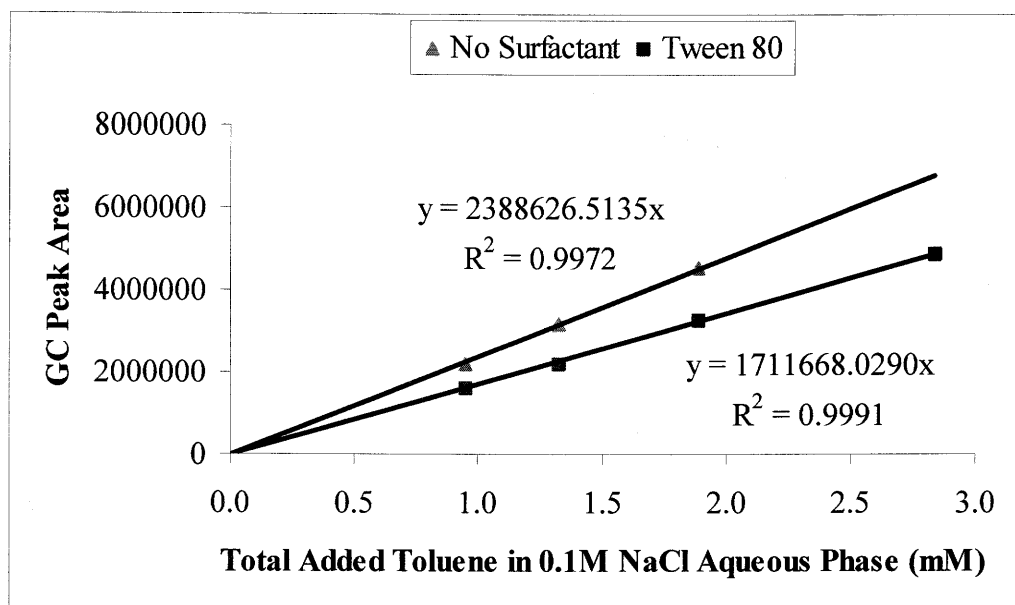


Figure C-9 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 0.1 M NaCl (Tween 80 = 3210 mg/L)

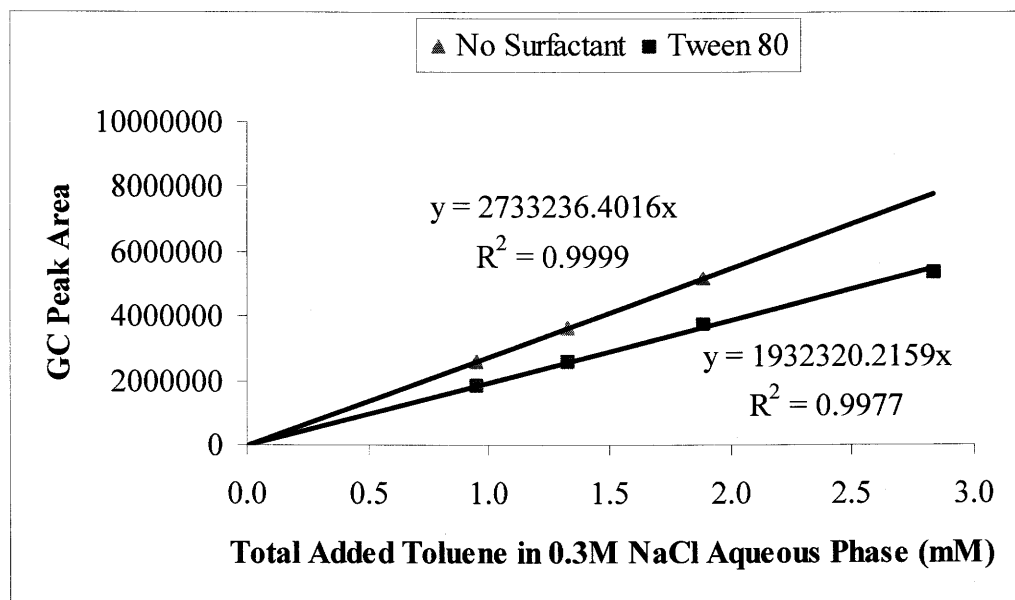


Figure C-10 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 0.3 M NaCl (Tween 80 = 3210 mg/L)

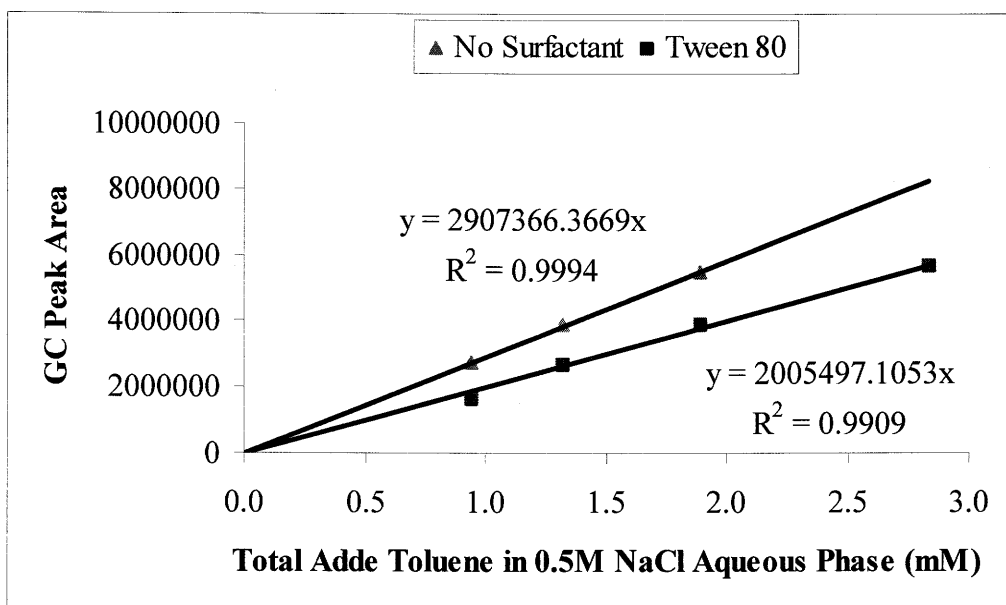


Figure C-11 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 0.5 M NaCl (Tween 80 = 3210 mg/L)

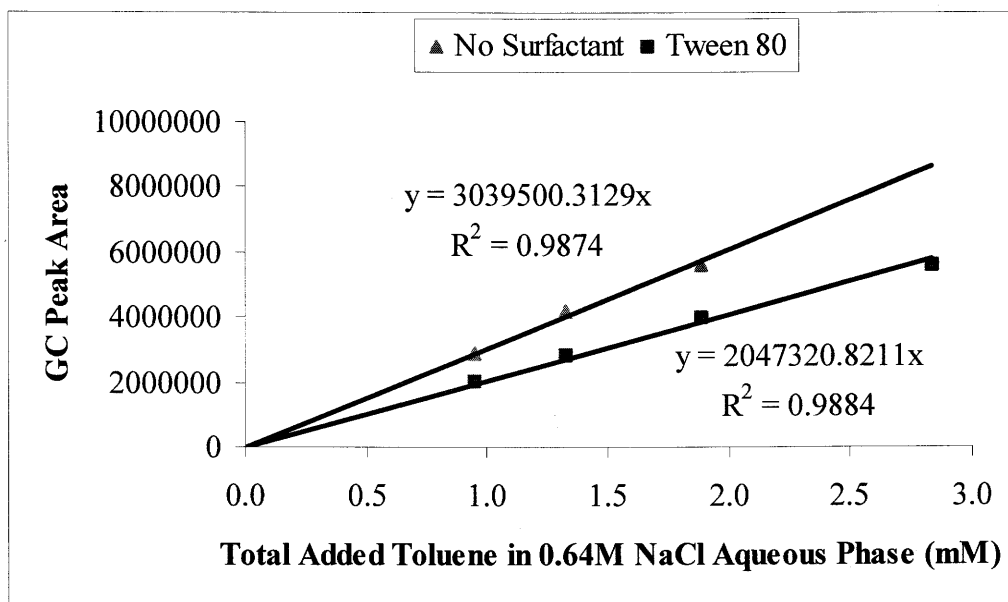


Figure C-12 Henry's Law Curve for Toluene in Water (upper) and Tween 80 Solution (lower) at 0.64 M NaCl (Tween 80 = 3210 mg/L)

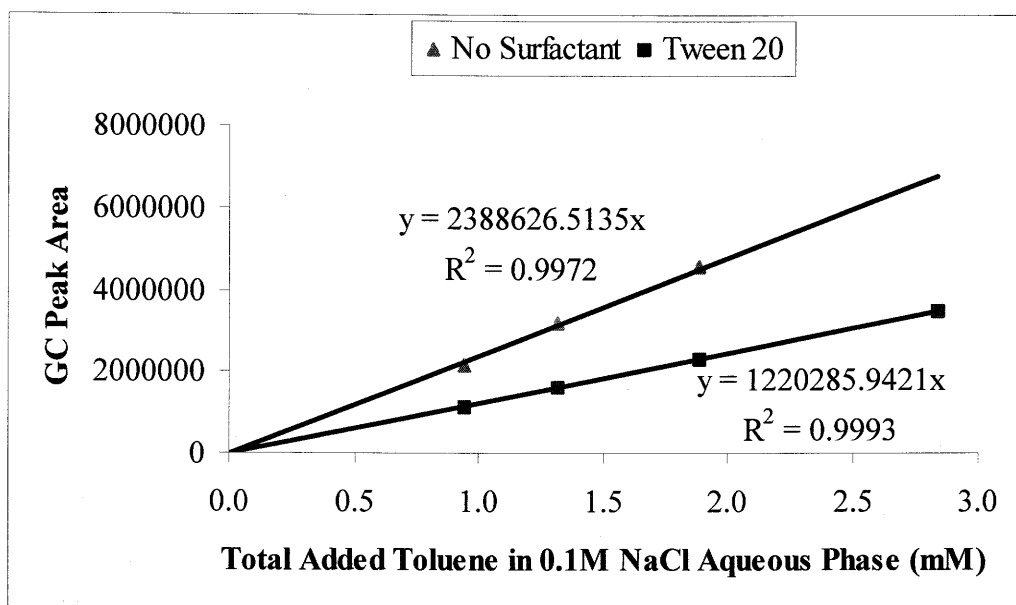


Figure C-13 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 0.1 M NaCl (Tween 20 = 13200 mg/L)

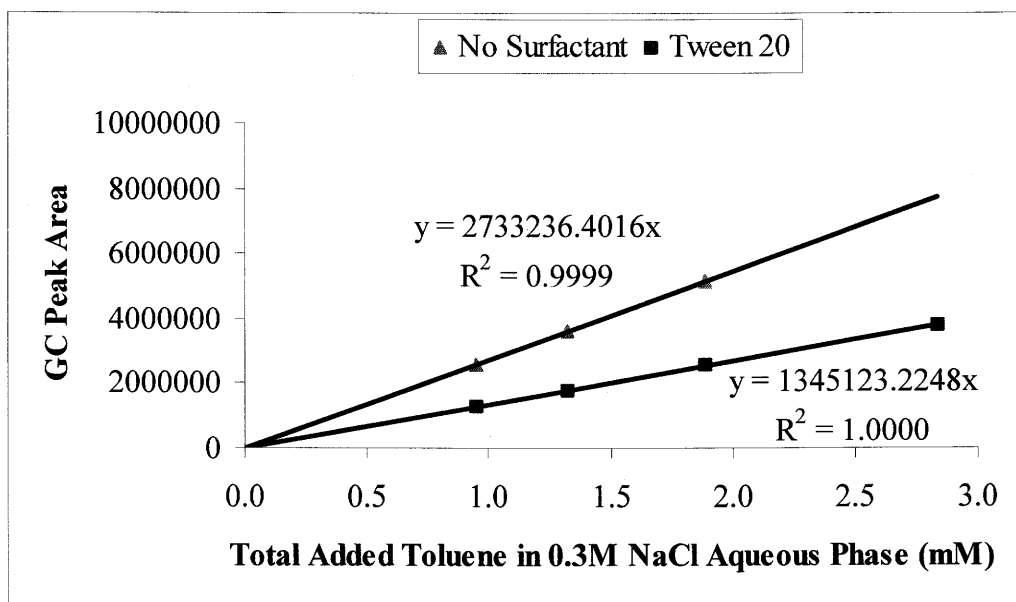


Figure C-14 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 0.3 M NaCl (Tween 20 = 13200 mg/L)

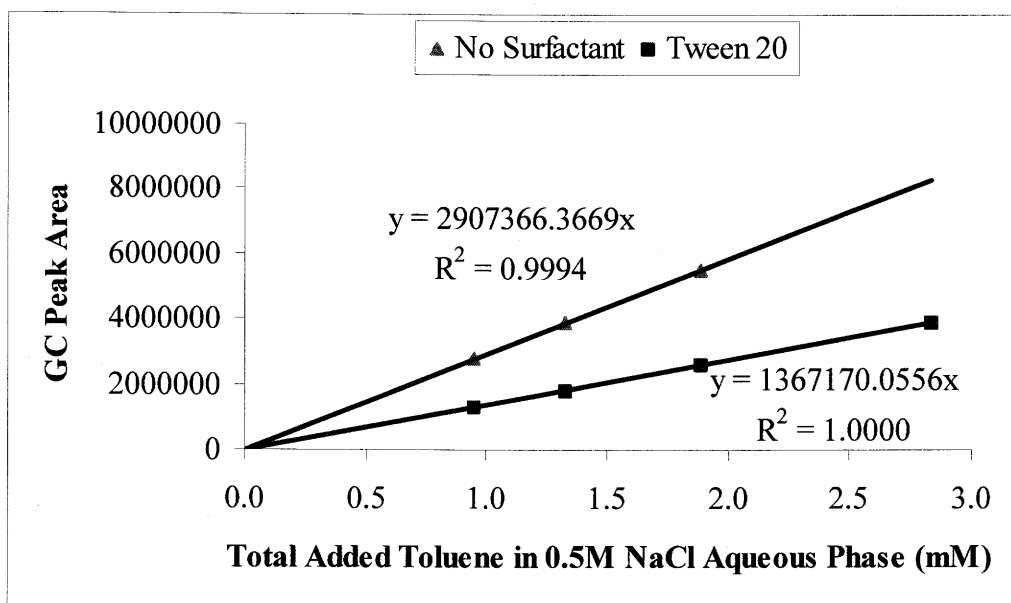


Figure C-15 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 0.5 M NaCl (Tween 20 = 13200 mg/L)

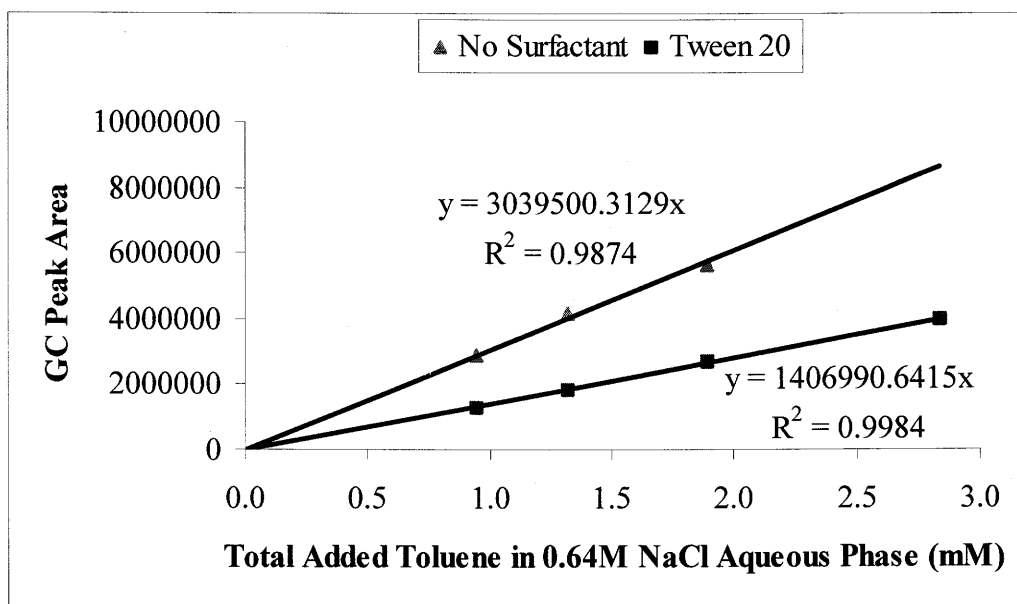


Figure C-16 Henry's Law Curve for Toluene in Water (upper) and Tween 20 Solution (lower) at 0.64 M NaCl (Tween 20 = 13200 mg/L)

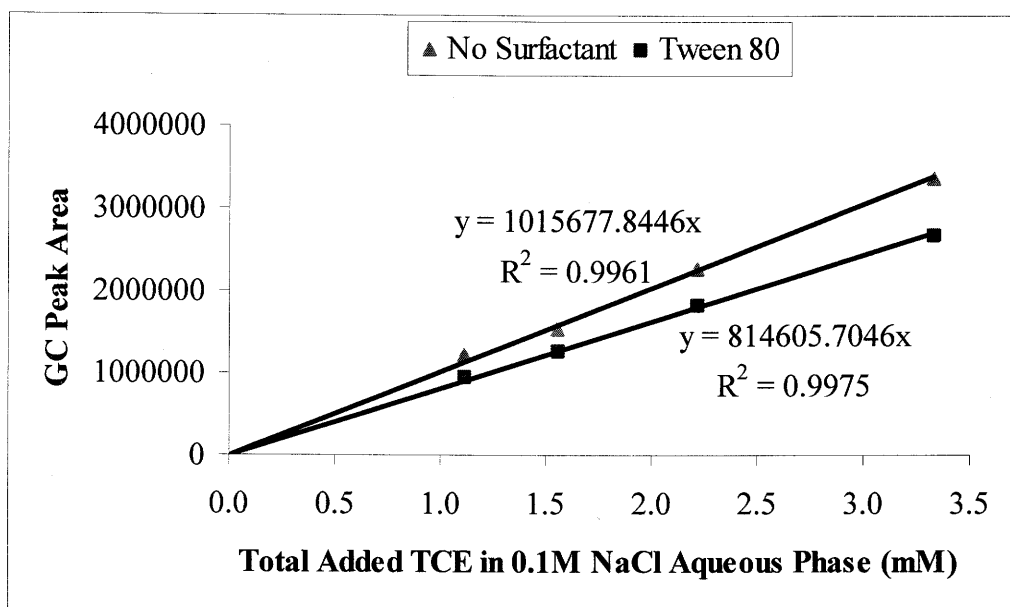


Figure C-17 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 0.1 M NaCl (Tween 80 = 3210 mg/L)

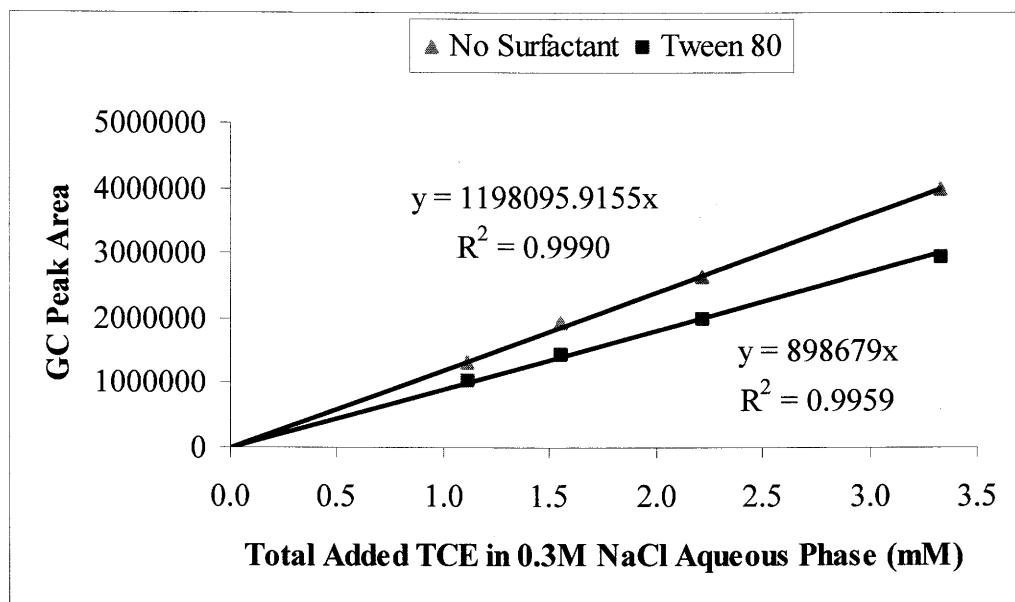


Figure C-18 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 0.3 M NaCl (Tween 80 = 3210 mg/L)

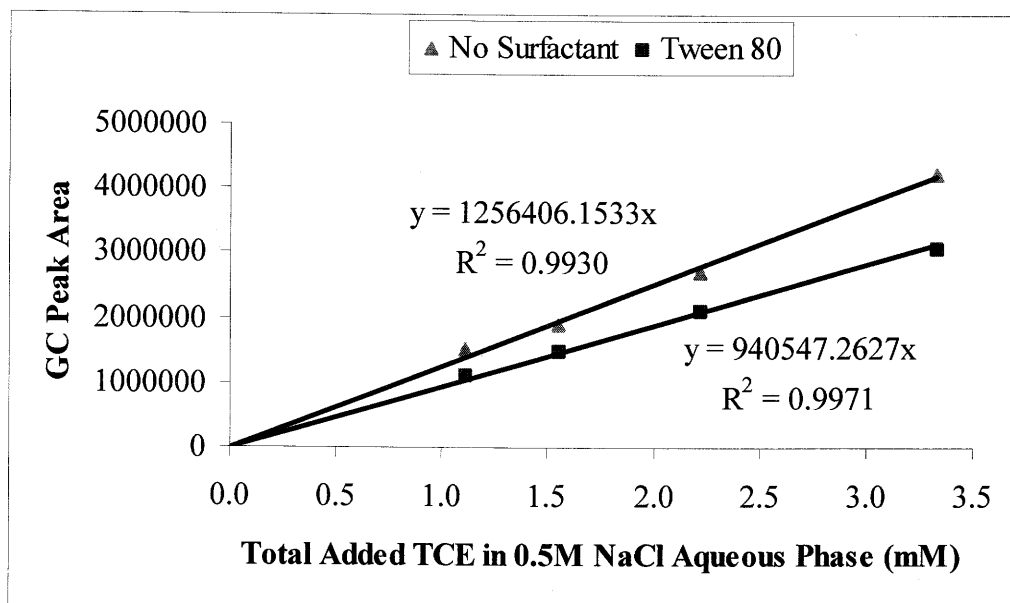


Figure C-19 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 0.5 M NaCl (Tween 80 = 3210 mg/L)

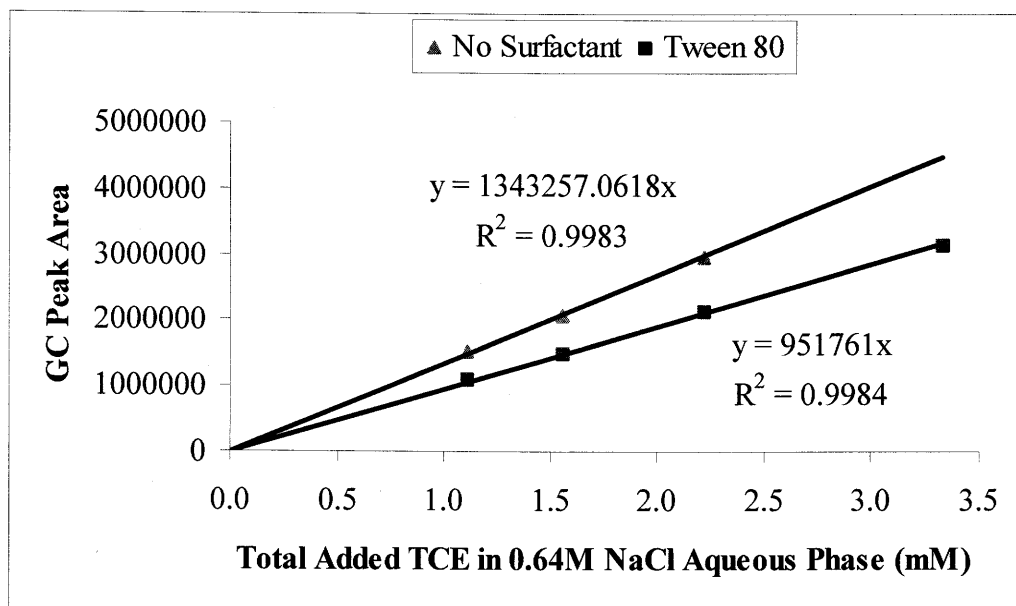


Figure C-20 Henry's Law Curve for TCE in Water (upper) and Tween 80 Solution (lower) at 0.64 M NaCl (Tween 80 = 3210 mg/L)

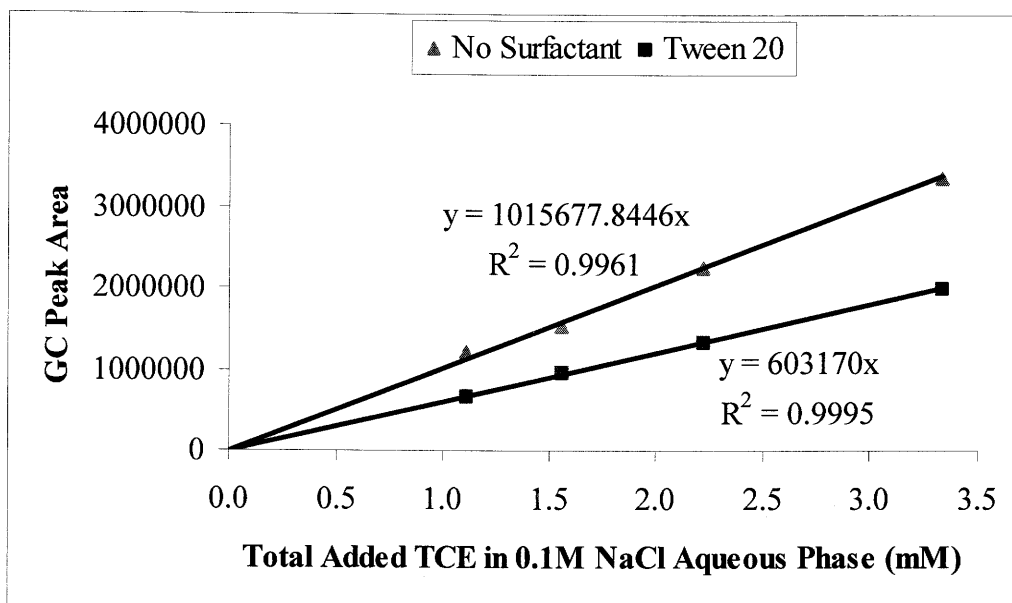


Figure C-21 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 0.1 M NaCl (Tween 20 = 13200 mg/L)

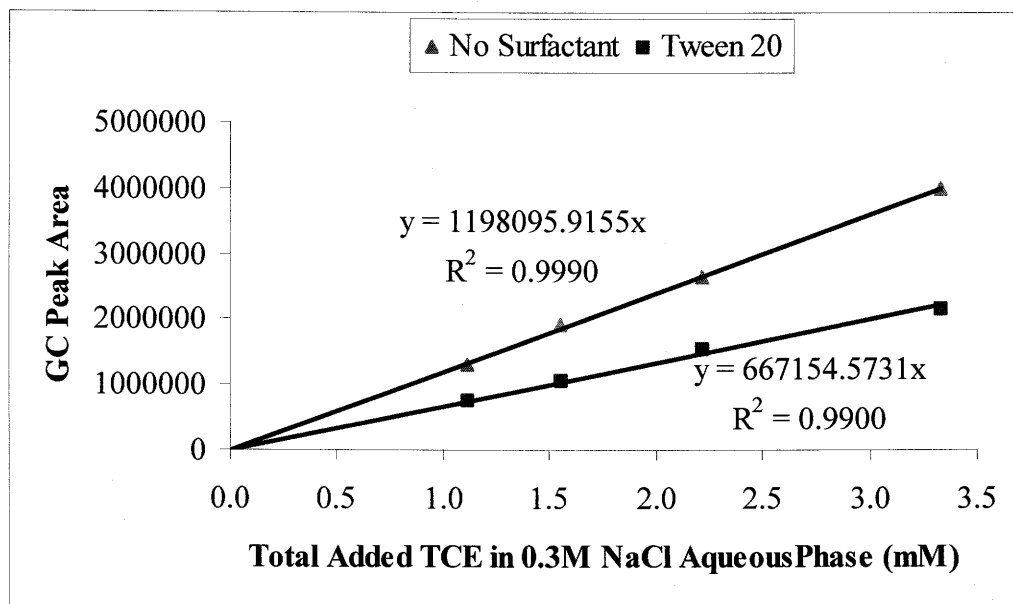


Figure C-22 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 0.3 M NaCl (Tween 20 = 13200 mg/L)

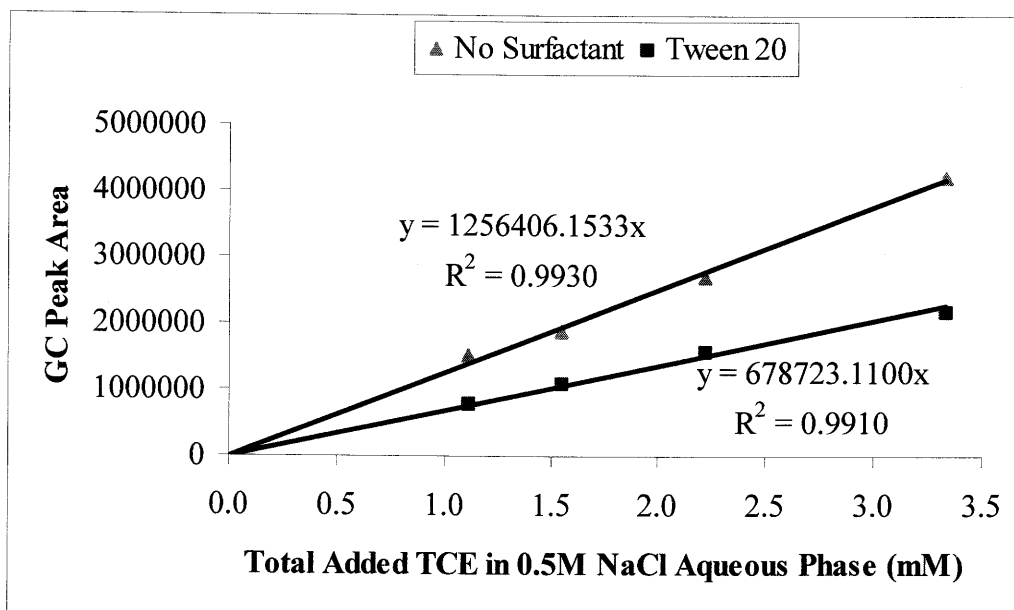


Figure C-23 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 0.5 M NaCl (Tween 20 = 13200 mg/L)

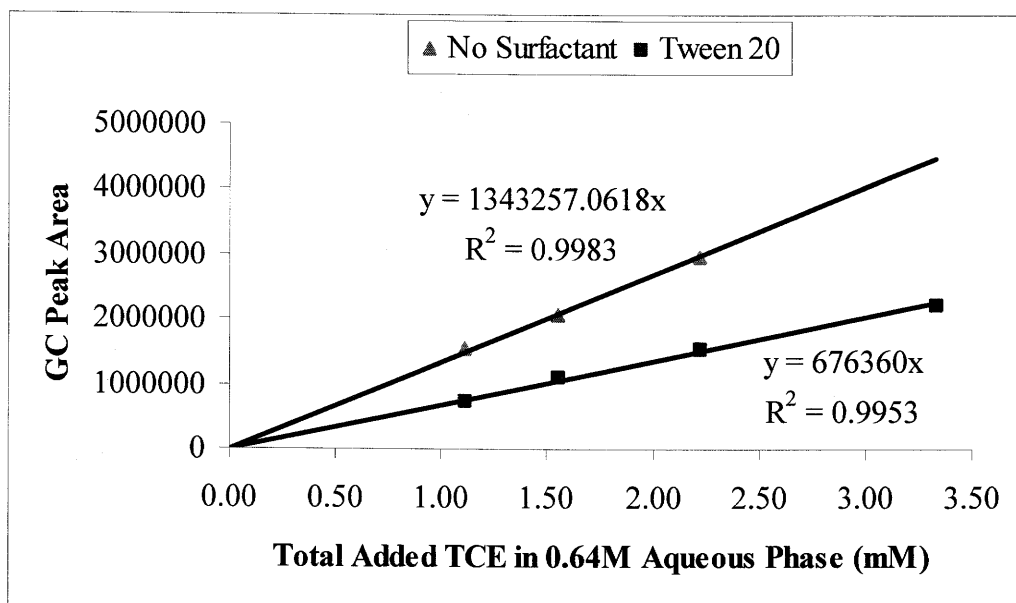


Figure C-24 Henry's Law Curve for TCE in Water (upper) and Tween 20 Solution (lower) at 0.64 M NaCl (Tween 20 = 13200 mg/L)