

**An-Najah National University
Faculty of Graduate Studies**

**SORPTION CHARACTERISTICS OF
NONIONIC SURFACTANT TRITON X-100 IN SOIL
CONTAMINATED WITH DIESEL**

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Signature

Sheheleh Jodeh

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.....
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Dedication

To my Mother, to my Family and every
one who helped and supported me in my
research achievement

Acknowledgment

Praise is to Allah, the most merciful, the most graceful for granting me the power and courage to finish this work.

I wish to express my sincere gratitude to my supervisor, Dr. S. Jodeh for his guidance and support during my research work, as well as his help in my thesis writing. I would like to thank Dr. S. Khalaf, Mr. A. Abu Ubaid, Dr. R. Dawoud, and all members of Chemistry Department for their advice and encouragement.

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I'm also greatly indebted to my mother and family for their support and help during my work.

إقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

SORPTION CHARACTERISTICS OF NONIONIC SURFACTANT TRITON X-100 IN SOIL CONTAMINATED WITH DIESEL

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة علمية أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

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The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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List of Symbols

$1/n$: constant which indicates the curvature of the isotherm.

a : a constant for correlation K_m and K_{ow} (L/mol).

b : a constant for correlating K_{oc} and K_{ow} (L/mol).

C : TPH liquid concentration (mol/L).

C_o : total initial concentration in solution (mg/mL).

CAC : critical aggregation concentration.

CMC : concentration at which surfactant monomers start to form micelles (mol/L).

C_{CMC} : apparent solubility of petroleum hydrocarbon compound as moles per liter at the CMC.

C_e : equilibrium concentration in solution (mg/mL).

CMC_{eff} : the concentration of surfactant in aqueous-soil system that gives the same surface tension in the absence of soil (mol/L).

C_{mic} : total apparent solubility of petroleum hydrocarbon Compound as moles per liter in micellar solution at a particular surfactant concentration greater than CMC.

C_s : is the concentration of the analyte in the aqueous phase (mg/mL).

C_{sorb} : the number of moles of surfactant sorbed per liter of solution evaluated at the particular bulk solution surfactant concentration (mol/L).

C_{surf} : surfactant concentration at which C_{mic} was evaluated (mol/L).

C_{surf} : aqueous-phase surfactant concentration (for the aqueous phase without soil) (mol/L).

$D_{s, \sigma}$: bulk surfactant dose in the soil/aqueous system that produces a surface tension value of σ in the supernatant (mol/L).

f_{oc} : fractional organic carbon content of soil or sediment.

HLB : Hypophile-Lipophile Blance

HOC : hydrophobic organic compounds.

K : sorption capacity.

K_d : overall distribution coefficient.

K_m : micelle water partition coefficient.

K_{oc} : organic carbon normalized distribution coefficient at equilibrium (L/kg).

K_{ow} : the octanol-water partition coefficient.

K_p : partition coefficient that measure the tendency of a chemical to be adsorbed by soil or sediment from liquid phase.

m : mass of soil (g).

MSR: molar solubilization ratio of a given hydrocarbon in surfactant solution (moles of hydrophobic organic contaminant solubilized per mole of surfactant above its CMC).

P_{mic} : concentration of HOC in the surfactant micelles (mol/L).

P_s : concentration of HOC in soil or sediment (mol/kg).

P_{surf} : concentration of HOC solubilized by both monomeric and micellar phases (mol/L).

P_w : concentration of HOC in the water (mol/L).

Q_g : the number of grams of nonionic surfactant sorbed per gram of the soil.

Q_{max} : maximum plateau value of sorption in moles per gram for the micelle-forming surfactant on the particular soil (mol/g).

Q_{surf} : number of moles of surfactant sorbed per gram of soil (mol/g).

S : concentration of surfactant in both monomeric and micellar forms (mol/L).

S_{mic} : concentration of surfactant in micellar form (mol/L).

TPH : Total Petroleum Hydrocarbons.

V_a : volume of aqueous solution (L).

$V_{a,mol}$: molar volume of water at the experimental temperature.

W_{soil} : weight of soils (g).

x : HOC concentration in soil (mg).

X : sorbed concentration (mg/gm)

X_a : mole fraction of organic solute in the micelle-free aqueous phase.

X_m : mole fraction of organic solute in the micelle phase.

X_{max} : maximum adsorbed concentration

β : constant relates K_m with K_{ow}

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Abstract

Surfactant with its amphiphilic nature toward polar and nonpolar substances may be used in mass transfer improvement of hydrophobic pollutants from solid or non-aqueous liquid phase into aqueous phase by decreasing interfacial tension and formation of micelles which surround these pollutants and solubilize them into aqueous phase. Micelles are often characterized according to their size and shape. The geometric properties of these micelles depend on the chemical structure of the surfactant and on the concentration and the nature of the aqueous environment. The adsorption of the surfactant on solid surfaces can lower the concentration of free surfactant in aqueous solution. If the degree of adsorption is high, surfactant concentration could drop below the Critical Micelle Concentration (CMC), rendering the surfactant solution with no ability to solubilize. Therefore, the amount of surfactant mass that will sorb should be accounted for when selecting injection concentration. In this study, diesel was used as an organic contaminant to study sorption characteristics

of non ionic surfactant, Triton X-100 onto soil below and above CMC. The surface tension measurement was used for calculating this kind of sorption. Nonionic surfactant Triton X-100 was used to study remediation enhancement of diesel contaminated soil. UV-Visible Spectrophotometer was used to determine the amount of diesel removed from contaminated soil by surfactant via solubilization and mobilization mechanisms at 254 nm. The results indicated that when the concentration of surfactant was lower than the CMC, the amount of surfactant sorbed on soil increased with increasing the surfactant concentration; the amount of desorbed diesel was relatively low compared with the original amount added to soil, but amount of diesel desorbed from soil at surfactant concentration above CMC was relatively high. Other factors such as temperature, pH, and ionic strength were also studied to examine whether they improve or inhibit diesel desorption from soil. The study has shown that high pH, low pH, high temperature, and ionic strength decreases the capacity of surfactant in desorption of diesel from soil.

CHAPTER 1

INTRODUCTION

1.1 Overview:

Petroleum and its derived products are considered to be increasingly menacing pollutants of our environment.

These natural products are introduced to the environment due to various anthropogenic activities, such as accidental spills from transportation processes, leaking underground storage tanks, and poor waste disposal practices.

These compounds are commonly found in soil groundwater aquifers in industrialized areas. Some special classes of petroleum hydrocarbons are commonly referred to as nonaqueous phase liquid (NAPL), they are difficult to recover from the subsurface system and represent a long-term source of soil and aquifer contamination [1, 2].

Limited solubility of petroleum hydrocarbons is a major constraint over biodegradation of these compounds. The soluble portion will be degraded at faster rates while less soluble or insoluble compounds will have limited bioavailability thus reducing the degradation rate of these compounds.

Petroleum hydrocarbons are recalcitrant contaminants in the natural

environment that make rehabilitation of contaminated sites difficult. In addition to their low aqueous solubility, petroleum hydrocarbons have high interfacial tension and a tendency to sorb onto soil particles. The high interfacial tension results in large capillary forces that resist washing by water. One of the most common types of groundwater contamination is from spills of petroleum based fuels and solvents from underground storage tanks.

When the problem of subsurface contamination begins, the initial remediation approach involves removing contaminated soil and pumping the contaminated water for treatment. Pump-and-treat remediation technology was initially prescribed for cleanup of subsurface contamination from both organic and inorganic contaminants. It is the most commonly used in situ remediation technology for contaminated aquifers [3].

The pump-and-treat remediation technology may take significantly long periods of time to treat the contaminated groundwater. Desorption of contaminants from soil media and dissolution of trapped immiscible phases limit the effectiveness of pump-and-treat remediation processes because of the high interfacial tension as mentioned above.

Other conventional treatment technologies for soil contamination involve landfill disposal and incineration. With landfill disposal only the location of pollutants is changed and the future liability is delayed. And so their complete

destruction is not achieved. Incineration of hazardous wastes is both costly and difficult to implement.

1.2 Scope:

It has been known that surfactants are able to improve the mass-transfer of hydrophobic pollutants from solid or nonaqueous liquid phase into aqueous phase by decreasing the interfacial tension and by accumulating the hydrophobic compounds in the micelles [4, 5, 6]. Therefore, surfactants have been extensively studied in recent years for enhancing the subsurface contaminants remediation [7, 8, 9].

Surfactant enhanced subsurface remediation is one of several technologies being developed for remediation of subsurface nonaqueous phase liquid NAPL contamination. The removal of total petroleum hydrocarbons TPH was increased by 60% in the presence of surfactants compared to water only [10].

The presence of surfactant in soil-water system dramatically increases the apparent solubility of hydrocarbons. The apparent solubility is increased due to increased micellar solubilization and reduction in interfacial tension between hydrophobic contaminants and the aqueous phase [11, 12].

With surfactants, more hydrophobic contaminants, including the sorbed

and entrapped ones, are mobilized in the aqueous phase. It is an emerging technology that has been demonstrated by a few pilot scale application to date, but currently is the focus of wide-spread research and optimism. Economic analyses indicate that this technology can be competitive with conventional pump-and-treat, landfill and incineration remediation if surfactant loss can be minimized, contaminant elution is maximized and surfactant-contaminant separation and surfactant reuse are implemented [13].

Surfactants can help to remove the contaminants from soil by solubilization and mobilization. Since surfactants can be adsorbed on soils, the concentration of free surfactant in the aqueous solution would be lower. If the degree of adsorption is significant, surfactant concentrations could drop below the CMC, rendering the surfactant solution unable to solubilize. Sorbed surfactant could also increase the soil organic carbon fraction, thereby potentially increasing contaminant partitioning into the soil. In addition, adsorption of surfactant on soil can cause the surfactant velocity to be lower than the groundwater velocity due to retardation.

The major cost of surfactant enhanced subsurface remediation is the cost of surfactant itself. Surfactant loss by adsorption onto soil is about 97% and only 3% is left for removing contaminants. Therefore, minimization of the loss of surfactant by adsorption would increase the process effectiveness. An

understanding of the sorption of surfactants is important not only for their efficient use during remediation applications but also for understanding their potential fate in the environment [14].

1.3 Objectives:

The aim of this research is to study the effect of a nonionic surfactant in enhancing the remediation of insoluble hydrophobic organic compounds by solubilization and mobilization mechanisms, which in turn increase the bioavailability and hence the biodegradability of petroleum hydrocarbons. To study the effect of sorption characteristics of surfactant on soil at different amounts of diesel in term of adsorption isotherms, and the effect of these components (i.e. soil and diesel) on the CMC value of the surfactant and interpretation of these effects in term of sorption behavior. To study different factors that may positively or negatively affect the sorption behavior of surfactant onto soil.

CHAPTER 2

BACKGROUND

2.1 Definition of Surfactant:

Surfactant or surface active agent is an amphiphilic substance with dual affinity. Each surfactant molecule consists of two parts, a hydrophilic (water loving) head that is attracted to water molecules and a hydrophobic (water hating) tail that repels water and simultaneously attaches itself to oil and hydrocarbons.

The structure of surfactant lower the surface tension of the medium in which it is dissolved. And consequently lower the interfacial tension between two immiscible media such as oil/water phases.

Surfactants in general may be natural (i.e. from vegetables or animal) which known as **oleo-chemicals** and may be synthetic (i.e. form petroleum derivatives) which are known as **petrochemicals**.

2.2 Types of Surfactant

There are four main types of surfactants used in laundry and cleaning products. Depending on the type of the charge of the head, a surfactant belongs to the anionic, cationic, non-ionic and amphoteric/zwitterionic family.

2.2.1 Anionic Surfactants

The head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps.

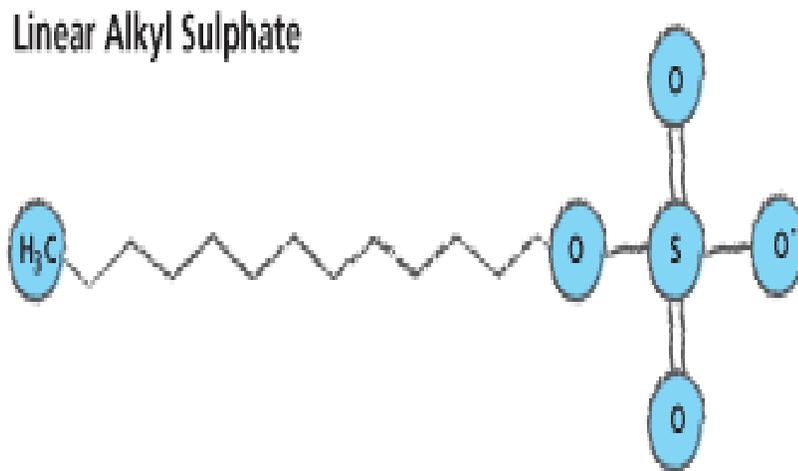


Fig.2. 1 : Example of an Anionic Surfactant.

2.2.2 Cationic Surfactant

The head is positively charged. There are three different categories of cationic surfactants each with their specific application:

- In fabric softener.
- In laundry detergents.
- In household and bathroom cleaners.

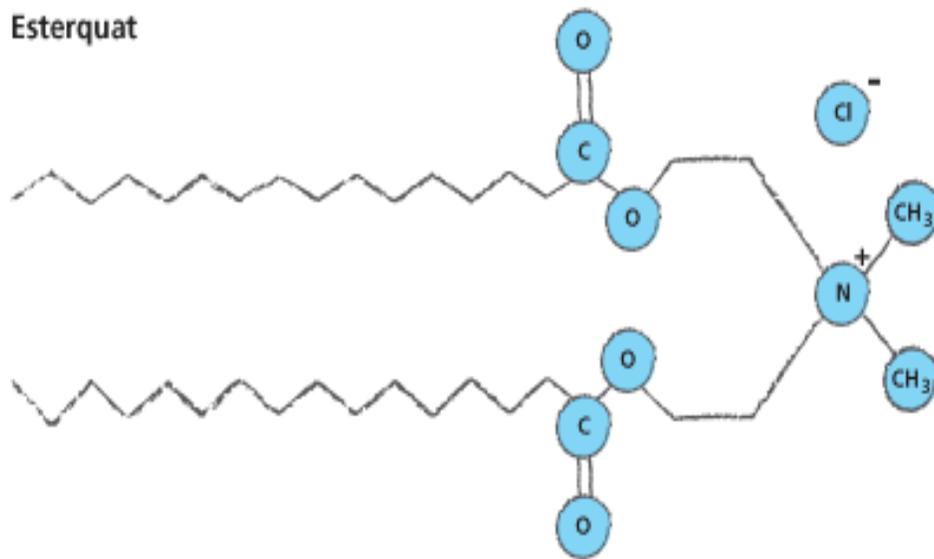


Fig.2. 2 : Example of a Cationic Surfactant.

2.2.3 Nonionic Surfactants

Because they don't have an electrical charge, nonionic surfactant is resistant to hard water and soluble in water and organic solvent, including hydrocarbons. It is a poor foamer and has no electrical effects (e.g. no strong adsorption onto charged surfaces) so it is suitable for subsurface remediation since it does not tend to be adsorbed onto soil.

Non Ionic Surfactants

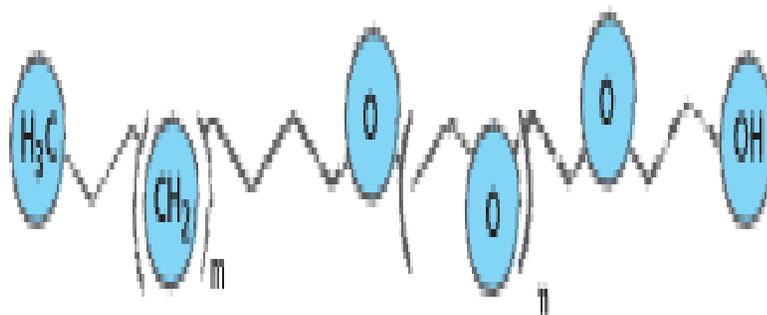


Fig.2. 3 : Example of a Nonionic Surfactant.

2.2. 4 Amphoteric/Zwitterionic Surfactant

They can be anionic, cationic, or nonionic in solution, depending on the acidity or pH of the water. These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate).

Alkyl Betaine

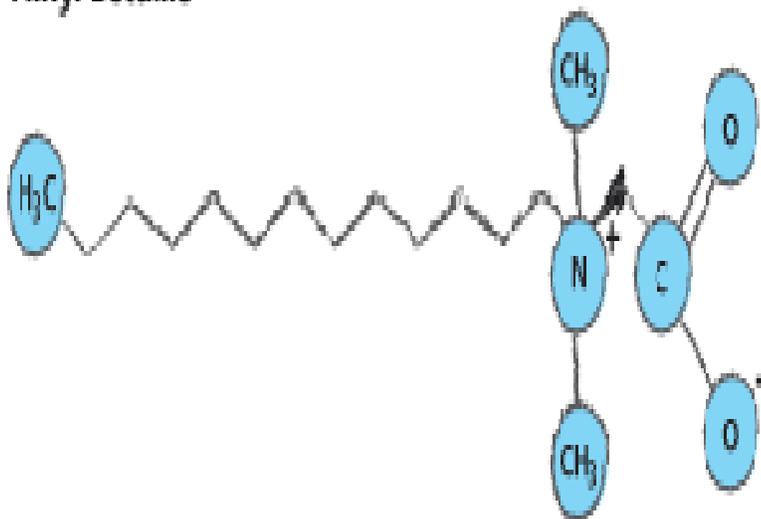


Fig.2. 4 : Example of an Amphoteric Surfactant.

Surfactants can be classified according to their hydrophile-lipophile balance (HLB) also. Surfactants with high HLB value are hydrophilic and thus are more water soluble, whereas surfactants with low HLB values are lipophilic and thus more oil soluble [15].

2.3 Physical Characteristics of Surfactants

Surface active agent or surfactant has the potential to alter the properties of fluid interface. Because surfactant molecules are typically composed of strongly hydrophilic head and hydrophobic tail [16], they accumulate at interfaces between two immiscible phases (air-water, oil-water, water-solid) for example, a surfactant will accumulate at an oil water

interface with its hydrophobic part (lipophilic tail) in the oil phase and its hydrophilic part (polar or ionic head) in the water phase; thus, both portions of the molecule are in a preferred phase and the free energy of the system is minimized. Accumulation of surfactants at the interfaces alters the nature of the interface, resulting in the designation of these molecules as surface active agent. Appendix A-1 shows some physical properties of Triton X-100. Figure 2.5 shows the accumulation of surfactant monomers at the NAPL-water interface.

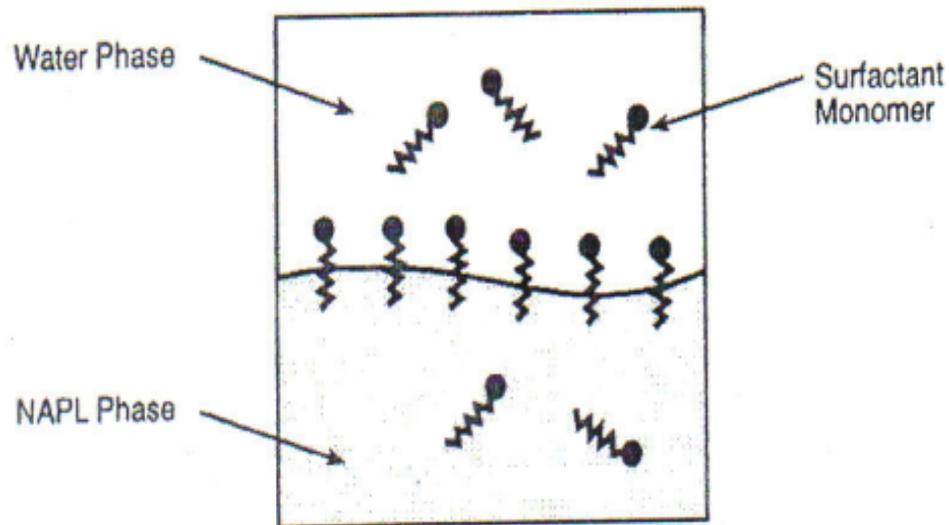


Fig.2. 5 : Surfactant Monomer Accumulations at the NAPL-Water Interface.

Aggregations of surfactant monomers referred to as micelles will form when a sufficient amount of surfactants are added to aqueous

solution. The threshold concentration at which micelles begin to form is termed the Critical Micelle Concentration (CMC). Micelles are often spherical in shape and can contain several hundreds of surfactant monomers. The CMC is a function of surfactant structure, composition, temperature, ionic strength, and the presence and type of organic additives in the solution [17, 18]. Beyond the CMC, any surfactant added to aqueous solution will not increase the number of monomers in aqueous solution, but rather it will contribute to the formation of additional micelles as shown in Figure 2.6.

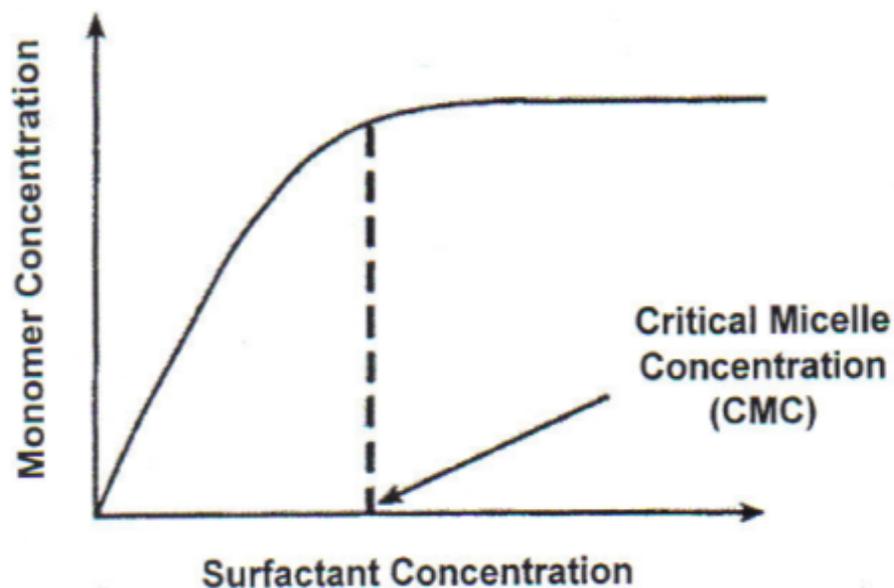


Fig.2. 6 : Formation of Micelles at Critical Micelle Concentration CMC.

The concentration of surfactant required to form micelles is typically small and is dependent on factors such as surfactant type, temperature and

water hardness [17]. Whenever surfactant is added to an aqueous solution, a number of property changes occur, as shown in Figure 2.7.

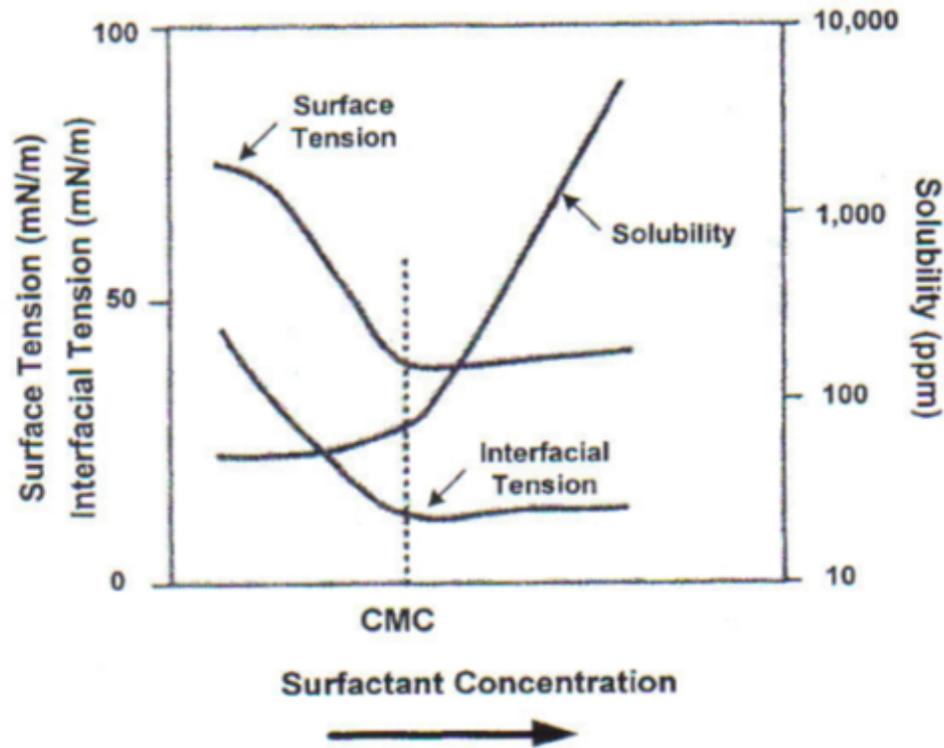


Fig.2. 7 : Variation of Surface Tension, Interfacial Tension and Contaminant Solubility with Surfactant Concentration.

The solubility of organic compounds in solution increases beyond the CMC as additional micelles are formed. This solubility represents both the contaminant molecules in free aqueous solution and contaminant molecules entrained in micelles. In general, the larger the octanol-water partitioning coefficient (K_{ow}) of a particular of contaminant, the greater its tendency to partition into the micellar phase. Due to the significant increase in

contaminant solubility beyond the CMC, surfactant flushing is considered as a promising technology for NAPL remediation [19].

2.4 Properties of Micelles

Micelle is formed by aggregation of number of surfactant molecules into a single structure. In aqueous solvents, the micelle consists of surfactant monomers that are oriented so that their nonpolar regions are in maximum contact with one another and their polar regions are in maximum contact with the water as shown in Figure 2.8 [20]. Yalkowsky and Zografı (1972) showed that most micelles that have fewer than 100 monomers are spherical. When micelles become very large, they take other shapes, such as prolate (cigar-shaped) ellipsoids or revolutions.

Micelles are often characterized according to their size and shape. These geometric properties depend on the chemical structure of the surfactant and on concentration and the nature of the aqueous environment. The size of micelle depends on the temperature and the type and concentration of the solutes in the solution, micelle size also pH-dependent for weak electrolyte surfactants. An increase in temperature generally produces slight decrease in the size of ionic surfactant micelles and very large increase in the size of non ionic surfactant micelles. Dissolved solutes, even in low concentration in an aqueous solution, can have profound effects on the aggregation surfactants. They can either favor or oppose micelle

surfactant above CMC. Similarly, the MSR is described as the moles of hydrophobic organic contaminant solubilized per mole of surfactant above its CMC [4, 18]. Most of the literature refers to MSR.

The micelle water partition coefficient (K_m) or some literature may express as K_{mic} is also used to quantify solubility enhancement by surfactant.

2.5.1 Molar Solubilization Ratio (MSR)

The MSR is the degree of solubility enhancement achieved with particular surfactant. It is defined as the ratio of the moles of solute solubilized to the moles of surfactant present as micelles. In the presence of an excess of hydrophobic organic compound, the MSR can be calculated as follows [21].

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

Where C_{mic} : total apparent solubility of petroleum hydrocarbon Compound as moles per liter in micellar solution at a particular surfactant concentration greater than CMC.

C_{CMC} : apparent solubility of petroleum hydrocarbon compound as moles per liter at the CMC.

C_{surf} : surfactant concentration at which C_{mic} was evaluated.

The MSR as well as WSR can be obtained from the slope of the solubility curve above the critical micelle concentration [22, 23].

A higher MSR indicates the greater solubilization ability for the surfactant. The amount of NAPL solubilized generally increase with increasing the size of micelles and the total surfactant concentration. Thus, anything that promotes increasing the micellar size or to increase aggregation number will promote solubilization. Surfactants with low CMC tend to be better solubilizers. This is one reason that nonionic surfactant have been used for solubilization in remediation projects.

2.5.2 Micelle-Water Partition Coefficient (K_m)

The micelle water partition coefficient, K_m , represents the distribution of organic molecules between surfactant micelles and the aqueous phase as:

$$K_m = \frac{X_m}{X_a} \quad (\text{Equation 2. 2})$$

Where X_m : mole fraction of organic solute in the micelle phase.

X_a : mole fraction of organic solute in the micelle-free aqueous phase.

The mole fraction of organic solute in micellar pseudo-phase, X_m , can be calculated in term of MSR [18].

$$X_m = \frac{\text{MSR}}{1 + \text{MSR}} \quad (\text{Equation 2. 3})$$

The mole fraction of organic solute in aqueous phase can be approximated for dilute solution by:

$$X_a = C_{CMC} \cdot V_{a,mol} \quad (\text{Equation 2. 4})$$

Where $V_{a,mol}$: molar volume of water at the experimental temperature.

C_{CMC} : estimated as solubility in water.

Javert et al; 1995 used the following equation to relate the octanol-water partition coefficient, K_{ow} to micelle-water coefficient, K_m .

$$K_m = \beta \cdot K_{ow} \quad (\text{Equation 2. 5})$$

Where β depends on the type of surfactant [24].

Chu and So (2001) studied partition of petroleum hydrocarbons between liquid and solid phases in the presence of soils and surfactant. They also proposed a model of micelle-water partition coefficient, K_m (L/mol) as:

$$K_m = \frac{[P]_{mic}}{[P]_w \cdot [S]_{mic}} \quad (\text{Equation 2. 6})$$

For nonionic surfactants, most CMC values are low, hence:

$$K_m = \frac{[P]_{surf}}{[P]_{mic} \cdot [S]} \quad (\text{Equation 2. 7})$$

Where K_m : micelle-water partition coefficient (L/mol).

$[P]_{mic}$: concentration of TPH in the surfactant micelles (mol/L).

$[P]_w$: concentration of TPH in the water (mol/L).

$[P]_{surf}$: concentration of TPH solubilized by both monomeric and micellar phases (mol/L).

$[S]_{mic}$: concentration of surfactant in micellar form (mol/L).

[S] : concentration of surfactant in both monomeric and micellar forms (mol/L).

2. 6 Solubilization and Mobilization

Harwell et al; (1995) investigated the use of surfactants in removing the contaminants from aquifer. They explained contaminant removal via two mechanisms: solubilization and mobilization. The first mechanism, solubilization, involves partitioning of contaminant within surfactant micelles. The surfactant is not used to release the hydrophobic contaminants from the pore, rather the solubility of the contaminant liquid in the water is increased because the water contains micelles which take-up some of the contaminant. The more micelles there are in the water, the more contaminant goes to the surface every time water is pumped to the surface. Figures 2.9 and 2.10 present the molecules solubilized in a normal micelle and how NAPL- swollen micelles increase the contaminant removal at rate as water is pumped to the surface, respectively.

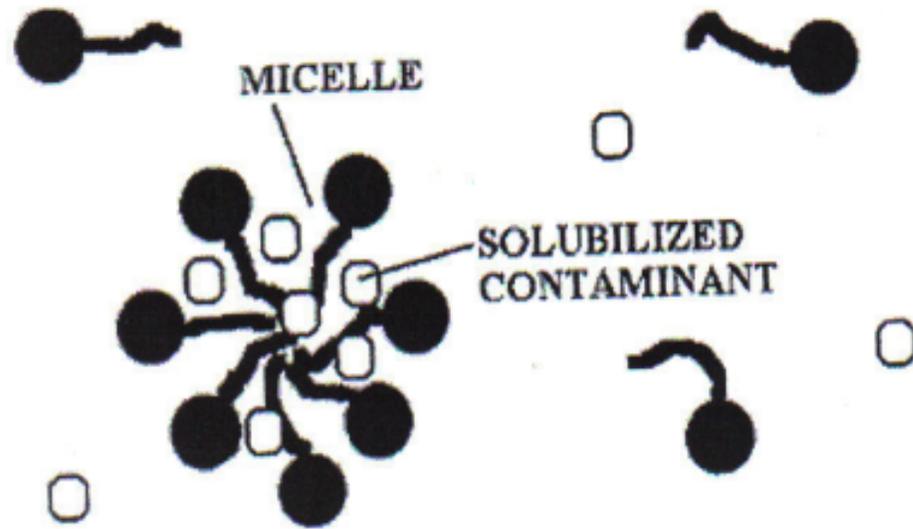


Fig.2. 9 : NAPL Molecules Solubilized in Normal Micelle.

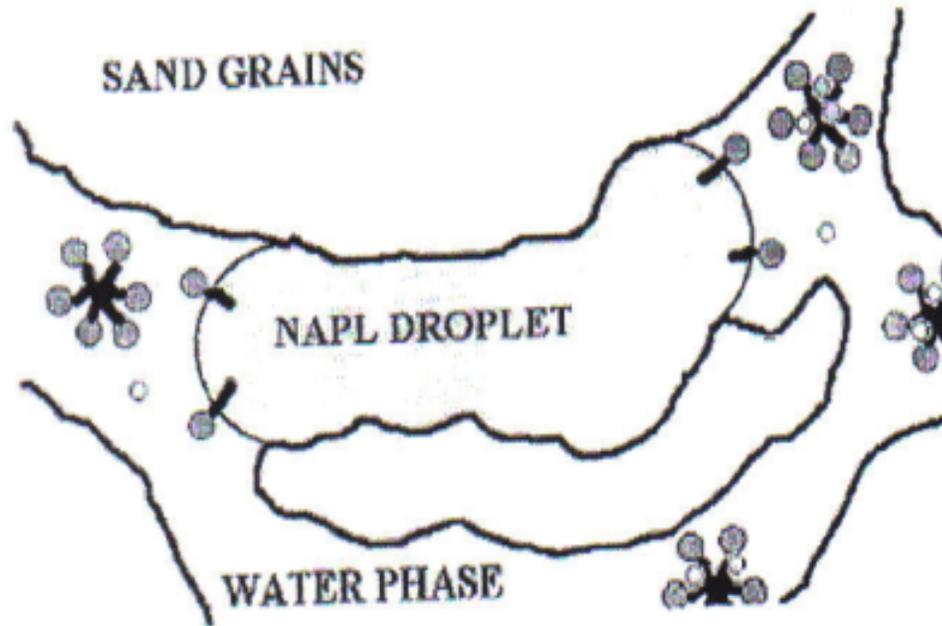


Fig.2. 10 : NAPL-Swollen Micelles Increase Contaminant Removal Rate as Water is Pumped to the Surface.

The second mechanism, mobilization; occurs as a result of reduction in NAPL-water interfacial tension by addition of a surfactant into the aqueous solution. Reduction of NAPL- water interfacial tension reduces the capillary forces which are responsible for the retention of residual NAPL and formation of pooled NAPL. If the NAPL/water interfacial tension is lowered below critical value (related to the capillary number), then the droplet of NAPL will flow out of the pore space between the sand grains in the aquifer (i.e. physical mobilization of NAPL can occur). Figure 2.11 shows mobilization process.

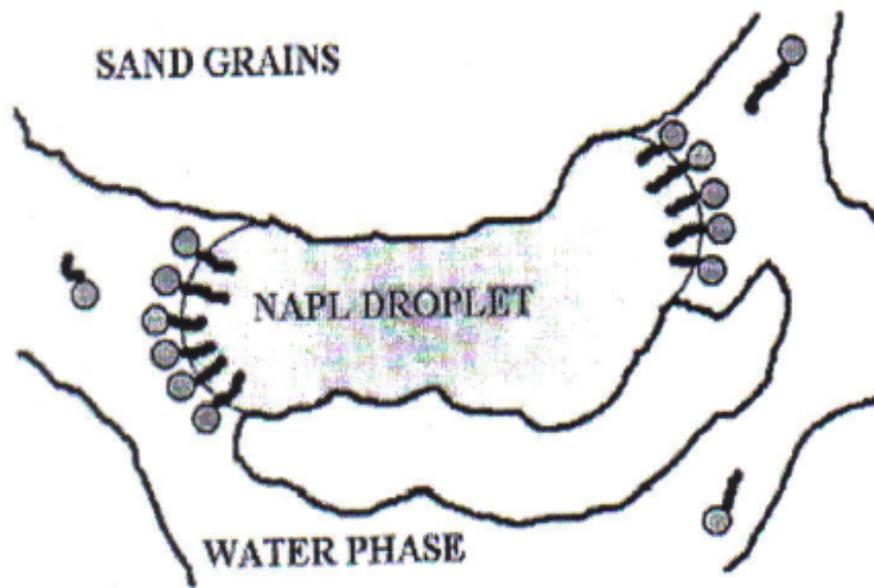


Fig.2. 11 : High Gibbs Adsorption at NAPL/Ground Water Interface Lowers Interfacial Tension.

Winsor Type I micro-emulsions occur when surfactant stays in aqueous phase to form NAPL swollen regular micelles. To achieve a Type I system, a water-soluble surfactant should be used.

Winsor Type II micro-emulsion consists of reverse micelles. If the surfactant transfers into the NAPL phase, it will form water swollen reverse micelles in the NAPL phase, which will be in equilibrium with nearly pure aqueous phase.

Winsor Type III micro-emulsions occur when the surfactant has nearly equal affinity for the aqueous phase and for the NAPL phase. Then it may form separate phase, with both NAPL and water in a new surfactant phase,

which is in equilibrium with both a nearly pure NAPL phase and nearly pure aqueous phase. The formation of this third phase associated with achieving ultra-low interfacial tensions. The primary recovery mechanism in such system is clearly NAPL mobilization due to the reduction of capillary forces.

Experiment by Harwell et al; 1995 showed that Winsor Type III micro-emulsion have higher removal efficiency of TPH from glass beads than Winsor Type I. however, the reason why Type I system is considered instead of a Type III system is because aquifers are heterogeneous and it is not easy to control the direction of either injected surfactant solution or mobilized Dense Non-aqueous Phase Liquid (DNAPL). If DNAPL is mobilized and the migration of the released DNAPL is not adequately controlled, the DNAPL might move downward out of the capture zone of the extraction wells, resulting in a spreading of the contamination rather than enhancement of the contamination removal rate.

2.7 Surfactant Sorption

The adsorption of surfactant to solid surfaces can lower the concentration of the free surfactant in aqueous solutions. If the degree of adsorption is high, surfactant concentration could drop below CMC, rendering the surfactant solution with no ability to solubilize. Therefore, the amount of surfactant mass that will sorb should be accounted for when selecting injection concentration. In addition to reducing the number of

monomers available for micelle formation, adsorption will cause soil organic carbon content to increase and the surfactant velocity to be lower than the groundwater velocity. This should be taken into account when calculating travel times and sampling intervals. In addition to adsorption to mineral surfaces, surfactant partitioning to the NAPL phase must be considered. All surfactants will have certain solubility in NAPL, the degree of which is indicated by HLB number. Significant partitioning of surfactant on the NAPL phase will cause reduction in the concentration of surfactant in aqueous solution and will lead to retardation of the surfactant velocity [19]. The degree of surfactant sorption in an aqueous system depends in the nature of the surfactant monomers hydrophilic head group [25, 26].

2.7.1 Sorption of Nonionic Surfactant onto Soil

Liu et al; (1992) studied Desorption of nonionic surfactant from soil by using the surface tension measurement, spectrophotometry and chemical oxygen demand. They found that a surface tension technique was effective for assessing the sorption of both micelle-forming surfactant and the lamellae-forming surfactants at aqueous phase concentrations less than the CMC or CAC, respectively. For solution of micelle-forming surfactants at concentrations greater than the CMC, the spectrophotometric technique with an azo dye was used. For solutions of the lamellae-forming surfactant, the chemical oxygen demand (COD) method gave satisfactory result. Sorption

of the micelle-forming nonionic surfactant onto soil was observed to be constant at a value of the bulk solution surfactant concentration exceeding surfactant monomer saturation, i.e. the critical micelle concentration. Liu et al; (1992) reported that sorption could be characterized for each surfactant/soil system by a Freundlich isotherm at surfactant concentrations up to the surfactant CMC [7].

Adeel and Luthy (1995) demonstrated that sorption and transport of a nonionic surfactant, triton X-100, in sand/aqueous systems was controlled by concentration-dependent phenomena [27]. Adeel and Luthy (1995) cited that other research (Vigon and Rubin, 1989; Abdul and Gibson, 1990; and Fountain and Klimek, 1991) have studied the use of surfactants to enhance organic contaminant removal for in-situ subsurface remediation and ex-situ soil treatment [28, 29]. The results from recent research include the following:

- Nonionic surfactant sorption exhibits different characteristic for soil aquifer sediments.
- The sorption of hydrophobic organic compound (HOC) onto a solid is influenced by the sorption of nonionic surfactant, and depends on the surface conformation of the sorbed surfactant.
- The kinetics of nonionic surfactant transport through and aquifer sediment are dependent also on sorbed surfactant conformation.

The sorption phenomena controlling partitioning of nonionic surfactant between natural media and aqueous phases are different for soils and sands. It is proposed that surfactant sorption may be governed by the amount naturally-occurring organic matter associated with the solid phase, the mineral composition of the solid medium and the surfactant concentration [30].

2.7.2 Sub-CMC Sorption

Figure 2.12 and Figure 2.13 adapted from Liu et al; 1992 show that the greater the soil/water weight-to-volume ratio, the greater the amount of surfactant that must be added to the system in order to decrease the surface tension by a given amount. The following represents the mathematical relationships developed by Liu et al; (1992) to estimate surfactant sorption onto soil [7].

$$C_{\text{sorb}} = D_{s, \sigma} - C_{\text{surf}} \quad (\text{Equation 2. 8})$$

$$Q_{\text{surf}} = (D_{s, \sigma} - C_{\text{surf}}) \cdot \left(\frac{V_a}{W_{\text{soil}}} \right) = C_{\text{sorb}} \cdot \left(\frac{V_a}{W_{\text{soil}}} \right) \quad (\text{Equation 2. 9})$$

Where V_a : volume of aqueous solution (L).

W_{soil} : weight of soils (g).

$D_{s, \sigma}$: bulk surfactant dose in the soil/aqueous system that produces a surface tension value of σ in the supernatant (mol/L).

C_{surf} : aqueous-phase surfactant concentration (for the aqueous phase without soil) (mol/L).

C_{sorb} : the number of moles of surfactant sorbed per liter of solution evaluated at the particular bulk solution surfactant concentration (mol/L).

Q_{surf} : number of moles of surfactant sorbed per gram of soil (mol/g).

Surfactant sorption may also be expressed as Q_g , the number of grams of nonionic surfactant sorbed per gram of the soil, using Freundlich isotherm as:

$$Q_g = K \cdot C^{\frac{1}{n}} \quad (\text{Equation 2. 10})$$

Where K : sorption capacity.

$1/n$: constant which indicates the curvature of the isotherm.

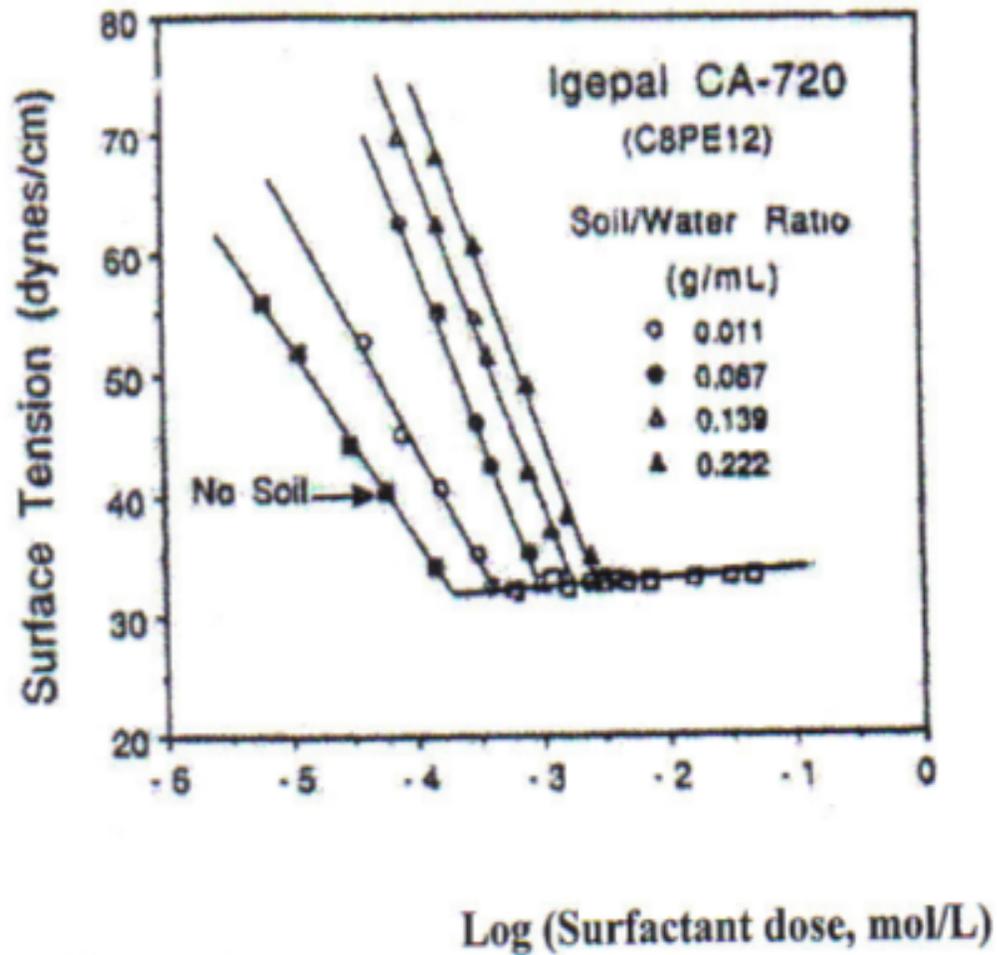


Fig.2. 12 : Plot of Surface Tension as a Function of the Logarithm of the C₈PE₁₂ Nonionic Surfactant Dose in Aqueous and Soil/Aqueous System of Varying Soil/Water Weight-to-Volume Ratios.

Urano et al; 1984 studied the adsorption of surfactant on sediments. They found that sorption could be characterized for each surfactant/soil system by a Freundlich isotherm at surfactant concentration up to the surfactant CMC, or initial micelle concentration [31].

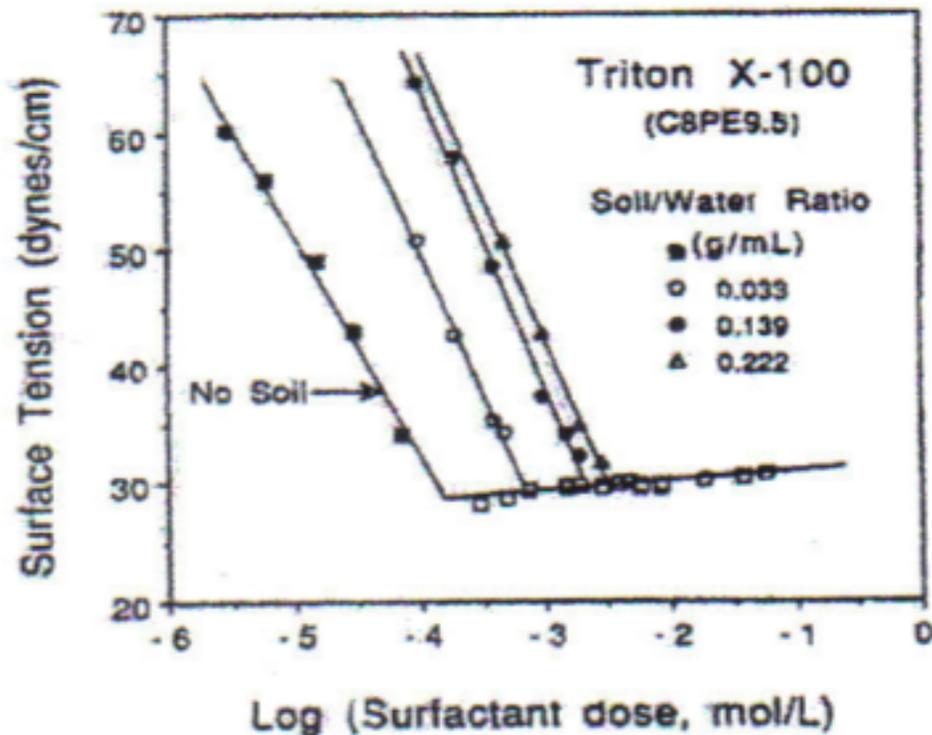


Fig.2. 13 : Plot of Surface Tension as a Function of the Logarithm of the $C_8PE_{9.5}$ nonionic surfactant dose in Aqueous and Soil/Aqueous Systems of Varying Soil/Water Weight-to-Volume Ratios.

2.7.3 Supra-CMC Sorption

Liu et al; (1992) observed that micelles do not sorb onto soil and the maximum number of moles of surfactant sorbed per gram of soil is constant (i.e. independent of the soil/water ratio for each micelle-forming surfactant) for all the soil/water weight-to-volume ratios studied [7]. The smallest surfactant dose that changes to the minimum plateau value of the surface tension for the soil/aqueous system gives, after subtracting the CMC and

multiplying by the ratio of V_a to W_{soil} , a specific value for Q_{surf} that is equal to Q_{max} . Q_{max} is the maximum plateau value of sorption in moles per gram for the micelle-forming surfactant on the particular soil (mol/gm). Q_{max} permits calculation of the concentration of the surfactant in micelle form in the system, an important parameter in predicting surfactant solubilization of HOC [18].

According to Zheng and Obbrad (2002), they used the surface tension measurements to determine Q_{max} and CMC to estimate CMC_{eff} in the soil/aqueous system as [8]:

$$CMC_{eff} = CMC + Q_{max} \left(\frac{W_{soil}}{V_{aq}} \right) \quad (\text{Equation 2. 11})$$

Where V_{aq} : volume of aqueous solution (L).

W_{soil} : weight of soil (g).

Chu and So (2000) studied the portioning of HOC between liquid and solid phases in the present of soil and surfactant by using hydrophobic dye, orange 11, as the HOC and nonionic surfactant Tween 80 [14]. They proposed an adsorption models for surfactant-aided soil washing.

The portioning of hydrophobic dye in soil-surfactant-water systems can be determined as:

$$\frac{x}{m} = (C_o - C_e) \frac{V}{W} \quad (\text{Equation 2. 12})$$

Where x/m : HOC concentration in soil (mg/gm).
 C_o : total initial concentration in solution (mg/mL).
 C_e : equilibrium concentration in solution (mg/mL).
 W : weight of soil (g).

Using: $K_m = a \cdot K_{ow}$ (Equation 2. 13)

HOC sorption onto soil can be calculated as:

$$K_{ow} = \frac{[P]_s}{[P]_w \cdot f_{ow}} \quad (\text{Equation 2. 14})$$

And $K_{oc} = b \cdot K_{ow}$ (Equation 2. 15)

Where K_{ow} : octanol-water partition coefficient.

K_{oc} : organic carbon normalized distribution coefficient at equilibrium (L/kg).

a : a constant for correlation K_m and K_{ow} (L/mol).

b : a constant for correlating K_{oc} and K_{ow} (L/mol).

Partitioning of HOC among soil, water and surfactant phases can be estimated from:

$$K_d = \frac{[P]_s}{[P]_w + [P]_{surf}} \quad (\text{Equation 2. 16})$$

Where K_d : overall distribution coefficient.

f_{oc} : fractional organic carbon content of soil or sediment.

$[P]_s$: concentration of HOC in soil or sediment (mol/kg).

K_d can be measured in the lab and it is the index to quantify the efficiency of a surfactant aided-soil-washing system. The derivation of the model can be concluded as:

$$K_d = \frac{\frac{b}{a} \cdot f_{oc}}{\frac{1}{a \cdot K_{ow}} + [S]} \quad (\text{Equation 2. 17})$$

Or written in reciprocal form:

$$\frac{1}{K_d} = \frac{1}{b \cdot K_{ow} \cdot f_{oc}} + \frac{a}{b \cdot f_{oc}} [S] \quad (\text{Equation 2. 18})$$

A plot of $1/K_d$ vs. $[S]$ will give a straight line with a slope $a/b \cdot f_{oc}$ and intercept of $1/b K_{ow} f_{oc}$.

Chu and So (2001) performed experiments with 5 different types of soil to study the partitioning of the dye (disperse orange 11) as a function of nonionic surfactant Tween 80. They found that soil washing performance ($1/K_d$) is minimal until the total surfactant concentration reaches 1.00×10^{-3} M, a value considerably higher than the CMC in pure water (10^{-5} M). This is likely due to sorption of surfactant onto soil. They also performed experiment to determine surfactant sorption by surface tension measurements. The result of their experiments is shown in Figure 2.14.

From the figure the difference between the two concentrations can be used to quantify the surfactant sorbed to soil.

Figure 2.15 shows the plot of surfactant dose $[D]$ against its corresponding monomer surfactant concentration $[S]_{\text{mon}}$. Chu and So (2000) concluded that 97% of the surfactant dose sorbed by the soil before the soil becomes saturated, and only small fraction ($\sim 3\%$) of $[D]$, in the monomer form, becomes effective as soil-washing agent.

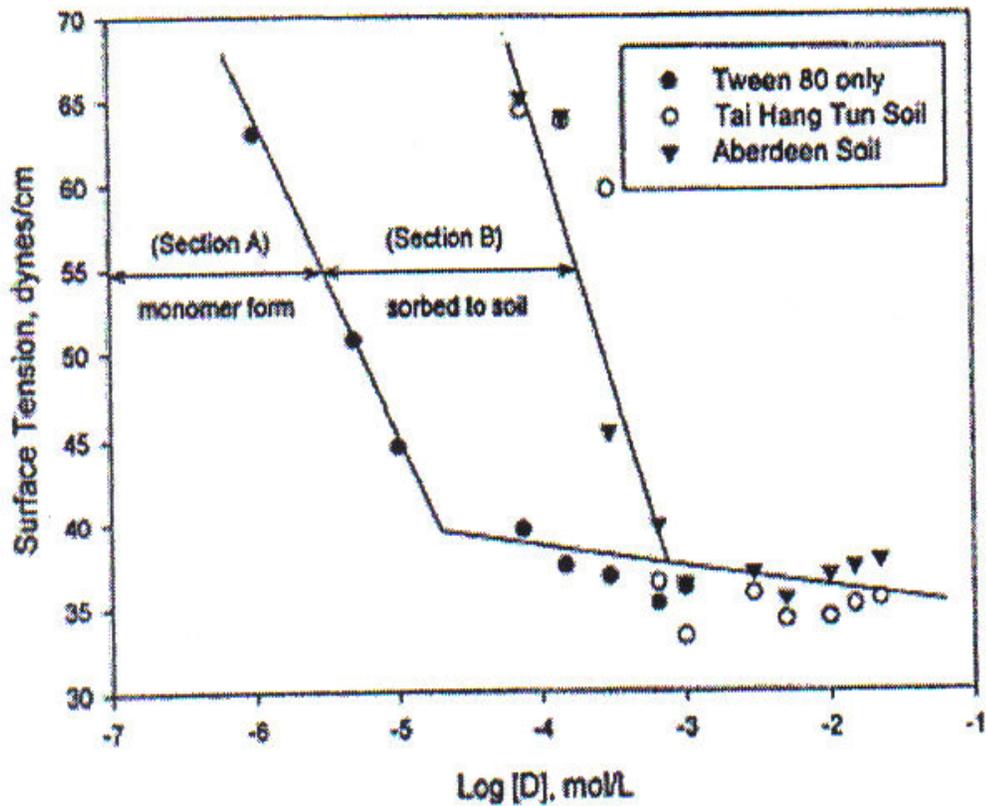


Fig.2. 14 : Surface Tension Change in Tween 80 Solution as a Function of Surfactant dose for Systems with and without Soils.

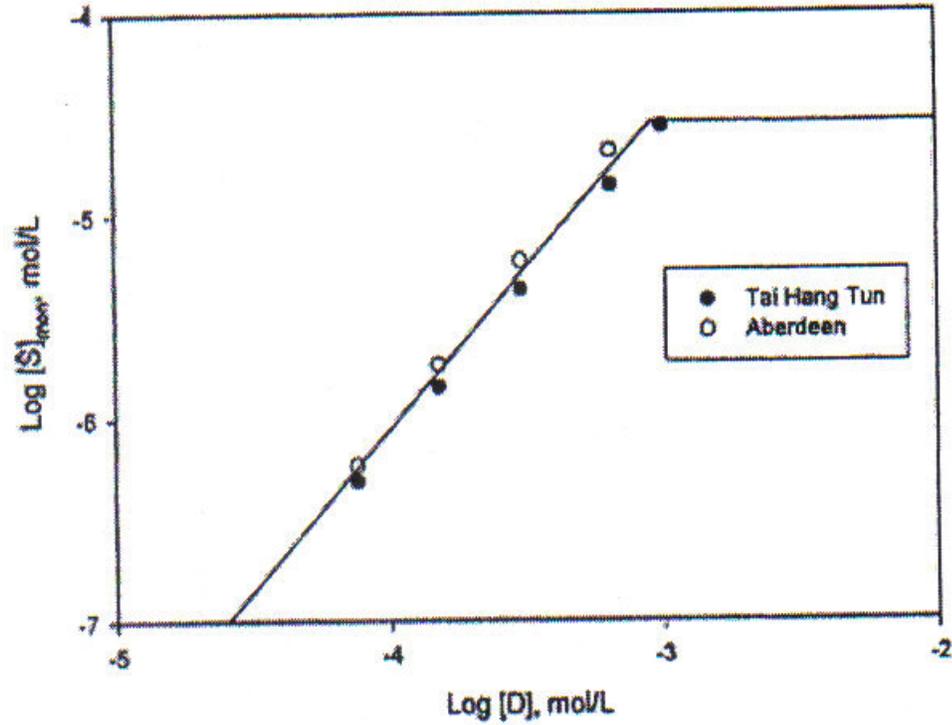


Fig. 2. 15 : A Linear Correlation between Surfactant Monomer ($\log [S]_{\text{mon}}$) and Surfactant Dose ($\log [D]$) in Two Different Soil/Water Systems Containing Tween 80 [14].

They also proposed the portioning of HOC in surfactant-aided soil washing system should be separated into two stages.

In stage 1, when $[D]$ is less than the effective CMC, only the free surfactant monomers $[S]_{\text{mon}}$ contribute to the soil washing, then:

$$\frac{f_{\text{oc}}}{K_d} = \frac{1}{b \cdot K_{\text{ow}}} + \frac{a}{b} [S]_{\text{mon}} \quad (\text{Equation 2. 19})$$

In stage 2, when [D] is higher than the needed for CMC to be obtained, therefore:

$$\frac{f_{oc}}{K_d} = \frac{1}{b \cdot K_{ow}} + \frac{a}{b}([D] - [S]_{sorb}) \quad (\text{Equation 2. 20})$$

They conclude that in stage 1, HOC can be extracted from soil by surfactant monomer, but most the surfactant (97%) is lost due to sorption on soil. Washing performance is directly proportional to the available monomer concentration in the liquid phase. In stage 2, sorption sites on the soil are saturated by surfactant hence surfactant micelles exist in bulk solution. The micelles can significantly increase the apparent HOC solubility. Soil washing performance is mainly dominated by the surfactant micelles available in the system and the organic content of soil [14].

2. 8 Hydrocarbon Compounds

2.8. 1 Total Petroleum Hydrocarbon (TPH)

Petroleum mixtures consist of approximately 200 different hydrocarbons. With each compound exhibiting different chemical and physical properties that control its behavior in a specific environment. The common hydrocarbon groups found in petroleum mixture include alkanes, alkenes, alkynes, aromatics, naphthalene, and other hydrocarbon derivatives of sulfur, oxygen and nitrogen. These hydrocarbons have different chemical and physical properties such as boiling point, vapor pressure and solubility.

The transport of petroleum hydrocarbon contamination in soils and in groundwater depends on both the physical and chemical characteristic of contaminants (i.e. petroleum hydrocarbons) and properties of contaminated media (i.e. soil phase, liquid phase, and air phase). The contamination in polluted zone affects the liquid phase, the solid phase, and the air phase in the soil layer above the groundwater level. Petroleum contaminants with high vapor pressure volatilize easily and are present in the air phase. The petroleum hydrocarbons with hydrophobicity tend to be sorbed on soil particle and the rest of the petroleum hydrocarbons are present in the liquid phase. When the contaminants reach the aquifer, the contamination affects the liquid phase and solid phase and the movement of the contaminants follow the groundwater flow direction. The transport characteristic depends on the properties of the soil and aquifer such as hydraulic conductivity of the contaminated aquifer and the organic content in the soil particle. The properties of the contaminants also play a significant role in the transport of the contaminants.

2.8.2 Contaminant Properties Affecting Fate and Transport

The chemistry of the contaminants will affect their transport and fate in the subsurface. Moore and Ramamoorthy (1984) divided these properties into two groups as: 1- physicochemical properties of contaminants such as solubility, vapor pressure, partition coefficient, sorption, and volatilization

and 2- chemical transformation such as oxidation-reduction behavior, halogenation/dehalogenation, hydrolysis, and photochemical breakdown [32].

2.8.3 Physicochemical Properties

2.8.3.1 Solubility

When organic chemical is in physical contact with water, it partitions into the aqueous phase. The equilibrium concentration of the chemical in the aqueous phase is referred as its solubility. The solubility of organic compounds varies considerably from the infinitely immiscible compounds such as alcohols (ethanol, methanol) to extremely low solubility compounds such as poly-nuclear aromatic compounds [33]. The precise determination of solubility remains elusive for many contaminant compounds, and some of the aqueous solubility values are only estimates. Solubility of organic compounds is affected by many factors such as pH, temperature, the presence of dissolved salts or minerals in water, etc. In general, the greater the molecular weight and structural complexity of the organic compound, the lower the solubility. Many environmentally sensitive compounds have very low water solubility.

2.8.3.2 Vaporization

The transfer of components from NAPL phase directly to the air phase is referred to as vaporization. Vaporization will lead to the formation of contaminant vapors in unsaturated media. The rate of vaporization and magnitude of air-phase concentration is proportional to a compound's vapor pressure [19]. Vapor pressure is that characteristic of the organic chemical that determines how readily vapors volatilize or evaporated from the pure phase liquid. Molecular activity in a liquid tends to free some surface molecules and this tendency towards vaporization is mainly dependent on temperature [33].

2.8.3.3 Volatilization

The volatilization of components from the water phase to air phase is referred to as volatilization. The volatility of a compound is described by its Henry's constant. Henry's law states that water-vapor partitioning is described by a linear relationship under equilibrium conditions. The factors that affect volatilization are the solubility, molecular weight, vapor pressure, and the nature of the air- water interface through which mass transfer occurs [33, 34].

2.8.3. 4 Interfacial tension

Interfacial tension refers to the tensile force that exists in the interface separating two immiscible fluids (i.e. phases). This force arises due to mutual attraction between molecules in the vicinity of the interface and like molecules in bulk solution [19]. The greater the interfacial tension between two immiscible liquids; the less likely emulsion will form; emulsions will be more stable if formed, and the better the phase separation after mixing. Interfacial tension decreases with increasing temperature, and may also be affected by pH, presence of surfactants and gases in solution [33, 35].

2.8. 4 Sorption of Hydrophobic Organic Compound

The portioning of components from the water phase to solid such as sand grains and fracture walls is referred to as sorption. The properties of a contaminant have a significant impact on its sorption behavior. Piwoni and Keeley (1990) discussed that the properties of a contaminant such as: water solubility, polar/ionic character, octanol/water partition coefficient, acid/base chemistry and oxidation/reduction chemistry have a significant role in its behavior. Sorption processes include adsorption, chemisorption, and adsorption and ion exchange [36].

Adsorption is the processes by which a solute clings to solid surface. If the adsorption occurs by London-van der Waals forces of the solid and adsorbate, it is called physical adsorption. Chemisorption occurs when solute

is incorporated on a sediment, soil, or rock surface by a chemical reaction or chemical bonding forces. Cation exchange is the process during which cations may be attracted to the region close to negatively charged clay-mineral surface and held there by electrostatic forces. Anion exchange can occur at positively charged sites on iron and aluminum oxides and the broken edges clay minerals. Absorption occurs when the aquifer particles are porous enough so that the solute can diffuse into the particle and be sorbed onto interior surfaces. Many organic compounds dissolved in ground water can be adsorbed on solid surface by the hydrophobic effect. These compounds exist as electrically-neutral species with differing degrees of polarity. The solubility of organic compounds in water is a function of the degree to which they are attracted by the polar water molecule. This attraction depends upon polarity of the organic molecule itself [23, 37].

Hydrophobic compounds can be dissolved in many nonpolar organic solvents but have a low solubility in water. When dissolved in water, these molecules tend to be attracted to surfaces that are less polar than water. There is a small limited amount of adsorption of organic compounds on pure mineral surfaces [23, 38, 39]. However, the primary adsorptive surface is the fraction of organic solids or aquifer [23, 40, 41, 42].

When an organic compound has been dissolved in the groundwater, it will be transported away from the source area in the groundwater flow

direction. The contaminants do not travel at the same velocity as the groundwater but slower due to adsorption process.

2.8.4.1 Adsorption Isotherm

The adsorption isotherm is the plot of the concentration of the contaminant in soil phase versus the concentration of contaminant in aqueous phase. Different types of adsorption isotherms have been defined according to their shape and mathematical representation as described below.

For a system where solid phase and liquid phase coexist, the adsorption isotherm describes the equilibrium relationship between the liquid and solid phases [43]. The most popular isotherms are Langmuir and the Freundlich isotherm. For the Langmuir isotherm, the concentration in the soil increases with increasing concentration in the groundwater until a maximum concentration in the soil is reached as shown in Figure 2.16. The Langmuir isotherm can be expressed as the following:

$$X = X_{\max} + \frac{KC}{1 + KC} \quad (\text{Equation 2. 21})$$

Where X : sorbed concentration.

C : liquid concentration.

K : equilibrium constant.

X_{\max} : maximum adsorbed concentration.

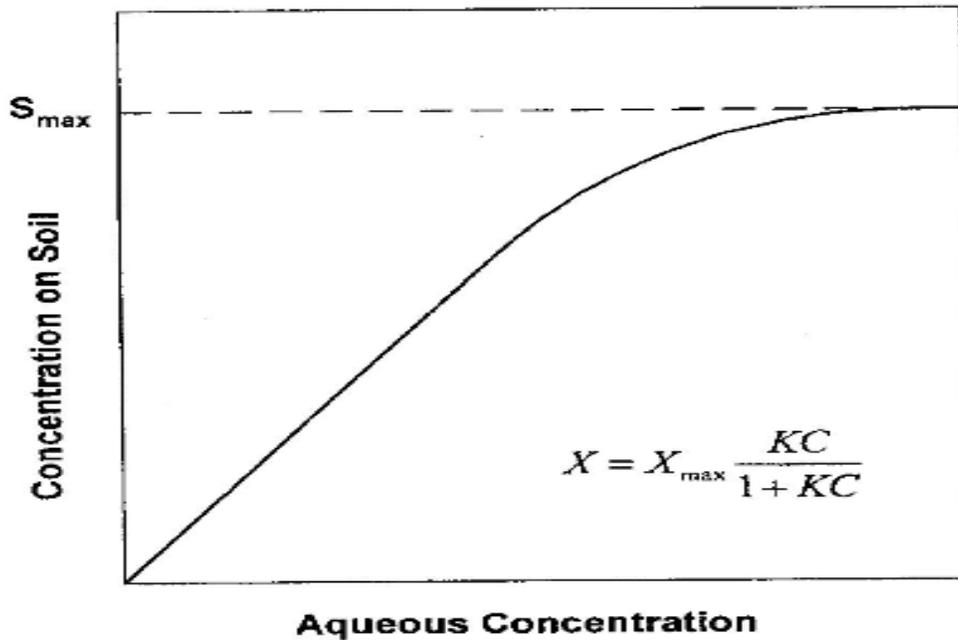


Fig.2. 16 : Langmuir Adsorption Isotherm.

The horizontal line represents the maximum adsorbed concentration

The Freundlich isotherm can be expressed in the following form:

$$X = KC^{\frac{1}{n}} \quad (\text{Equation 2. 22})$$

Where K : Freundlich adsorption constant.

$1/n$: constant.

These constants are different for different compounds. The shape of the Freundlich isotherm depends on the value of n . if n is less than 1, the isotherm becomes steeper with increasing concentration in the aqueous solution. If n is greater than 1, the isotherm becomes steeper at lower concentration as shown in Figure 2.17.

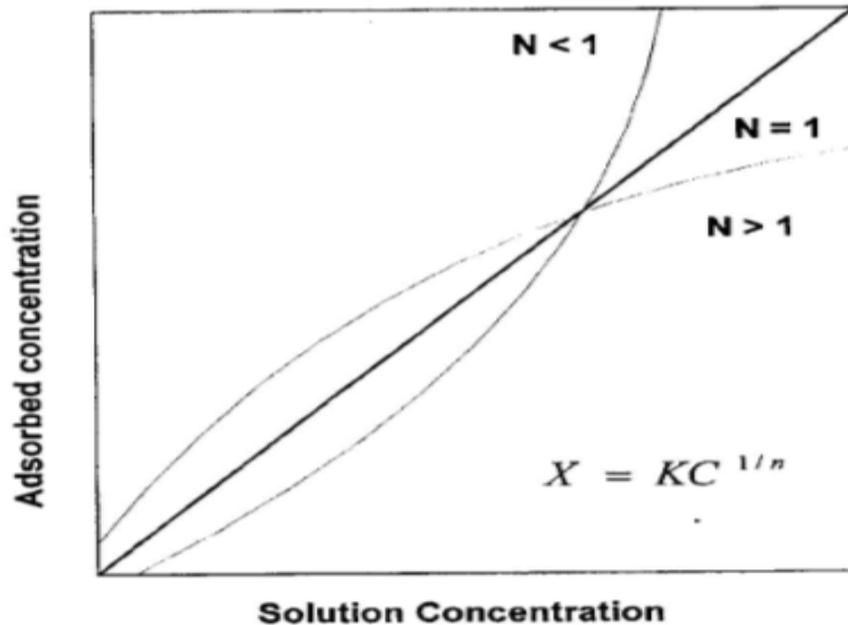


Fig.2. 17 : Freundlich Isotherm in its 3 Cases of the Exponential n

For many environmental processes, the linear form of the Freundlich isotherm applies. It is called the linear adsorption isotherm, since $1/n=1$, thus: $X = KC$ (Equation 2. 23)

The linear isotherm are particular interest because (1) many nonpolar, hydrophobic organic compounds tend to follow the linear isotherm over wide range of conditions and (2) the application of a linear isotherm simplifies the mathematical model used to estimate the rate of contaminant movement in the subsurface and reduces the number of parameters that need to be obtained to characterization [44].

2.8.4.2 Partition Coefficient

Another way to represent the partitioning between the soil phase and aqueous phase is by partition coefficient, K_p . The partition coefficient is a measure of the distribution of a given compound in two phases and is expressed as a concentration ratio, assuming simple dissolution. In reality the situation could be more complex as a result of molecular change. Sorption and Desorption, as stated by Moore and Ramamoothy (1984), means that the more hydrophobic the organic compound is, the more likely it is to be sorbed to the sediment [32]. The solubility of an organic compound depends on the characteristic of that compound and sorbent geologic matrix. Sorbent characteristic of the geologic matrix include surface area, nature of charge, charge density, presence of hydrophobic areas, presence of organic matter, and strength of sorption. The partition coefficient is also called “soil distribution coefficient” or “distribution coefficient”. As mentioned above, the Freundlich isotherm can be used for many environmental applications.

The Freundlich isotherm can be written as linear adsorption isotherm as follows:

$$X = K_p \cdot C \quad \text{or} \quad K_p = \frac{X}{C} \quad (\text{Equation 2. 24})$$

Where K_p : partition coefficient that measures the tendency of a chemical to be adsorbed by soil or sediment from liquid phase.

X : mass of chemical sorbed per unit dry mass of soil.

C : liquid concentration.

The soil distribution becomes the Freundlich adsorption coefficient when $n = 1$. Both the Freundlich and Langmuir isotherms approximate linear behavior for dilute solute concentration [45].

The partition coefficient of an organic chemical is not constant for every soil type. In general K_p increases as the fraction of organic carbon f_{oc} , increase in the soil [40, 44]. In other words, the sorption of nonpolar, hydrophobic organic compounds in soils is primarily an equilibrium partitioning process in soil organic matter.

The K_p can be represented as follows:

$$K_p = f_{oc} K_{oc} \quad (\text{Equation 2. 25})$$

Where K_{oc} : organic carbon partition coefficient.

f_{oc} : fraction of organic carbon within the soil matrix.

K_{oc} can be determined by the slope of K_p versus f_{oc} curves. The fraction of organic carbon f_{oc} must be measured for a particular soil. The partitioning of contaminant onto mineral surface or organic carbon content of the soil or aquifer is almost exclusively onto the organic carbon fraction, f_{oc} , if it constitutes at least 1% of the soil or aquifer on a weight basis [40]. The K_{oc} also can be estimated from other physical properties of pollutants such as aqueous solubility or octanol/water partition coefficient (K_{ow}). The octanol-water partition coefficient, K_{ow} represents the distribution of a chemical

between octanol and water in contact with each other at equilibrium conditions.

$$K_{ow} = \frac{\text{concentration in octanol phase}}{\text{concentration in aqueous phase}} \quad (\text{Equation 2. 26})$$

The K_{ow} is a key parameter in studies of the environmental fate of organic chemicals. It is related to water solubility and soil-sediment adsorption coefficient. In general, K_{ow} is a measure of the hydrophobicity of an organic compound. The more hydrophobic the contaminant is, the more likely it is to partition onto soils and to have a low solubility in water.

2.8.5 Chemical Transformation

Oxidation and reduction (redox) involve reactions which liberate electrons (oxidation) and reactions that consume electrons (reduction). Many organic compounds can either accept or donate electrons. This is environmentally significant since the oxidized or reduced form of the organic compounds may have different physical and/or chemical properties.

Hydrolysis involves the reaction of hydrogen, hydroxyl radical, or water molecules with organic compound, depending on the pH and polarity of the reaction site on the molecule.

Halogenation or Dehalogenation of organic compounds occurs mostly under synthetic conditions or in specific environment. Moore and Ramamoorthy (1984) stated that mild chlorination reactions are possible in

natural waters with effluent that contain residual chlorine. Dehalogenation may occur under varying reaction of hydrolysis disproportionation [32].

Photochemical breakdown processes involve structural changes in a molecule induced by radiation in the near ultraviolet-visible light range. The structure of an organic compound generally determines whether or not a photochemical reaction is possible.

2.8.5.1 Physical and Chemical Processes in Subsurface

For the optimum condition of sub surface remediation, the critical questions such as how much water must pass through an aquifer to remove contaminants or how much time is required must be answered. The answer of these questions depends on the physicochemical processes within subsurface. The physical and chemical processes in the subsurface are dissolution, volatilization, and sorption.

2.8.5.2 Transformation, Retardation, and Attenuation of Solutes

Solutes dissolved in groundwater are subject to a number of different processes through which they can be removed from the groundwater. They can be sorbed onto surfaces of the mineral grains of the aquifer, sorbed by organic carbon that might be present in the aquifer, undergo chemical precipitation, be subjected to abiotic as well as biodegradation and participates in oxidation-reduction reaction. As a result of sorption processes,

some solutes will move much more slowly through aquifer than the groundwater that transporting them. The process of slowing down the movement of contaminants in soil called **retardation**. Biodegradation, radioactive decay, and precipitation will decrease the concentration of solute in the plume but may not necessarily slow rate of plume movement [45].

2.9 Diesel

2.9.1 Diesel Definition

Diesel or diesel fuel is a specific fractional distillate of petroleum fuel oil or a washed form of vegetable oil that is used as fuel in a diesel engine.

Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) [37]. The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approx. $C_{10}H_{20}$ to $C_{15}H_{28}$.

Sulphur occurs naturally in crude oils and must be removed to an acceptable level during the refining process. Sulphur in diesel fuel contributes to formation of particulate matter (PM) in engine exhaust and affects the performance of vehicle emissions control equipment. It therefore has an indirect effect on emissions of CO, hydrocarbons and NO_x .

Diesel fuel containing 500 ppm of sulphur is generally referred to as Low Sulphur Diesel (LSD). Fuel containing 50 ppm sulphur or lower is referred to as Ultra Low Sulphur Diesel (ULSD). "Sulphur-free" diesel generally refers to levels below 10 ppm.

Lower sulphur levels in diesel can be achieved by using a combination of lower sulphur feed stocks and sulphur removal. Hydrodesulphurisation of diesel uses hydrogen to release the sulphur from the feed and form H_2S which is removed and treated to recover the sulphur. A similar process occurs in hydro cracking.

2.9.2 Diesel Properties

Density is a measure of a fuel's mass per unit volume. It is temperature dependent and for diesel fuel is normally referenced to 15°C. Diesel is made up of a mixture of many different hydrocarbon compounds of various densities and molecular weights, and thus the overall density is a function of the composition of the fuel. For this reason, density is strongly correlated with other fuel parameters, particularly cetane number (normal hexadecane), aromatics content, viscosity and the distillation characteristics (boiling range or volatility). Appendix A-1 shows some physical properties of diesel. Reducing the high end distillation temperatures will reduce the maximum density by excluding the heaviest components.

Viscosity is a measure of a fuel's resistance to flow. It affects the performance of diesel fuel pumps and injection systems. Viscosity is dependent on fuel composition and so is reflected in the distillation parameters, density and cold flow properties.

2.9.3 Diesel Combustion Effects

Diesel combustion exhaust is an important source of atmospheric fine particles, which is a fraction of air pollution implicated in human heart and lung damage. Diesel exhaust also contains nanoparticles which have been found to damage the cardiovascular system in a mouse model. The study of nanotoxicology is still in its infancy, and the extent of health and societal effects caused by diesel combustion is unknown. Biodiesel and biodiesel blends result in greatly decreased pollution [46].

2.10 Ultraviolet-Visible Spectrophotometer

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis **spectrophotometer**. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the *transmittance*, and is usually expressed as a percentage (%T). The absorbance, A , is based on the transmittance: $A = -\log(\%T)$

The basic parts of a spectrophotometer are a light source (often an incandescent bulb for the visible wavelengths, or a deuterium arc lamp in the ultraviolet), a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

2.10.1 Types of UV/vis Spectrophotometer Beam

A spectrophotometer can be either *single beam* or *double beam*. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam. Samples for UV/Vis

spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, L , in the Beer-Lambert law.) Test tubes can also be used as cuvettes in some instruments. The best cuvettes are made of high quality quartz, although glass or plastic cuvettes are common. (Glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths) [47].

CHAPTER 3

MATERIALS AND METHODS

3.1 Surfactant Analysis and CMC Determination

The surfactant used to prepare surfactant aqueous solutions was nonionic surfactant, Triton-X 100 purchased from Segma Aldrich Company. It was used as received at 97% purity; Triton-X 100 is an alkyl phenol ethoxylate surfactant with low CMC but reported to be an environmental persistent. However, it was selected because of its widespread use in other studies, and as representative of the class of nonionic surfactants. Surface tension measurements were used to determine the CMC of the surfactant. Surfactant solutions were prepared at ten different concentrations by diluting stock surfactant aqueous solution. The selected surfactant concentrations as percent volume by volume in deionized water were 2.0, 1.0, 0.5, 0.1, 0.05, 0.01, 0.005, 0.001, 0.0005, and 0.0001. These concentrations range approximately from below CMC to above CMC. Surface tensions of surfactant solutions were measured by Fischer Surface Tensiometer Model 21 and the procedure of measuring surface tension by ASTM D 1331-89 (Reapproved 1995) “Standard Test Method for Surface and Interfacial Tension of Solutions of Surface-Active Agent”.

The instrument consists of platinum-iridium ring suspended from torsion balance and the force in dynes per centimeter required to pull the ring free from the solution is measured. The room temperature while performing the surface tension measurement was recorded and it ranged between 19.5 and 21°C during the entire experimental phase. Each sample was tested at least four times to ensure that consistent values were obtained. The platinum-iridium ring was cleaned after each measurement with acetone and heated until the ring glow red in the gas flame. All glassware was cleaned between each measurement and air-dried before use in the next measurement.

The averages from the measurements of each solution were plotted as a function of surface tension against the logarithm of surfactant concentration to identify the concentration at CMC. The surfactant concentration at which the surface tension no longer decreases significantly with increasing surfactant concentration is taken the representative surfactant CMC [48].

3.2 Soil

Three replicates of agricultural soil were obtained from Al-Jeftlick, north of Nablus city, Palestine. Moisture content of each sample was determined by drying for 24 hours in Ari J. Levy oven at 500 °C. pH was determined by Jenway 3510 pH meter. Organic carbon and organic matter of each replicate was determined by Walkley-Black Titration Method. Nitrogen percent of each sample was determined by Kjeldahl determination method.

The organic content was determined by Walkley-Black titration method. A 0.5 g of oven-dried and sieved (< 2mm) soil was placed in 250 mL conical flask and 5mL of 1N $K_2Cr_2O_7$ was added and swirled. A 10 mL sample of conc. H_2SO_4 was added into the suspension and swirled gently until the soil was mixed, then swirled more vigorously for about one minute. The flask was left to cool for 30 minutes. One hundred mL of deionized water was added to the flask and the suspension was filtered. A 0.3 mL of Ortho-phenanthroline-ferrous complex (0.025M) was added to the flask as an indicator and titrated with 0.5N $FeSO_4$. As the endpoint was approached, the solution changed sharply from greenish-blue to red-brown. The amount of $FeSO_4$ used was recorded. The percent of organic carbon and organic matter were calculated by using the following equations:

$$\text{Normality(N)}FeSO_4 = \frac{\text{mL } K_2Cr_2O_7 \times N K_2Cr_2O_7}{\text{mL } FeSO_4}$$

$$\text{meq } FeSO_4 = \text{mL } FeSO_4 \times N FeSO_4$$

$$\text{Organic carbon (\%)} = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4) \times 0.3 \times 1.33}{\text{weight of dry soil}}$$

$$\text{Organic Matter (\%)} = 1.72 \times \text{organic carbon \%}$$

Nitrogen percent of each replicate was determined by Kjeldahl method,

1.0 g of each soil sample was placed in digestion tube. A 10 mL sample of conc. H_2SO_4 was added and swirled until the acid was mixed with the sample. The sample was allowed to cool. Two and half g of a catalyst mixture (K_2SO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, TiO_2 and anatase) was added and the mixture was heated until the digestion mixture become clear, and then boiled gently for 5 hrs. The mixture was allowed to cool and 20 mL of deionized water was added slowly with shaking. The tube was swirled to bring any insoluble material into suspension then the tube was transferred to the distillation apparatus. The tube was rinsed three times with water to complete the transfer. A 5 mL sample of boric acid (20 g/L) was added to 250 mL conical flask and the flask was placed under the condenser of the distillation apparatus in such a way that the end of the condenser was dipped into the solution. Twenty mL of NaOH (10 mol/L) was added to the funnel of the apparatus and the alkali was run slowly into the distillation chamber. About 100 mL of the condensate was distilled. The condenser was rinsed and few drops of indicator (0.1 g bromocresol green, 0.02 g methyl red in 100 mL ethanol) was added to the distillate and titrated with sulfuric acid to the violet end point. The percent nitrogen in each replicate was calculated using the following equations:

$$\% \text{ N} = \frac{(V_1 - V_0) \times c(\text{H}^+) \times M_{\text{N}}}{m \times m_t} \times 100\%$$

Where V_1 : is volume, in mL, of the H_2SO_4 used in titration of sample.

V_0 : is the volume, in milliliters, of the sulfuric acid used in the titration of the blank test.

$c(H^+)$: is the concentration of H^+ in the H_2SO_4 in mol/L (e.g. 0.01 mol/L H_2SO_4 is used, $c(H^+) = 0.02$ mol/L).

M_N : is the molar mass of N, in g/mol (=14).

m : is the mass of test sample.

m_t : is the dry residue, expressed as g/100 g on the basis of oven dried material.

After removal of the surface litter and drying the soil, the +2 mm fraction was removed by dry sieving. The soil texture of each replicate was determined by ASTM 152-H hydrometer.

3.3 Optimum Time for Surfactant Sorption onto Soil

The purpose of this task is to determine the optimum time for the process of surfactant adsorption onto soil to reach equilibrium. Twenty one samples were prepared in 125 mL Erlenmeyer flask containing 50 mL of surfactant aqueous solution at 0.005% (V/V). Mercuric chloride (0.7 mL)

corresponding to 18 mg was added in the surfactant solution as degradation inhibitor [49]. The samples were separated into 3 groups (i.e. each group consists of 7 samples). One g of each soil replicate was added to each sample of the same group. The samples in Erlenmeyer flasks were closed with Teflon screw caps and mounted on Wrist Action Shaker Model 75, purchased from BURELL at 300 R.P.M and each sample was kept on the shaker for 1, 2, 4, 6, 12, 24 and 36 hours. Soil particles in the sample batch test was allowed to settle for at least 36 hours to make sure that the supernatant was free of suspended soil particles. After 36 hours of settling time, the supernatant was centrifuged for 15 minutes to remove the suspended particles. After centrifuging, 30 mL of the supernatant was placed into a 100 mL beaker for surface tension measurement. The result of surface tension reading from each sample was plotted against shaking period.

3. 4 Diesel Sorption onto Soil without Surfactant

The task of this experiment was first to study the sorption behavior of diesel in soil without surfactant, and second to determine the amount of diesel sorbed at various diesel concentrations. Three mixtures were prepared by mixing 1 g of soil with 10 mL solution of diesel dissolved in methanol at three different concentrations; 0.25%, 0.50% and 1.00% (v/v). The mixtures were shaken for two hours, and then left in hood for 24 hours for evaporation of methanol. Five hundreds μL of liquid phase of each were taken and

diluted with methanol in 10 mL volumetric flask, to test the amount of diesel remained after the completion of sorption process by UV-Visible spectrophotometer at 254 nm.

3.5 Surfactant Sorption onto Soil without Contaminant

The purpose of this task is to test the sorption behavior of surfactant onto uncontaminated soil. Seven mixtures, each one consists of 1 g of uncontaminated soil and 50 mL of surfactant aqueous solution at concentration 0.0005%, 0.001%, 0.005%, 0.1%, 0.5%, 1.0% and 2.0% (v/v) (i.e. each concentration for 1 mixture). The mixtures were shaken for 2 hours at 300 RPM then left for 36 hours for soil to settle. A 30 mL of the aqueous phase of each were taken for surface tension measurements.

3.6 Surfactant Sorption onto Contaminated soil at Different Diesel Concentrations

The purpose of this task is to determine the effect of diesel concentration on surfactant sorption onto soil. Sixty three samples were prepared in 250 mL Erlenmeyer flasks and separated into 3 groups for each soil replicate, 1, 2 and 3 (i.e. 21 samples for each soil replicate). The diesel concentrations were 0.25%, 0.50% and 1.0% (v/v) dissolved in methanol. Methanol was the preferred solvent because it showed no effect on surfactant solubilization; higher alcohols would affect CMC values significantly [18].

Seven surfactant concentrations were used in this test, 0.0005%, 0.001%, 0.005%, 0.1%, 0.5%, 1.0% and 2.0% (v/v). The surfactant aqueous solutions used in this test were prepared and measured for surface tension.

In each group of soil, the samples were separated into three diesel concentrations, 0.25%, 0.50% and 1.0% (v/v).

The artificially contaminated soil was made by adding 10 mL of diesel dissolved in methanol to 1 g soil at different diesel concentrations. The artificially contaminated soils in the flasks were closed by Teflon screw caps and shaken for 2 hours to make sure that the contaminant was completely adsorbed on the soil. After shaking, the contaminated soil samples were opened and left in hood for 24 hours to evaporate the methanol. The amount of contaminant evaporated with methanol in each sample was assumed to be equal in every group samples. Fifty mL of surfactant aqueous solution was added to the artificially contaminated soil after methanol was evaporated for 24 hours and 0.7 mL of mercuric chloride (corresponding to 18 mg) was added into each sample to inhibit the biodegradation process during the experiment. The samples were shaken for 2 hours and left to settle for 36 hours. The supernatants were taken from the samples and centrifuged for 15 minutes. Thirty mL of the supernatant was placed in 100 mL beakers to measure the surface tension at room temperature, (it was between 20.5 and

22.5°C). The results from the surface tension readings were plotted versus the logarithm of surfactant concentration in mol/L.

3. 7 Sorption Behavior of Surfactant in the Presence of Acid or Base

Two mixtures, each one consists of 1 g soil with 10 mL of 0.50% (v/v) diesel dissolved in methanol were shaken for two hours, and then left in hood for 24 hours for evaporation of methanol. Fifty mL of 0.1% surfactant aqueous solution was added to each one. A 10 mL sample of diluted HCl was added to the first, and a 10 mL sample of diluted NH₄OH was added to the second. Mixtures were shaken for two hours and were left for 36 hours for soil to settle. Surface tension measurement and UV-Visible Spectrophotometer test at 254 nm were performed for each mixture.

3. 8 Sorption Behavior of Surfactant at Different Temperature

Two mixtures, each one consists of 1 g soil and 10 mL Of 0.50% (v/v) diesel dissolved in methanol were shaken for two hours. Mixtures were left in hood for 24 hours for methanol evaporation. Fifty mL of 0.1 % surfactant aqueous solution was added to each one. The first mixture was shaken for two hours on a hotplate with magnetic stirrer keeping the temperature of the mixture between 50-60°C, while the second mixture was shaken by the same way keeping the temperature between 70-80°C. Mixtures were left for 36 hours for soil to settle. Surface tension measurement and UV-Visible Spectrophotometer test at 254 nm were performed for each one.

3.9 Surfactant Sorption Behavior in the Presence of NaCl Solution at Three Different Concentrations (Ionic Strength)

Three mixtures, each one consists of 1 g soil with a 10 mL sample of 0.50% (v/v) diesel dissolved in methanol were shaken for two hours, then they were left in hood for 24 hours for evaporation of methanol. Fifty mL of 0.1% surfactant aqueous solution was added to each one. A 10 mL sample of 0.05 M of NaCl was added to first mixture, a 10 mL of 0.1 M NaCl was added to the second and a 10 mL of sample 0.5 M NaCl was added to the third. They were shaken again for 2 hours and left for 36 hours for soil to settle. Surface tension measurement and UV-Visible Spectrophotometer test at 254 nm were performed for each one.

3.10 Calibration Curve for Diesel

Three standard solutions of diesel (dissolved in methanol) were prepared at concentration, 0.25%, 0.50% and 1.00% (v/v). Then, 500 μ L of each solution is taken and diluted with methanol in 10 mL volumetric flask. The cell of UV-Visible Spectrophotometer model 1601 purchased from Shimadzu was filled with diesel solution to test the absorbance at wavelength of 254 nm taking methanol as a baseline. Concentration of diesel versus absorbance graph was plotted as standard curve and this standard curve was used as a reference to define the concentration of dissolved diesel in samples. A 2 mL of aqueous phase of each sample (i.e. the studied sixty three

samples) was taken and diluted with methanol in 10 mL volumetric flask. The UV-Visible Spectrophotometric cell was filled and the absorbance at 254 nm was measured and compared with the standard curve for the determination of the solubilized diesel by surfactant.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Surface Tension Measurements and CMC Determination

Surface tension measurement is a well-established method for determining the CMC of surfactants. The surface tension for each concentration of surfactant Triton X-100 was measured at least four times. The average surface tension, the standard deviation, and the coefficient of variance for the surface tension measurement are shown in Table 4.1. The average surface tension of each surfactant concentration was plotted as a function of surface tension in dynes per centimeter against the logarithm of surfactant concentration; $\log [M]$, to identify the CMC points as shown in Figure 4.1. A logarithmic plot was chosen in order to clearly demonstrate where the CMC value occurs. The surface tension curve is composed of two linear segments; the intersection of the two linear portions represents the CMC. For the first linear segment, a sharp decrease of surface tension from 71.1 to 40.2 dynes/cm occurred between 0.0001% (v/v) and 0.01% (v/v) surfactant concentration. A slight decrease of surface tension from 40.2 to 35.2 dynes/cm occurred between 0.01% (v/v) and 0.05% (v/v) surfactant concentration. For the second linear segment, the surface tension did not decrease significantly with increasing surfactant concentration above 0.05%

(v/v). The surfactants concentration at which the two linear segments intersect represent the CMC [8].

From the graph in figure 4.1, the CMC point was found as the point (-3.47, 35.2) where the concentration of surfactant solution is 3.388×10^{-4} mol/L and the surface tension of the surfactant mixture 35.2 dynes/centimeter. CMC values of Triton X-100 from the previous research are shown in Table 4.2. The range of CMC determined by other researchers was from 6.89×10^{-5} to 3.3×10^{-4} mol/L [4, 8, 49, 50].

The variation in this number depends on the different techniques used to test CMC and the room temperature during measurements.

Table.4. 1 : Surface tension of surfactant Triton X-100 at different concentrations.

Surfactant solution (% V/V)	Concentration (mol/L)	log [M]	Average measured surface tension (dynes/cm)	Standard Deviation	Coefficient of Variance	Calculated surface tension (dynes/cm)
0.0001	1.710E-7	-5.7670	71.1	0.717	1.01	73.1
0.0005	8.550E-6	-5.0681	63.2	0.523	0.83	61.8
0.0010	1.710E-5	-4.7670	53.9	0.478	0.88	56.9
0.0050	8.550E-5	-4.0681	44.3	0.912	2.05	45.5
0.0100	1.710E-4	-3.7670	40.2	0.369	0.89	40.6
0.0500	8.550E-4	-3.0681	35.2	0.512	1.47	34.4
0.1000	1.710E-3	-2.7670	36.1	0.811	2.25	34.6
0.5000	8.550E-3	-2.081	35.2	0.724	2.01	34.9
1.0000	1.710E-2	-1.7670	34.3	0.502	1.46	35.0
2.0000	3.420E-2	-1.466	35.9	0.641	1.78	35.2

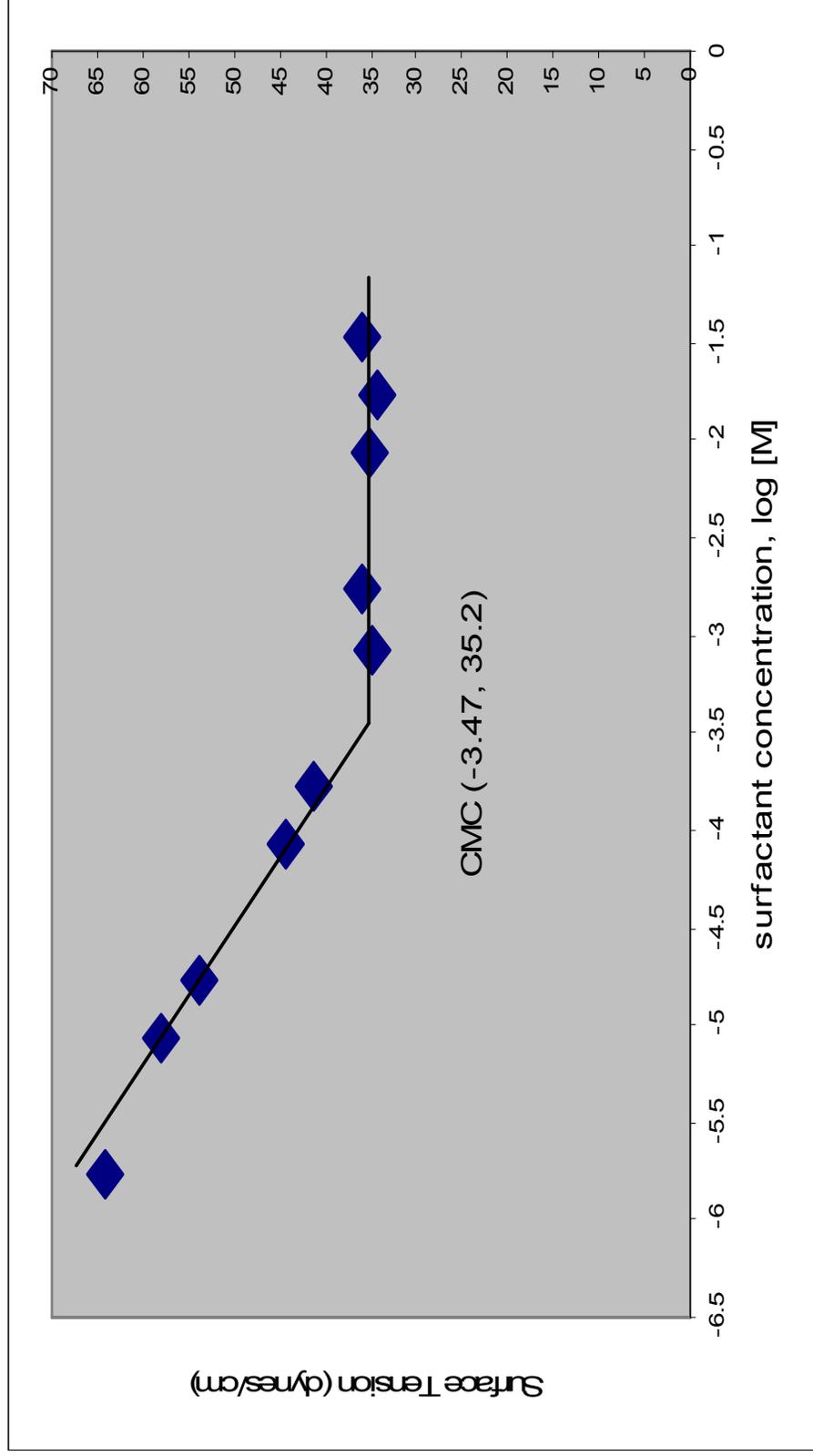


Fig.4. 1 : Surface tension of surfactant Triton X-100 at different concentrations.

Table.4. 2 : CMC of Triton X-100 from Previous Researches.

Chemical Name	Average Molecular formula	Symbol	Average MW (g/mol)	Surface Tension Tests CMC (M)	Reference
octylphenylethoxylate	$C_8H_{17}-C_6H_4-O(CH_2CH_2O)_{9.5}H$	$C_8PE_{9.5}$	628	1.70×10^{-4}	Liu and Luthy, 1992
polyoxyethylene (10) octylphenol	N/A	N/A	N/A	1.70×10^{-4} 3.18×10^{-4}	Zheng and Obbard, 2002
octylphenylethoxylate with average $x=9.5$	$C_8H_{17}-C_6H_4-O(CH_2CH_2O)_xH$	N/A	628	2.00×10^{-4} $(3.00-3.30) \times 10^{-4}$	Laha and Chen, 2002
N/A	N/A	N/A	624	2.24×10^{-4} 6.89×10^{-5}	Li and Chen, 2002
Octylphenoxypolyethoxy-ehtanol	$C_{33}H_{60}O_{10.5}$	N/A	624	3.39×10^{-4} 4.21×10^{-4}	this study section 4.1 prepared solution 100ml section 4.4 prepared solution 1000ml

4.2 Soil

Each soil replicate was analyzed in order to evaluate moisture, the organic carbon percent, organic matter, and nitrogen percent.

Table 4.3 presents moisture content, pH, organic carbon percent, organic matter percent and Nitrogen percent of each sample.

Table.4. 3 : Moisture content, pH, organic carbon, organic matter, and Nitrogen percent for soil samples.

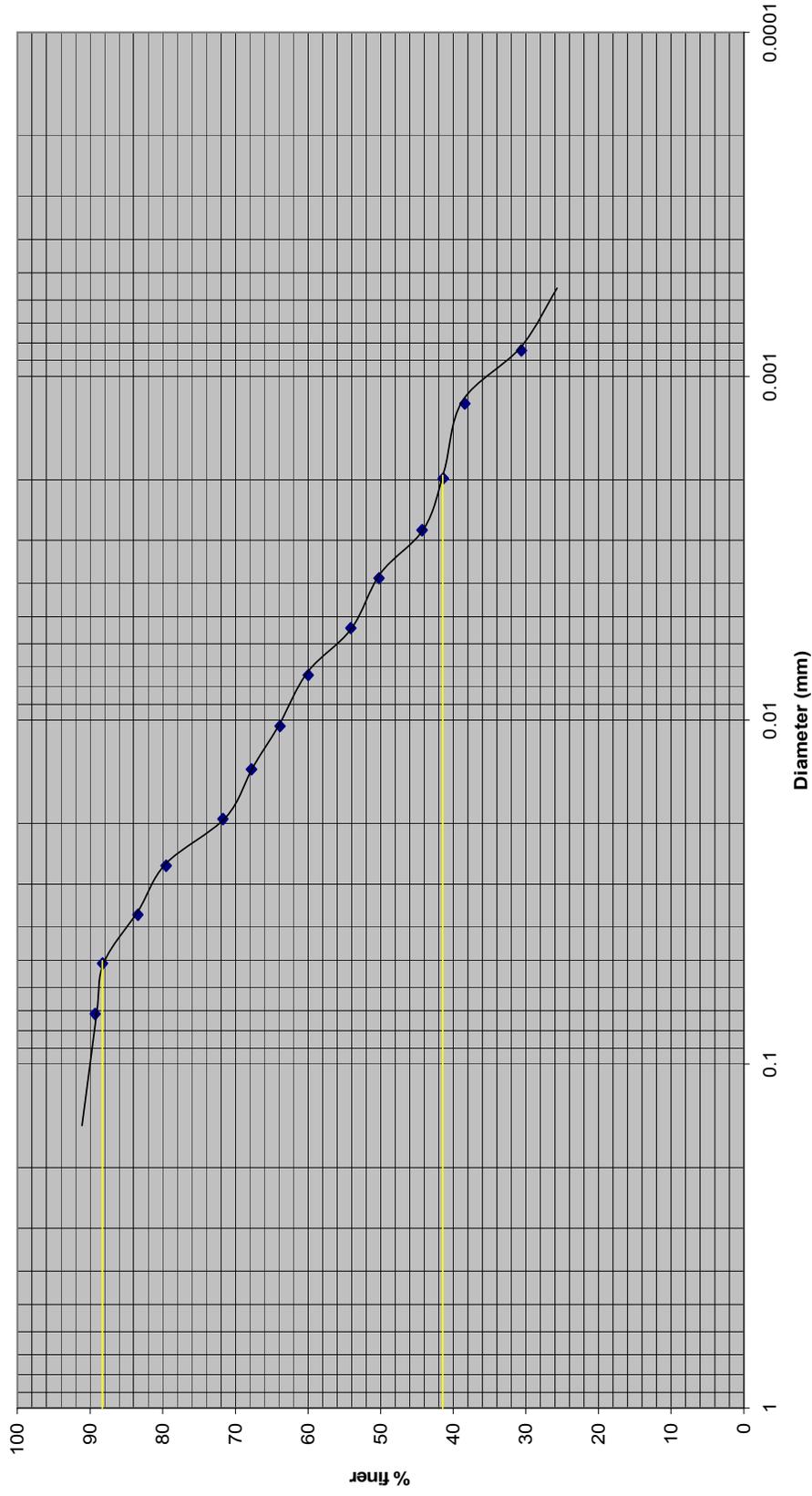
	Replicate (1)	Replicate (2)	Replicate (3)
pH	8.46	8.74	8.08
Moisture content (%)	19.3	26.2	27.0
Organic carbon (%)	1.85	1.73	1.76
Organic matter (%)	3.18	2.98	3.03
Nitrogen (%)	0.29	0.33	0.41

After drying them each replicate was sieved and hydrometer test was performed in order to evaluate the soil texture of each replicate. Table 4.4 presents soil texture of each replicate.

Table.4. 4 : Soil texture of the soil samples.

Soil texture	Replicate (1)	Replicate (2)	Replicate (3)
Sand fraction 2-0.06 mm (%)	12	10	11
Silt fraction 0.06-0.002 mm (%)	46	56	69
Clay fraction < 0.002 mm (%)	42	34	22

Figures 4.2, 4.3 and 4.4 show graphs obtained from Hydrometer tests for the three samples of soil.



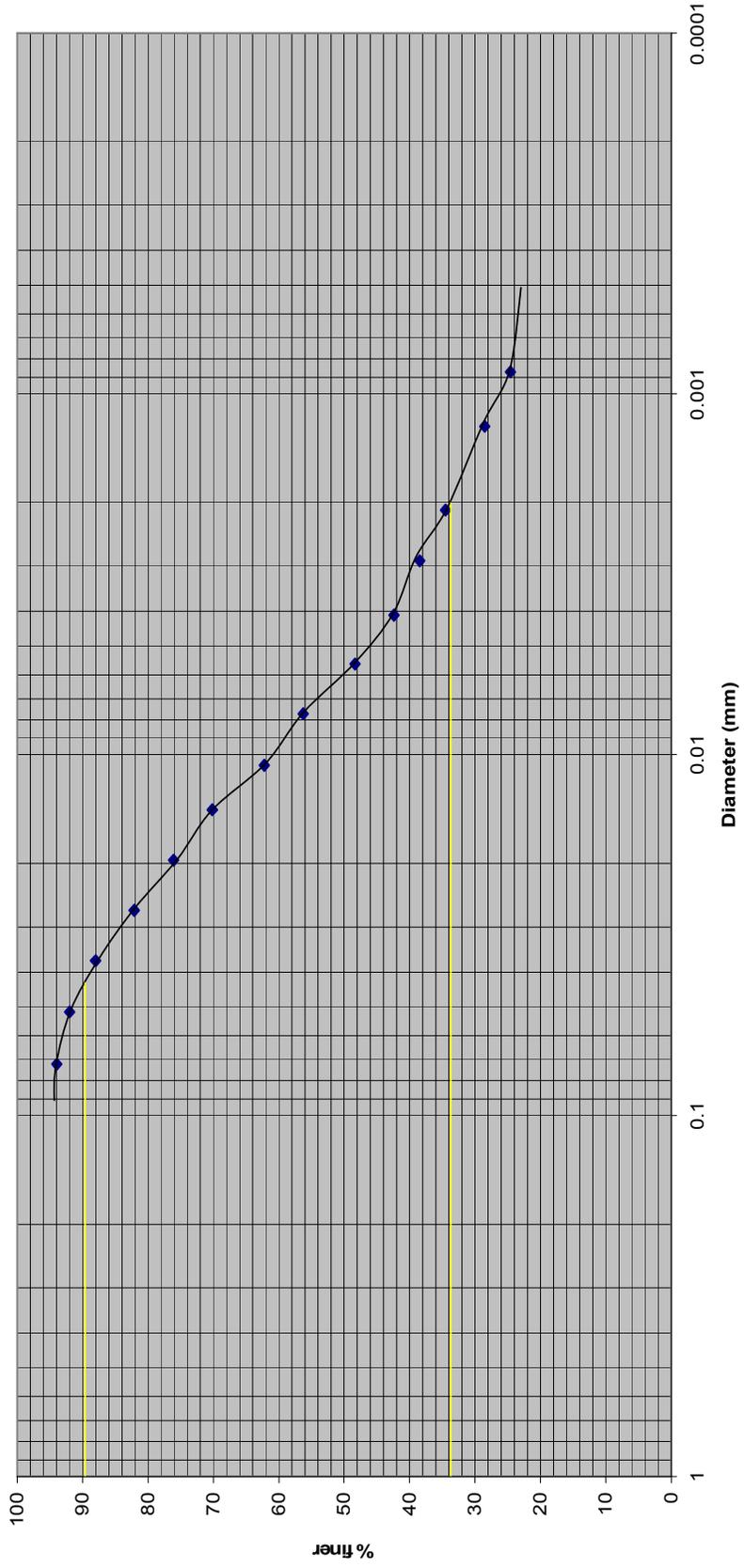


Fig.4.3 : Particle Size Distribution Curve (hydrometer test) for Replicate “2” as 34% clay, 56% silt, and 10% sand.

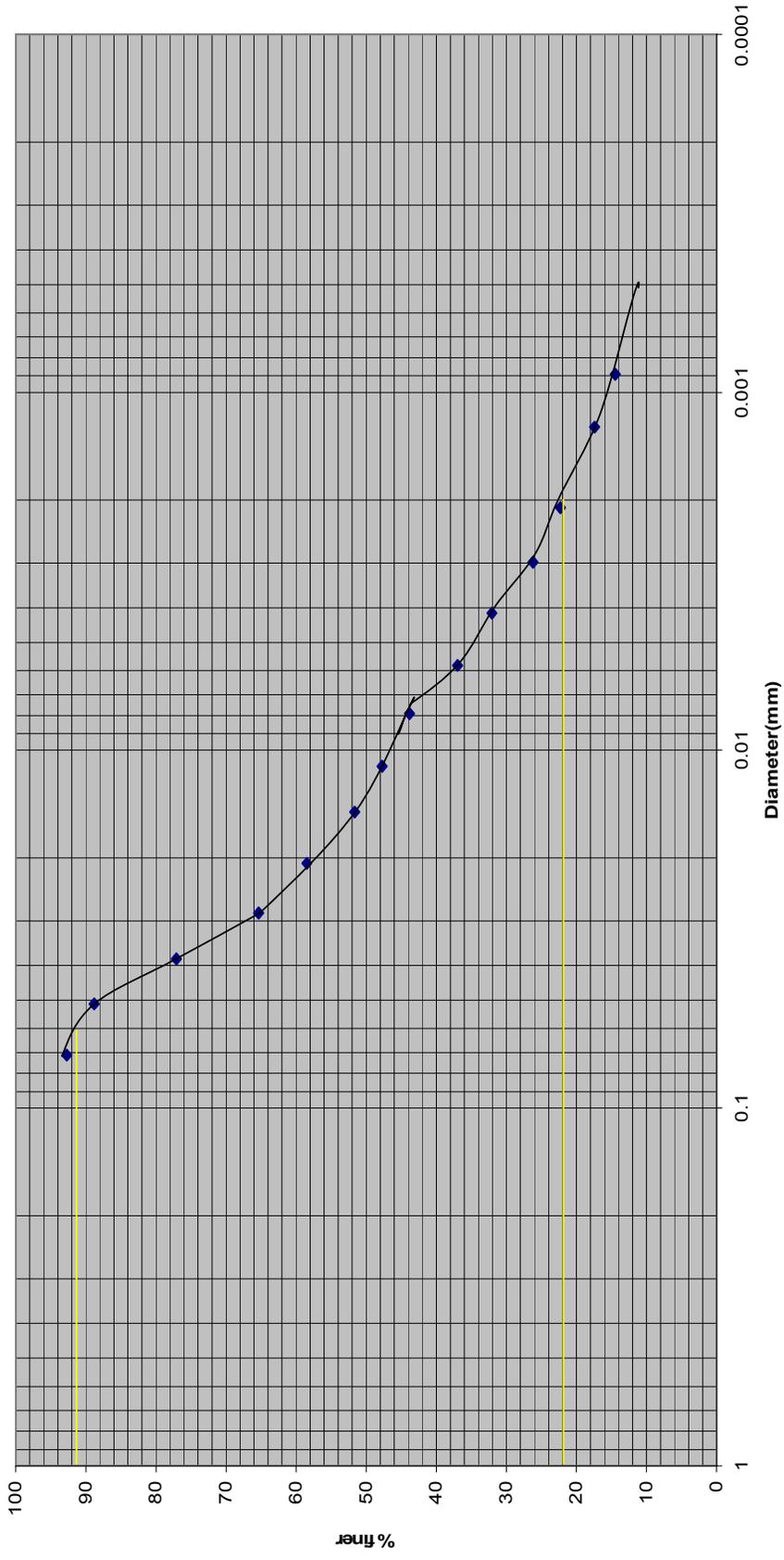


Fig.4.4 : Particle Size Distribution Curve (hydrometer test) for Replicate “3” as 22% clay, 69% silt, and 11% sand

4.3 Optimum Time for Surfactant Sorption

Table 4.5 shows the average surface tensions from the three replicates of soil. Appendix B-1 shows all the surface tension readings (at least four times for each sample), the average, the standard deviation, and the coefficient of variation from each sample.

The results show that the surface tensions of the supernatant taken from the mixture of aqueous surfactant solution at concentration of 0.005% (v/v) with 1 g of the three soil samples at different mixing time (1, 2, 4, 6, 12, 24 and 36 hours) were not significantly different (the three soil replicates have given the same results and approximately the same values for surface tension), (between 44.2 and 44.9 dynes/cm).

The room temperature during the surface tension readings was between 20.5 and 22.0°C. The pH values of surfactant solutions mixed with soil were between 5.82 and 6.01. Figure 4.5 shows graph of surface tension versus mixing time.

Table.4. 5 : Surface Tension Measurements at Different Mixing Times.

Sample	Mixing time	Temp (°C)	pH	Surface Tension (dynes/cm)
	1	21.0-22.0	5.89	44.5
	2	20.5-21.0	5.94	44.2
	4	21.0-22.0	5.84	44.9
	6	21.0-22.0	5.98	44.8
	12	20.5-21.0	6.01	44.8
	24	20.5	5.86	44.4
	36	22.0	6.00	44.7

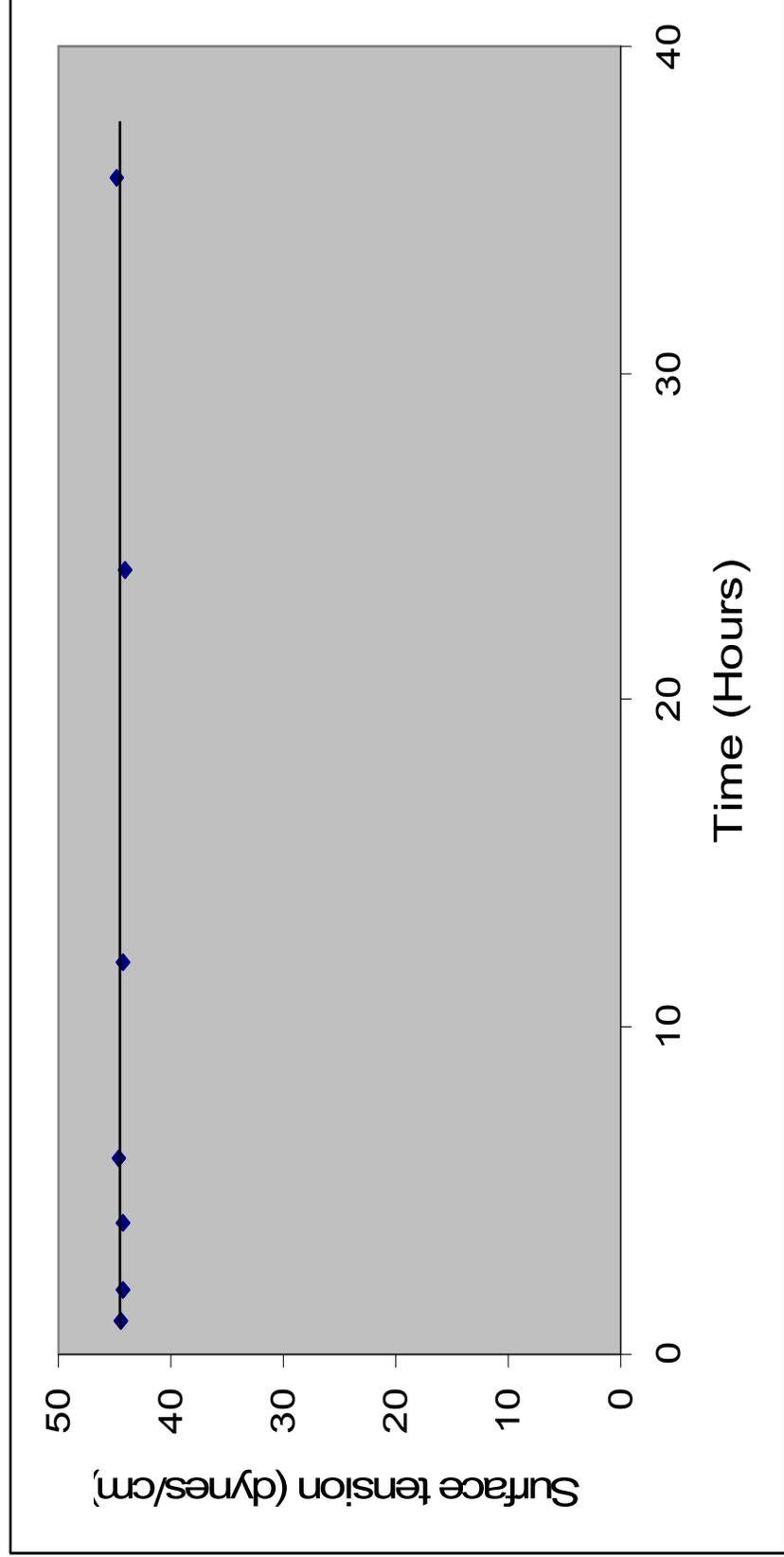


Fig.4. 5 : Surface tension measurements at different mixing time.

4.4 Diesel Sorption onto Soil without Surfactant

The experiment in this part of the research was to evaluate the amount of Diesel sorbed onto soil at the three concentrations of diesel, 0.25%, 0.50% and 1.00% (v/v). Five hundreds μL of solution of diesel dissolved in methanol was taken after the sorption process has equilibrated, and diluted with methanol in a 10 mL volumetric flask. The cell of UV-Visible Spectrophotometer was filled from the diluted solution and tested. The results were compared with calibration curve from UV-Visible Spectrophotometer. The comparison has shown that the amount of diesel sorbed on soil was ranging from 7% to 13% of the original amount. These amounts of sorbed diesel were slightly low; this probably was due to the low organic content of the soil itself which decreased the tendency of diesel to be sorbed onto it.

4.5 Surfactant Sorption onto Soil without Diesel

Results of this experiment have shown that the seven surfactant concentrations; 0.0005%, 0.001%, 0.005%, 0.1%, 0.5%, 1.0% and 2.0% (v/v) mixed with 1 g soil were slightly sorbed onto it. The surface tension of the supernatant of each sample mixture was measured and compared with surface tension of surfactant solution without soil to determine the amount of surfactant sorbed at each concentration (Q_g). Figure 4.6 shows a plot of the surface tension reading versus surfactant concentration. Figure 4.7 shows the comparison between surface

tension measurement with and without soil. From figure 4.7 we can calculate C_{sorb} and by equation (2.9) Q_g can be determined. It was observed that Q_g of surfactant was ranging between 9-15% for all seven concentrations.

This small amount of sorbed surfactant may probably be due to the low organic content of soil itself.

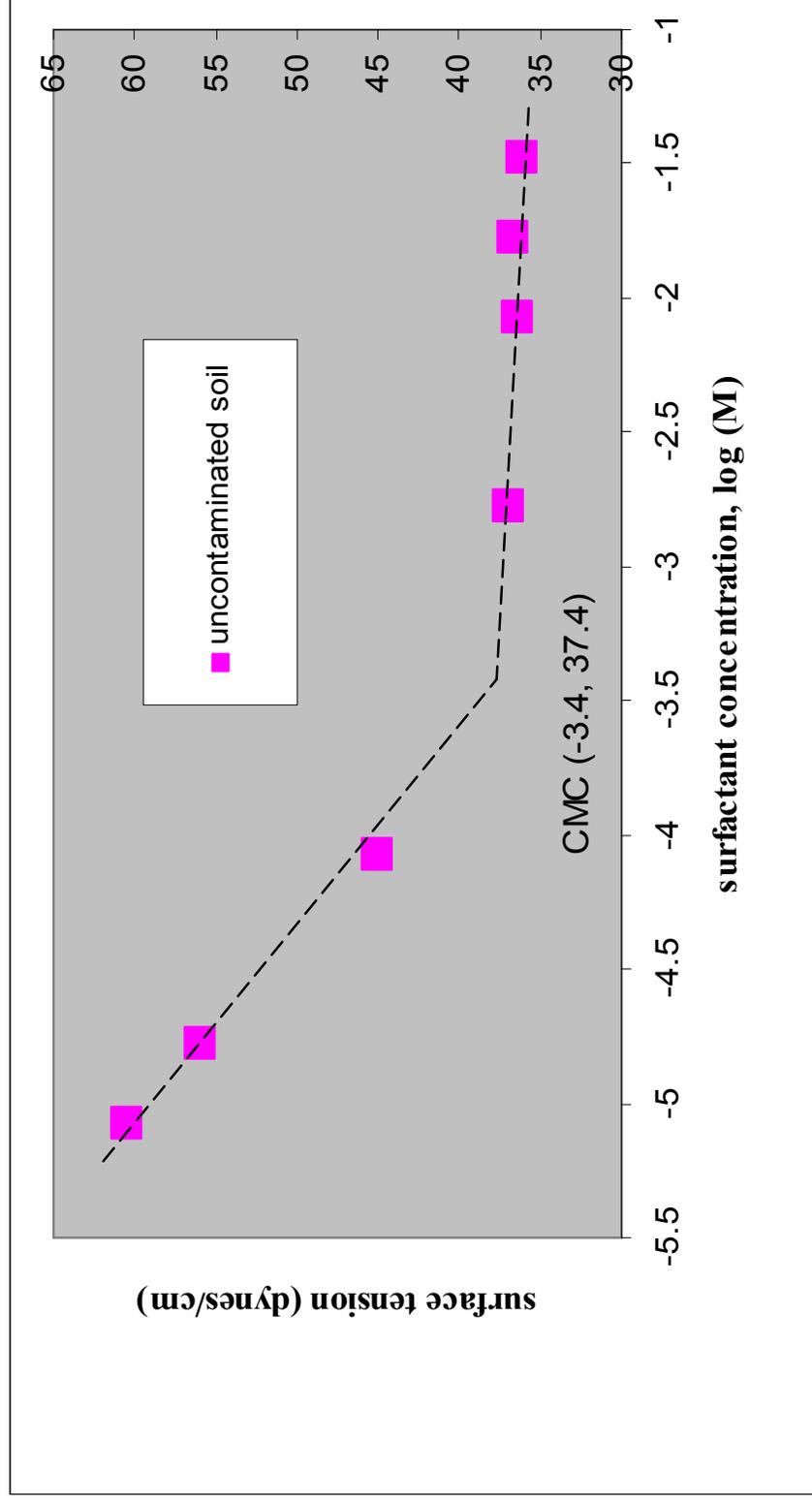


Fig.4. 6 : Surface Tension of surfactant solutions with uncontaminated soil.

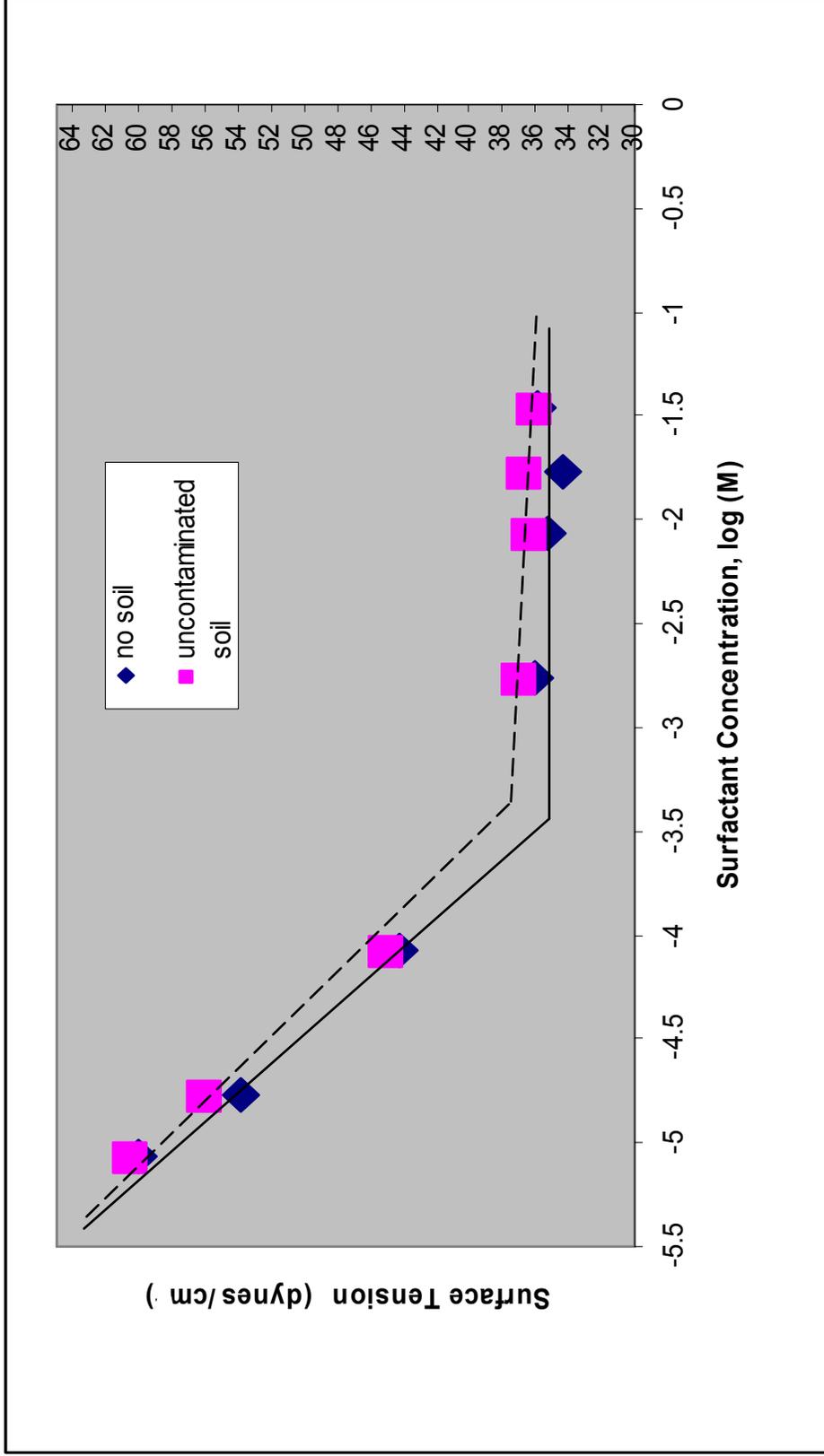


Fig.4. 7 : Comparison of Surface Tension of Surfactant with and without Uncontaminated Soil.

4.6 Effect of Contaminant on Surfactant Sorption on Soil

The Experiments in this section were performed in batch mode. Diesel dissolved in methanol was used as a contaminant in soil at different concentration 0.25%, 0.50% and 1.00% (v/v) to study how the contaminant affects the amount of surfactant sorbed onto soil. The contaminant was mixed with soil to produce an artificially contaminated soil and surfactant solutions were added and agitated for the sorption process to equilibrate. Then the aqueous phase was removed from the sample and the surface tension measurements were performed.

The average surface tension results for each sample of aqueous phase removed from contaminated soil at different diesel concentrations are shown in Table 4.6. Appendix B-2 shows all surface tension readings from each sample, repetition of readings at least four times, the standard deviation and coefficient of variance of each sample. The average surface tension readings from each sample were plotted against the logarithm of the surfactant concentration for each soil at 0.25%, 0.50% and 1.00% (v/v) diesel concentration as shown in Figure 4.8, 4.9, and 4.10 respectively. The surface tension curve is composed of two linear sections and the intersection of the two segments represents the CMC of diesel contaminated soil/aqueous system. The results have shown that, the presence of diesel with surfactant in solution together enhance the

sorption for each onto soil; especially at surfactant concentration lower than CMC.

From the graphs presented in Figures 4.8 to 4.10, soil with 0.25% diesel reached CMC at (-3.315, 35.12) or the surfactant Triton X-100 dose 4.84×10^{-4} mol/L, soil with 0.50% diesel reached CMC at (-3.23, 36.31) or 5.89×10^{-4} mol/L and soil with 1.00% diesel reached CMC at (-3.11, 37.64) or 7.76×10^{-4} mol/L.

Table.4. 6 : Surface Tension of Surfactant Solutions Mixed with Diesel Contaminated Soil at Different Concentrations.

% (v/v) diesel	Surfactant concentration (%) (v/v))	pH	Temp °C	Surface tension (dynes/cm)
0 % diesel	0.0005	6.08	21.0	63.2
	0.0010	6.09	21.0	53.9
	0.005	6.06	21.0	44.3
	0.1000	6.11	21.0	36.1
	0.5000	6.32	21.0	35.2
	1.0000	6.23	21.0	34.3
	2.0000	6.42	21.0	35.9
0.25% diesel	0.0005	5.99	21.5	64.2
	0.0010	6.02	21.0	62.3
	0.0050	6.07	22.0	45.9
	0.1000	5.93	20.5	37.1
	0.5000	6.21	21.0	36.1
	1.0000	6.13	21.5	34.2
	2.0000	6.06	21.5	35.7
0.50% diesel	0.0005	6.08	22.0	65.8
	0.0010	6.12	22.0	62.6
	0.0050	6.01	21.5	54.1
	0.1000	5.97	22.0	36.1
	0.5000	5.86	20.5	37.5
	1.0000	5.94	20.5	35.9
	2.0000	6.11	21.0	38.3
1.00% diesel	0.0005	5.93	20.5	67.4
	0.0010	5.87	20.5	64.2
	0.0050	6.02	21.0	57.2
	0.1000	6.07	20.5	38.1
	0.5000	5.86	21.5	39.2
	1.0000	5.91	21.0	37.8
	2.0000	6.04	21.0	37.3

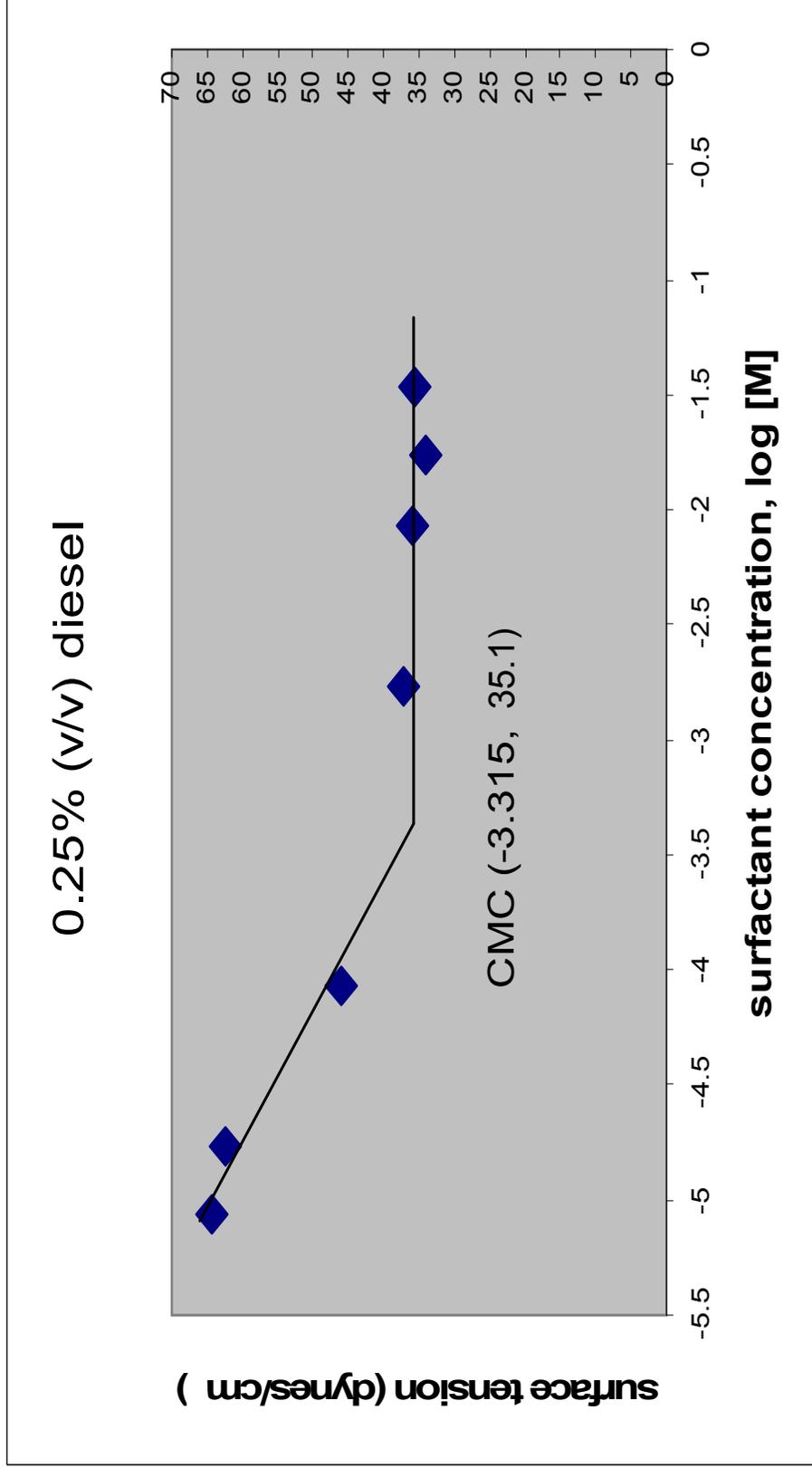


Fig.4.8 : Surface Tension of Surfactant Solutions at 0.25% (v/v) Diesel.

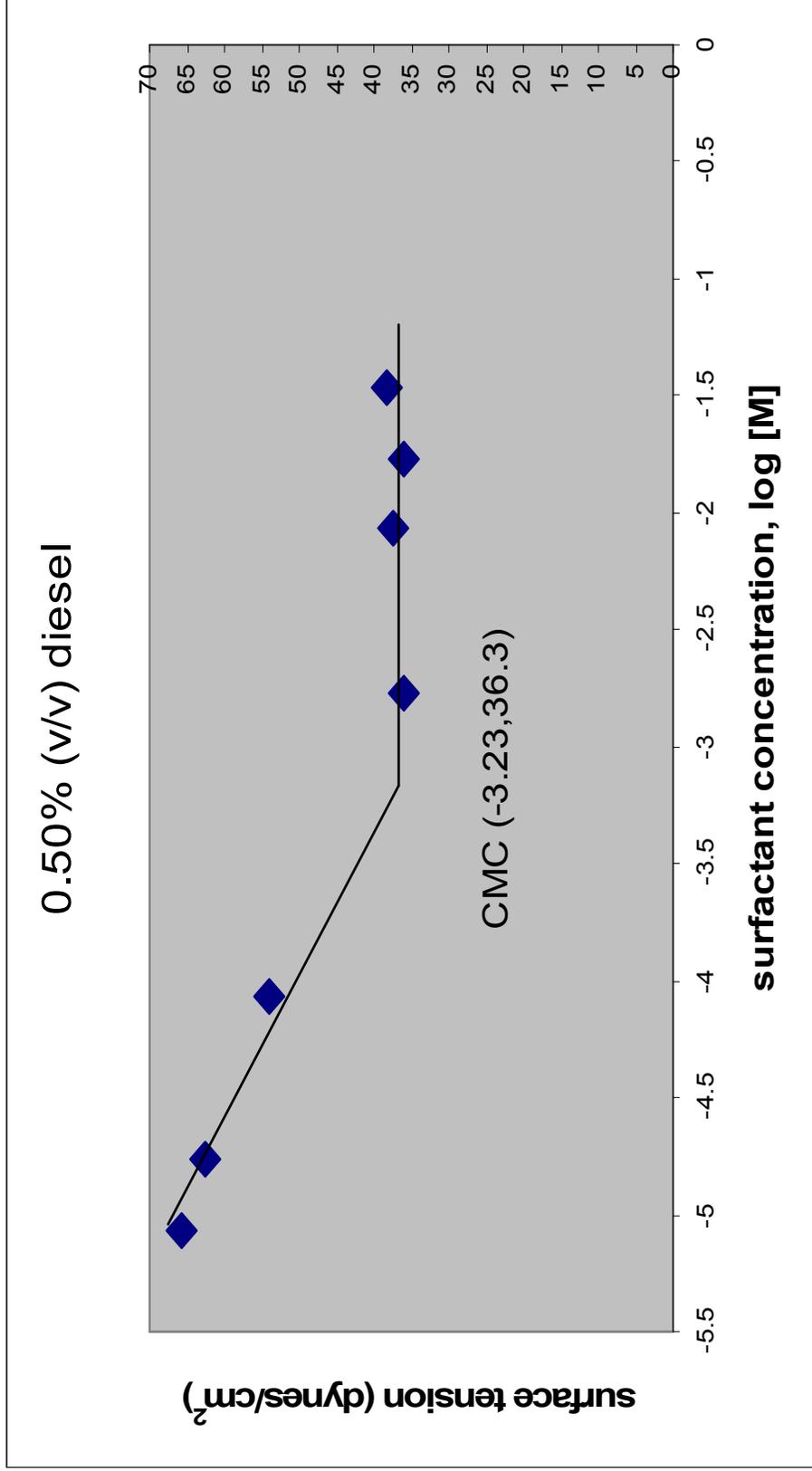


Fig.4. 9: Surface Tension of Surfactant Solutions at 0.50% (v/v) Diesel.

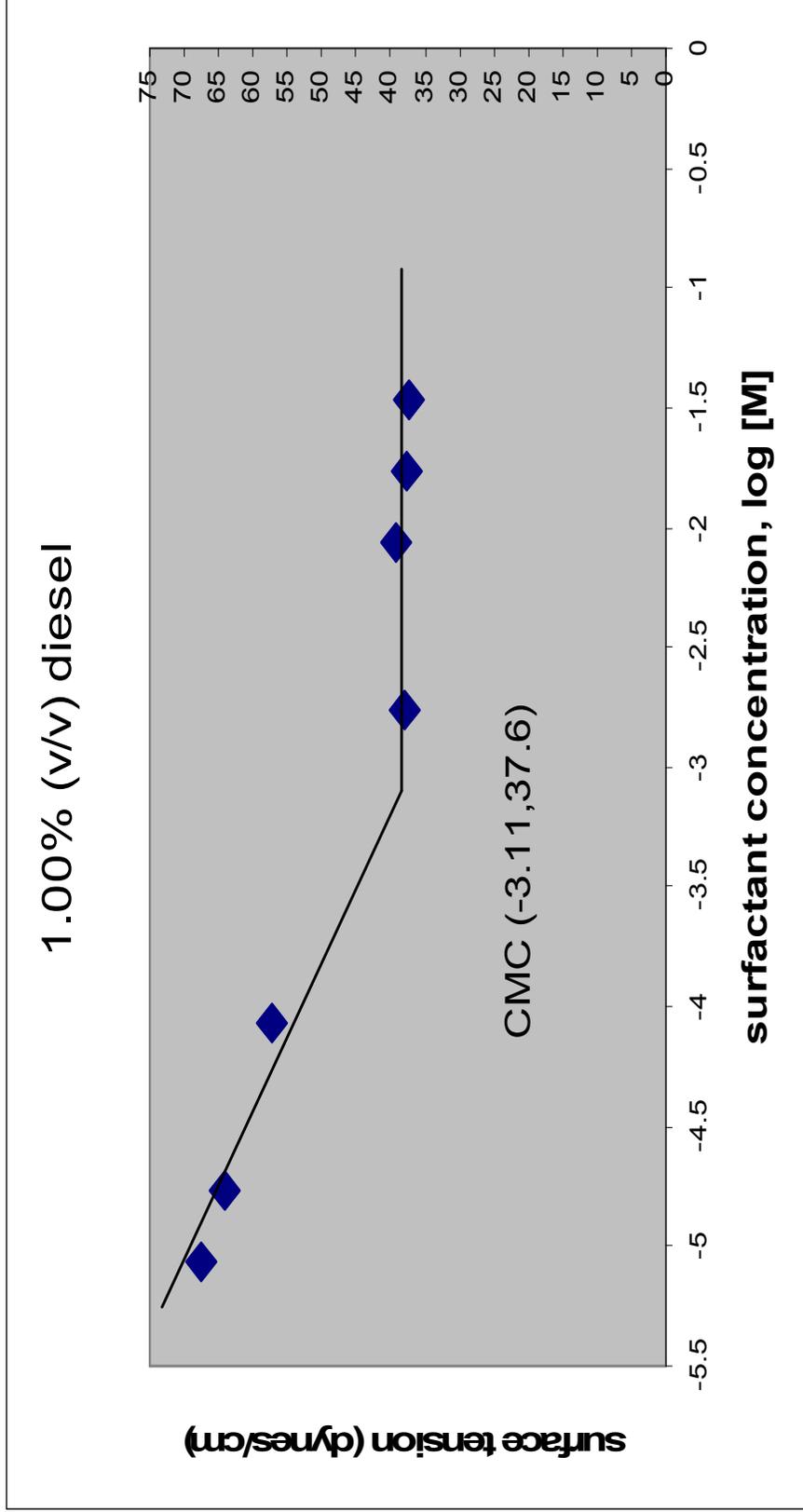


Fig.4. 10 : Surface tension of surfactant solutions at 1.00% (v/v) Diesel.

Figure 4.11 shows the graph plotted to compare among the results of surface tensions in the presence of soil containing different diesel concentrations, 0.25%, 0.50% and 1.00% (v/v), and the surface tensions of surfactant solution without soil.

The data shows that the greater the diesel concentration in the soil, the greater the amount of surfactant needed to be added into the system in order to reduce the surface tension by a given amount. The amount of surfactant sorbed on soil at any aqueous phase surfactant concentration can be calculated by using the data from surface tension plots [3, 8].

Referring to Figure 4.11 , the abscissa for a selected data point on the surface tension curve for the aqueous system without soil gives an aqueous-phase surfactant concentration, C_{surf} (-4.03 from Figure 4.11 or 9.33×10^{-5} mol/L). The corresponding ordinate, a particular value of the surface tension, σ (43 dynes/cm), is then located on the surface tension plot for the soil/aqueous system.

The abscissa on this plot that corresponds with this value of σ yields a value for, $D_{s, \sigma}$ (-3.76 from figure 4.11 or 1.74×10^{-4} mol/L) the bulk surfactant dose in soil/aqueous system that produces surface tension of σ in the supernatant. The difference between this value of $D_{s, \sigma}$ and the selected value of C_{surf} is equal to C_{sorb} (8.07×10^{-5}), the number of moles of surfactant sorbed per liter of solution, evaluated at the particular bulk solution

surfactant concentration. The product of C_{sorb} and the ratio V_a to W_{soil} , the volume of the aqueous solution in liters divided by the weight of the soil in grams, yields a value for Q_{surf} (4.035×10^{-3} g/g of soil), the number of moles of surfactant sorbed per gram of soil or gram surfactant per gram of soil.

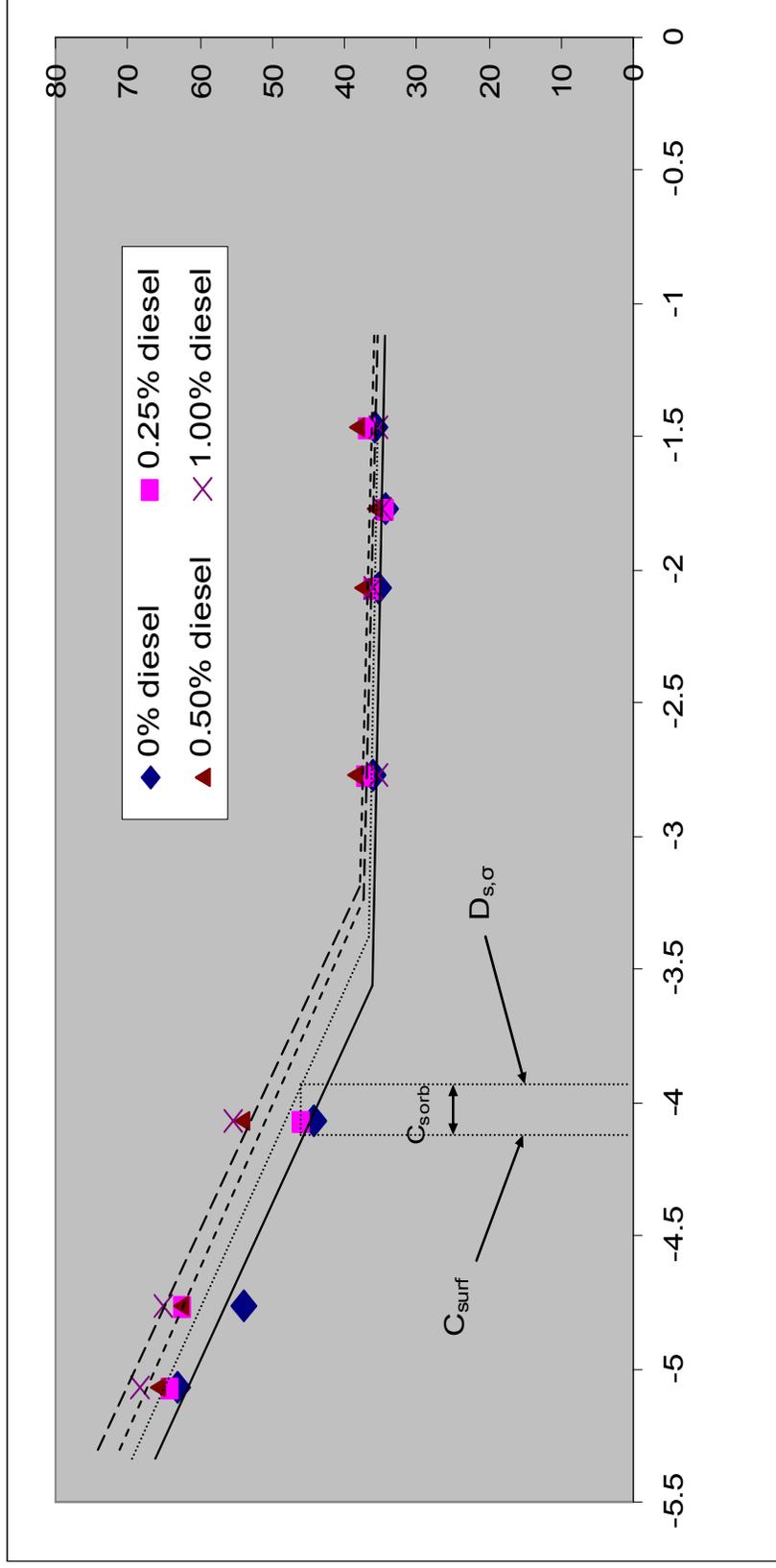


Fig.4.11 : Comparison of Surface Tension Measurements for Systems with and without soil Contaminated with Diesel at Different Concentrations.

The amount of surfactant adsorbed onto soil can be calculated by the following equation from Liu et al; 1992.

$$C_{\text{sorb}} = D_{\text{s},\sigma} - C_{\text{surf}} \quad (\text{eq.4. 1})$$

$$Q_{\text{surf}} = (D_{\text{s},\sigma} - C_{\text{surf}}) \cdot \left(\frac{V_{\text{a}}}{W_{\text{soil}}} \right) = C_{\text{sorb}} \cdot \left(\frac{V_{\text{a}}}{W_{\text{soil}}} \right) \quad (\text{equ.4. 2})$$

Where:

V_{a} : volume of aqueous solution (L).

W_{soil} : weight of soil (g).

$D_{\text{s},\sigma}$: the bulk surfactant dose in the soil/aqueous system that produces a surface tension value of σ in the supernatant (mol/L).

C_{surf} : aqueous-phase surfactant concentration (for aqueous phase with out soil) (mol/L).

C_{sorb} : the number of moles of surfactant sorbed per liter of solution, evaluated at particular bulk solution surfactant concentration (mol/L).

Q_{surf} : the number of moles of surfactant sorbed per gram of soil (mol/g).

Surfactant sorption may also be expressed as Q_{g} , the number of grams of non-ionic surfactant sorbed per grams of the soil, using the Freundlich isotherm:

$$Q_{\text{g}} = K \cdot C^{\frac{1}{n}} \quad (\text{equ.4. 3})$$

Where K : a measure sorption capacity.

$1/n$: an indicator of the curvature of the isotherm.

Table 4.7 shows the amount of surfactant sorbed per gram of soil contaminated with diesel at different concentrations calculated from the equations (4.1) and (4.2) by (Liu et al; 1992). This is the surfactant sorption at sub-CMC level and the surfactants sorb onto soil are in the form of surfactant monomers.

Figure 4.12 shows number of grams surfactant sorbed per gram of soil at 0.25%, 0.50% and 1.00% (v/v) diesel. Using the Freundlich isotherm, the values of K and n can be calculated, they are shown in Table 4.8.

At 0.25% diesel	$y = 2.3531x^{0.7775}$	$R^2 = 1$
At 0.50% diesel	$y = 13.138x^{0.8527}$	$R^2 = 1$
At 1.00% diesel	$y = 17.631x^{0.8448}$	$R^2 = 1$

However, in many environmental applications, the linear form of the Freundlich isotherm applies [42]. For the linear adsorption isotherm, $1/n=1$. From the result, the values of n at 0.25%, 0.50% and 1.00% (v/v) diesel are close to 1. If the value of n assumed to be equal 1, the following linear equations are obtained:

At 0.25% diesel	$y = 14.972x + 0.0003$	$R^2 = 0.9579$
At 0.50% diesel	$y = 36.760x + 0.0014$	$R^2 = 0.8303$
At 1.00% diesel	$y = 50.488x + 0.0018$	$R^2 = 0.9066$

Table.4. 7 : Surfactant Sorbed onto soil at Different Diesel Concentrations in gm/gm soil.

Surface tension (dynes/cm)	Surfactant Concentration , (mol/L)				C _{sorb} (g surf/g soil)			
	Soil-Free Surfactant Solution	0.25% Diesel	0.50% Diesel	1.00% Diesel	0.25% Diesel	0.50% Diesel	1.00% Diesel	1.00% Diesel
55	1.63E-5	3.76E-5	5.02E-5	6.18E-5	6.65E-04	1.06E-03	1.42E-03	1.42E-03
54	1.99E-5	3.89E-5	5.62E-5	6.61E-5	5.93E-04	1.13E-03	1.44E-03	1.44E-03
53	2.37E-5	4.07E-5	6.03E-5	7.59E-5	5.30E-04	1.14E-03	1.63E-03	1.63E-03
52	2.63E-5	4.68E-5	6.76E-5	1.00E-4	6.40E-04	1.29E-03	2.30E-03	2.30E-03
51	2.95E-5	5.13E-5	7.76E-5	1.23E-4	6.80E-04	1.50E-03	2.92E-03	2.92E-03
50	3.19E-5	5.48E-5	8.32E-5	1.34E-4	7.14E-04	1.60E-03	3.19E-03	3.19E-03
49	3.78E-5	6.03E-5	1.21E-4	1.48E-4	7.02E-04	2.60E-03	3.44E-03	3.44E-03
48	4.17E-5	6.92E-5	1.45E-4	1.58E-4	8.58E-04	3.22E-03	3.63E-03	3.63E-03
47	4.89E-5	7.76E-5	1.62E-4	1.91E-4	8.95E-04	3.53E-03	4.43E-03	4.43E-03
46	5.81E-5	8.71E-5	1.78E-4	2.29E-4	9.05E-04	3.74E-03	5.33E-03	5.33E-03
45	6.57E-5	1.00E-4	2.04E-4	2.88E-4	1.07E-03	4.31E-03	6.94E-03	6.94E-03
44	7.64E-5	1.32E-4	2.40E-4	2.95E-4	1.73E-03	5.10E-03	6.82E-03	6.82E-03
43	8.72E-5	1.45E-4	2.63E-4	3.16E-4	1.80E-03	5.48E-03	7.14E-03	7.14E-03
42	9.96E-5	1.66E-4	3.09E-4	3.89E-4	2.07E-03	6.53E-03	9.03E-03	9.03E-03
41	1.17E-4	1.91E-4	3.31E-4	4.07E-4	2.31E-03	6.68E-03	9.05E-03	9.05E-03
40	1.43E-4	2.27E-4	3.73E-4	4.36E-4	2.62E-03	7.18E-03	9.14E-03	9.14E-03
39	1.79E-4	2.63E-4	3.98E-4	4.89E-4	2.62E-03	6.83E-03	9.67E-03	9.67E-03
38	2.01E-4	3.16E-4	4.37E-4	5.62E-4	3.59E-03	7.36E-03	1.13E-02	1.13E-02
37	2.52E-4	3.72E-4	4.79E-4	6.31E-4	3.74E-03	7.08E-03	1.18E-02	1.18E-02

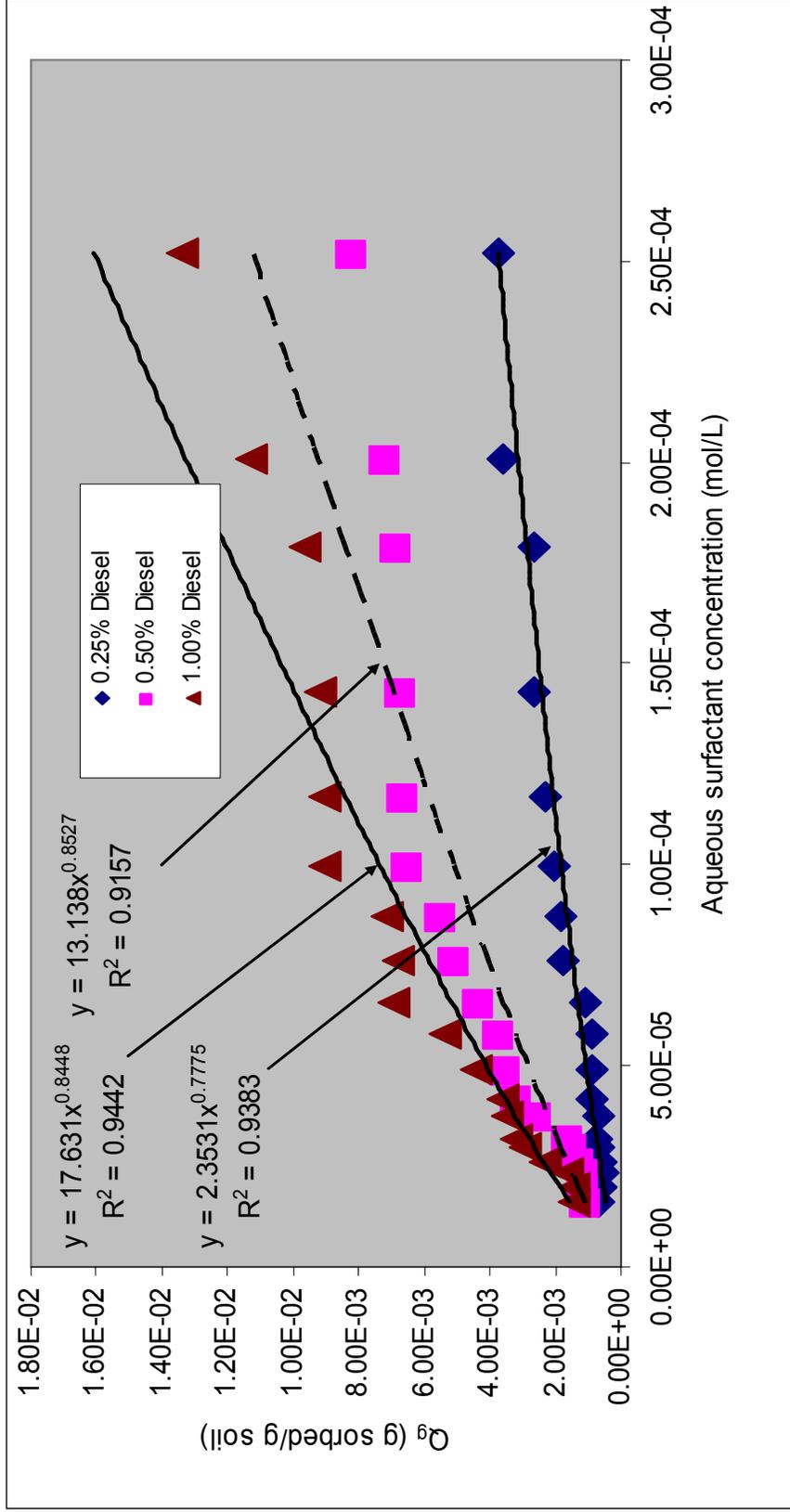


Fig.4. 12 : Linear equation for surfactant Triton X-100 sorbed on soil at Different Diesel Concentrations.

Table.4. 8 : Value of K, 1/n and n from Freundlich Isotherm at Different Diesel Concentrations.

% diesel in soil	K	1/n	n
0.25	2.3531	0.7775	1.286
0.50	13.138	0.8527	1.173
1.00	17.631	0.8448	1.183

Table 4.9 shows CMC values at different levels of diesel, 0.25%, 0.50% and 1.00% (v/v) and figure 4.13 shows the variation of CMC (log M) in relation to diesel concentration. The CMC values increase as the diesel concentration increases. Since the higher diesel concentration tends to adsorb more surfactant monomers, the amount of surfactant monomer left to form micelle is reduced. Therefore, the CMC of the higher diesel concentration in soil is reached at the higher surfactant concentration.

According to other researchers [7, 8, 43], the smallest surfactant dose that corresponds to the minimum plateau value of surface tension for the soil/aqueous system gives, after subtracting the CMC and multiplying by the ration of V_a to W_{soil} , a specific value for Q_{surf} that is equal to Q_{max} , i.e. the maximum value of sorption for surfactant on that particular soil. From Q_{max}

the effective CMC, CMC_{eff} can be estimated by surface tension technique [8] as the following:

$$CMC_{eff} = CMC + Q_{max} \left(\frac{W_{soil}}{V_{aq}} \right) \quad (\text{equ.4. 4})$$

Q_{max} is an important parameter in predicting surfactant solubilization of organic contaminant. From Figure 4.8 to 4.10 the CMC_{eff} and CMC were determined. Therefore the amount of surfactant sorbed onto soil and Q_{max} can be calculated from equation (4.3). Table 4.9 shows the amount of surfactant sorbed onto soil in mol/L and by percent lost the amount Q_{max} at each diesel concentration. The amount of surfactant sorbed on soil are 19.6%, 33.9% and 49.9% and the Q_{max} are 2.96E-3, 2.24E-3 and 1.2E-2 g/g of soil, for the diesel concentration 0.25%, 0.50% and 1.00% (v/v) respectively.

The surfactant dose required for micelle formation in soil-water system (CMC_{eff}) is shown in Table 4.9, at different concentrations of diesel. Figure 4.13 shows the plot of effective CMC (log M) versus percent diesel concentration. At higher percent diesel in soil, higher surfactant dose are required to initiate micellization. From the graph, it is observed that the effective CMC and diesel percent are related linearly. Comparison of Figure 4.8 with Figure 4.9 shows that diesel in soil affects the effective CMC at higher concentration.

Table.4. 9 : Surfactant Doses Required for Micelle Formation and Amount of Surfactant Sorbed onto Soils with Different Diesel Concentration in the Soil-Water Systems.

Diesel Concentration in Contaminated soil (%)	Surfactant Doses for Micelle Formation (CMC_{eff})		Surfactant Adsorbed onto soil		Q_{max} (g/g soil)
	log (M)	mol/L	mol/L	%	
0.00	-3.47	$3.89E-4$			
0.25	-3.32	$4.84E-4$	$9.50E-5$	19.6	$2.96E-3$
0.50	-3.23	$5.89E-4$	$2.00E-4$	33.9	$6.24E-3$
1.00	-3.11	$7.76E-4$	$3.87E-4$	49.9	$1.21E-2$

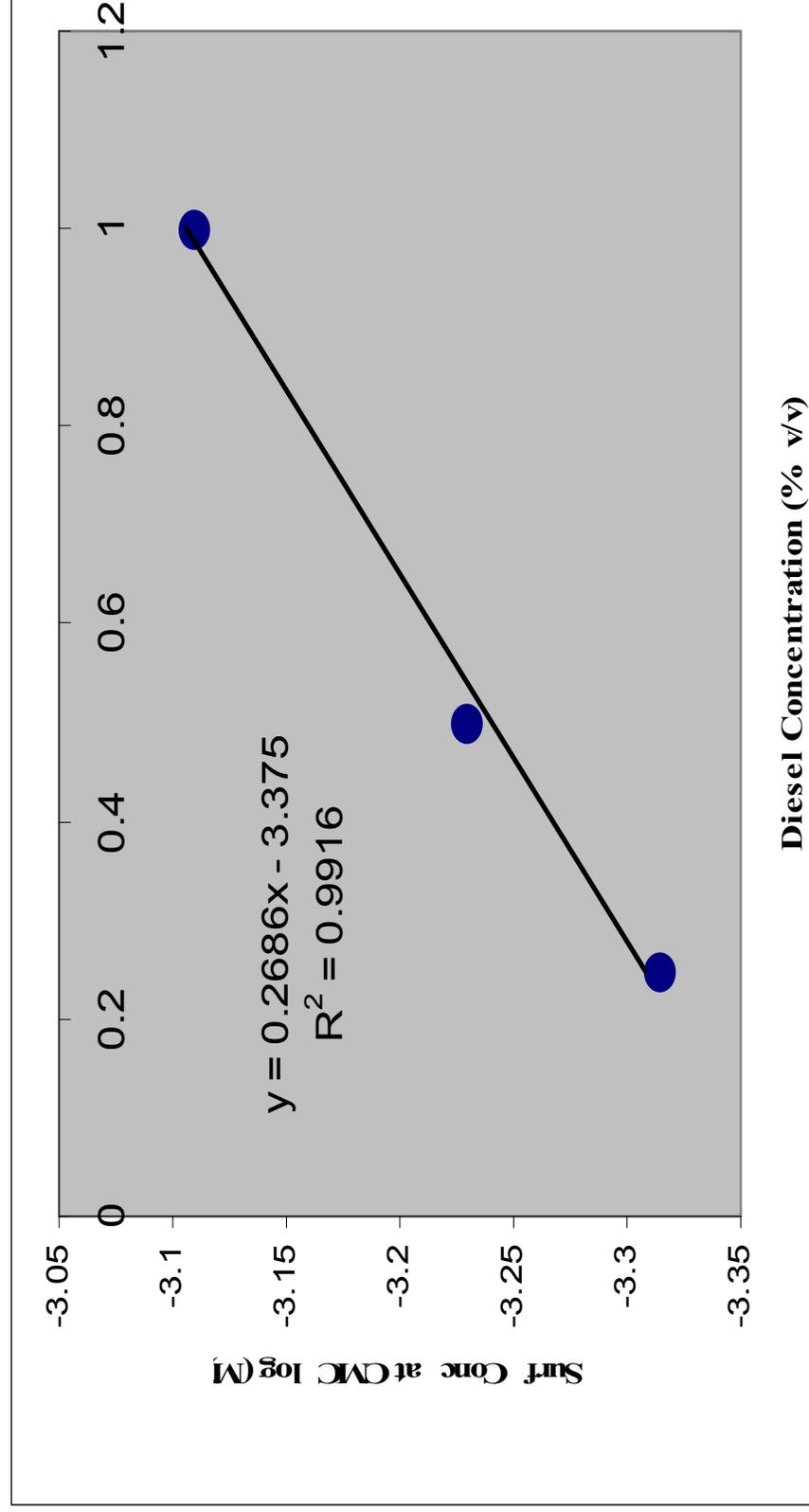


Fig.4. 13 : Effective CMC at Different Diesel Concentrations

4.7 Effect of Presence of Acid or Base on Sorption Behavior of Surfactant onto Contaminated Soil

One g of soil was mixed with 10 ml of diesel at concentration 0.50% (v/v) and 50 mL of surfactant solution at concentration 0.1% (v/v) was added with 10 mL of diluted HCl. The mixture was agitated for sorption process to equilibrate. A 30 mL sample of supernatant was tested for surface tension measurement. The surface tension was 53.3 dynes/cm. The result indicated that the sorption of surfactant onto soil was increased, so the removal of diesel from contaminated soil was decreased. The same effect appeared when 10 mL of diluted NH_4OH was added to the mixture of soil with diesel and surfactant, the surface tension reading was 54.2 which indicated that the amount of sorbed surfactant was increased and amount of removed diesel was decreased. These results probably were due to conversion of solution to more electrolytic by the effect of acid and base which in turn makes the surfactant more active in its movement which cause more amount to be sorbed onto soil. When the acid or base was added to surfactant solution without soil, there was no effect on surface tension and this approved that the result in increasing surface tension was due to adsorption not anything else.

4. 8 Effect of Temperature on Sorption Behavior of Surfactant onto Contaminated Soil

One g of soil was mixed with a 10 mL diesel sample at 0.50% (v/v), 50 mL of 0.1% surfactant solution was added. The mixture was agitated by magnetic stirrer on a hot plate for 2 hours for sorption process, keeping the temperature 50-60°C for. The experiment was repeated again with the same procedure but at temperature 70-80°C. After the mixtures were left for 36 hours for soil to settle, the surface tension reading was taken. The temperature increased the surface tension reading of the tested samples and decreased the amount of removed diesel. The surface tension was 53.8 and 51.1 dynes/cm for 50-60°C and 70-80°C respectively. These results may be attributed to the enhancement of adsorption of Triton X-100 and decreasing its solubility at high temperature which in turn weaken the micelle formation which cause less removal of diesel from mixture [50].

4. 9 Effect of Ionic Strength on Sorption Behavior of Surfactant onto Contaminated Soil

The experiment of this section was to study the effect of presence of NaCl solution with different concentrations on sorption behavior of surfactant onto contaminated soil. A 10 mL sample of 0.05, 0.1 and 0.5 NaCl was added to three mixture of contaminated soil at 0.50% (v/v) diesel and 0.1% surfactant. The result showed that as the concentration of NaCl

increased the surface tension reading increased. The surface tensions of mixtures at 0.05, 0.1 and 0.5 NaCl were 46.4, 47.8 and 49.1 dynes/cm respectively. The increase in surface tension reading probably was due to presence of NaCl not due to increase of surfactant sorption onto soil. There is a different case; NaCl increases the surface tension of water in normal cases [51]. On the other hand, some researches have shown that under the effect of ionic strength, Triton X-100 have tendency to aggregate in bulk solution which decrease the number of micelles and thus decrease the ability of removal of diesel by surfactant.

4. 10 UV-Visible Spectrophotometric Analysis of Diesel Concentration

Soil samples were contaminated with diesel by three different concentrations 0.25%, 0.50% and 1.00% (v/v). Fifty mL of surfactant solution (Triton X-100) at concentration of 0.0005, 0.001, 0.005, 0.1, 0.5, 1.0 and 2.0 % (v/v) were used to wash diesel from contaminated soil. The aqueous phase was separated from the soil to analyze the concentration of diesel solubilized from the soil by surfactant solution Triton X-100. Two mL of aqueous phase of each sample were diluted with methanol in 10 mL volumetric flask. UV-Visible Spectrophotometer was used to analyze the concentration of diesel in the aqueous phase. The results from UV-Visible Spectrophotometer were compared with standard curve prepared as

described in section 3.10 to determine the diesel concentration in each sample. Figure 4.14 shows the standard curve of diesel absorbance at 254nm.

The results of diesel solubilized by Triton X-100 are shown

in Table 4.10 and appendix C-1 shows peak height reading from UV-Visible spectrophotometer and concentration of each sample. Appendix C-2 shows a graph presents the diesel absorbance at 254nm. From the results, diesel concentration in deionized water at surfactant concentrations (0.0005, 0.001 and 0.005) were not observed to be different, lying in the range of 55.4 mg/L to 74 mg/L, 177 mg/L to 266 mg/L and 506 mg/L to 708 mg/L for 0.25%, 0.50% and 1.00% diesel respectively. In contrast, the concentration of diesel increases significantly at higher surfactant concentrations (0.1, 0.5, 1.0 and 2%) ranging from 277 mg/L to 370 mg/L, 531 mg/L to 797 mg/L and 1518 mg/L to 1605 mg/L for 0.25%, 0.50% and 1.00% diesel respectively. Figure 4.15 shows the bar chart comparing dissolved diesel versus Triton X-100 concentrations for the soils at different diesel concentrations. At lower surfactant concentration of 0.0005, 0.001, and 0.005 and in deionized water, results show that the concentration of diesel (of each 0.25%, 0.50% and 1.00%) removed from the soil slightly affected because the amount of surfactant was not sufficient to solubilize diesel from the soil and some diesel may have formed a separate phase in the mixture of samples.

At low surfactant concentrations, the amount of surfactant was not sufficient to form micelles which play an important role in the solubilization mechanism. As the number of surfactant monomers is increased in the aqueous solution, aggregates of surfactant monomers referred to as micelles form. The threshold concentration at which micelles begin to form is called critical micelle concentration (CMC). Beyond CMC, any surfactant added into the aqueous solution will not increase the number of monomers in aqueous solution, but rather will contribute to the formation of additional micelles. As a result, the more micelles there are in the water the more of the contaminant removed from soil.

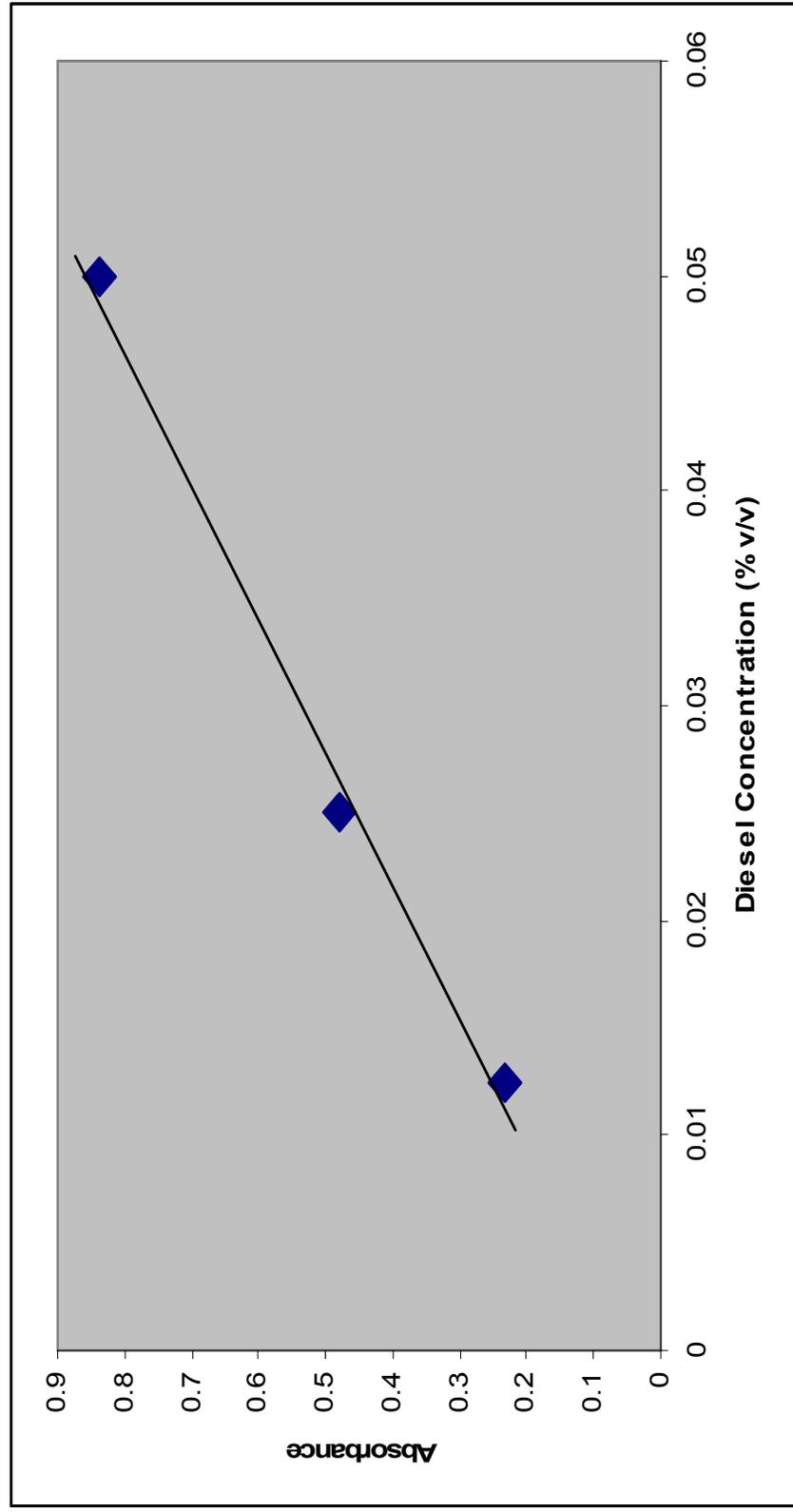


Fig.4. 14 : Standard Curve of Diesel Absorbance Obtained by UV-Visible Spectrophotometer at 254 nm.

Table.4. 10 : Dissolved Diesel in Triton X-100 solution from contaminated soil at different concentrations.

Triton X-100 Concentration		Diesel Dissolved in Triton X-100					
(% V/V)	(mol/L)	0.25% diesel		0.50% diesel		1.00% diesel	
		(mg/L)	(mol/L)	(mg/L)	(mol/L)	(mg/L)	(mol/L)
0.0000	0						
0.0005	8.55E-6	55.4	2.41E-04	177	7.70E-04	506	2.20E-03
0.0010	1.71E-5	64.2	2.79E-04	212	9.22E-04	564	2.45E-03
0.0050	8.55E-5	74	3.22E-04	266	1.16E-03	708	3.08E-03
0.1000	1.71E-3	280	1.22E-03	532	2.31E-03	1520	6.61E-03
0.5000	8.55E-3	306	1.33E-03	614	2.67E-03	1550	6.74E-03
1.0000	1.71E-2	334	1.45E-03	736	3.20E-03	1560	6.78E-03
2.0000	3.42E-2	370	1.61E-03	798	3.47E-03	1600	6.96E-03

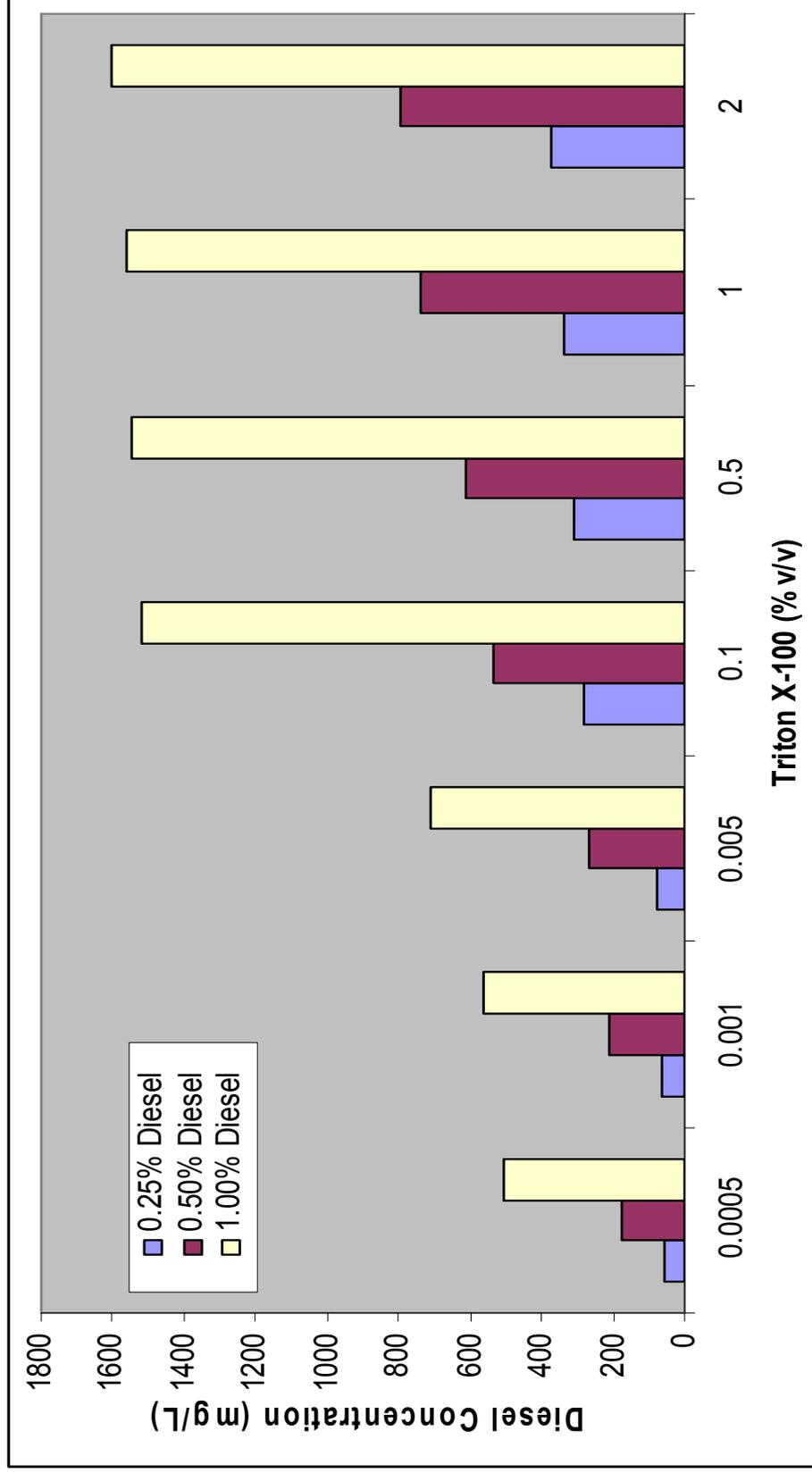


Fig.4. 15 : Diesel Concentration of Aqueous Phase from Diesel Contaminated Soil Washed by Triton X-100.

The increase in concentration of diesel in aqueous phase can be observed clearly at surfactant concentration of 0.1, 0.5, 1.0 and 2.0 % (v/v). Diesel concentrations are highest at 1.00%, lower at 0.50% and lowest at 0.25% in soil.

From the results of the previous experiment in section 4.6, the effective CMC determined from the supernatant of the mixture of Triton X-100 and diesel contaminated soil at 0.25% and 0.50% (v/v) diesel was in the range of 0.05-0.1% (v/v), while at 1.00% diesel concentration, was in upper range of 0.05-0.1% (v/v). Therefore, diesel removed from the soil would increase at the Triton X-100 concentration between 0.1% and 0.5% (v/v) by a micellar solubilization mechanism. Diesel concentrations analyzed by UV-Visible spectrophotometer confirmed the results from the experiments described in section 4.6.

Many researchers have studied the degree of solubility enhancement using particular surfactants. A measure of effectiveness of a particular surfactant in solubilizing a given contaminant is the molar solubilization ratio (MSR). It is defined as the ratio of the moles of solute solubilized to the moles of surfactant present as micelles and can be calculated as:

$$\text{MSR} = \frac{C_{\text{mic}} - C_{\text{CMC}}}{C_{\text{surf}} - C_{\text{CMC}}} \quad (\text{equ.4. 5})$$

Where C_{mic} is the total apparent solubility of TPH compounds as moles per liter in micellar solution at particular surfactant concentration greater than the CMC, C_{CMC} is the apparent solubility of a TPH compounds as moles per liter at the CMC and C_{surf} is the surfactant concentration at which C_{mic} was evaluated. The MSR can be obtained from the slope of the solubility curve above the critical micelle concentration [4, 21].

The slope of the solubility curve above the CMC is estimated from the concentration of surfactant Triton X-100 above 0.1% (v/v) or 1.71E-3 mol/L which is the range of the CMC point defined in section 4.1. Figure 4.16 shows the linear equation for diesel concentration solubilized by Triton X-100 the higher CMC concentration and the slope of the linear equations are the molar solubilization ratio (MSR). From the graph, the linear equations are as follows:

$$\text{At 0.25\% diesel} \quad Y = 0.0181X + 1.22E-3 \quad R^2 = 0.979$$

$$\text{At 0.50\% diesel} \quad Y = 0.0353X + 2.37E-3 \quad R^2 = 0.906$$

$$\text{At 1.00\% diesel} \quad Y = 0.0101X + 6.62E-3 \quad R^2 = 0.967$$

MSRs can be estimated from the slope of the graph as 0.0181, 0.0353 and 0.0101 for the soils with diesel concentration 0.25%, 0.50% and 1.00% (v/v) respectively.

The results show that at 0.25% and 0.50% diesel, as the diesel concentration in soil increased the removed diesel by surfactant solution above CMC increased but the MSR at 1.00% was the lowest one.

Therefore, the MSR value of the soil with 0.50% diesel is higher than the MSR value of soils with 1.00% and 0.25% diesel.

.ation Ratio (MSR).

An alternative approach in quantifying surfactant solubilization consists of characterizing the portioning of the diesel contaminant between micelles and monomeric solution with a mole fraction micelle-phase/aqueous-phase portion coefficient. The micelle-phase/aqueous-phase partition coefficient, K_m , is the ratio of the mole fraction of the compound in the micellar pseudo phase, X_m , to the mole fraction of the compound in the aqueous pseudo phase, X_a , [18].

$$K_m = \frac{X_m}{X_a} \quad (\text{equ.4. 6})$$

$$X_m = \frac{\text{MSR}}{1 + \text{MSR}} \quad (\text{equ.4. 7})$$

$$X_a = C_{\text{CMC}} \cdot V_{\text{a,mol}} \quad (\text{equ.4. 8})$$

Where C_{CMC} is the estimated solubility of the compound in water, $V_{\text{a, mol}}$ is the molar volume of water, 0.01805 L/mol at 25°C [4, 18].

K_m is normally presented in terms of $\log K_m$. In this study, the values of $\log K_m$ calculated from the MSR values and the diesel solubility in water (5.2 mg/L) are equal to 4.63, 4.91 and 4.37 for 0.25%, 0.50% and 1.00% diesel in soil, respectively.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The amount of surfactant Triton X-100 sorbed onto soil increased with increasing surfactant concentration. After the sorption process has been completed, the additional amount of surfactant added into soil/aqueous system was no longer sorbed by soil but formed micelles which play an important role in the solubilization of hydrophobic organic compounds. The minimum concentration of surfactant at which micelles start to form is called “critical micelle concentration” (CMC). In the soil/aqueous system, the CMC is higher than the CMC of surfactant solution without soil or it is called the elevated CMC or effective CMC (CMC_{eff}).

From the experiments performed in this study, it was observed that CMC_{eff} value increased with increasing diesel concentration in soil. In soil/aqueous systems with no contaminant present in the soil, the CMC_{eff} depends on the organic content of soil itself. The CMC of surfactant Triton X-100 in aqueous system without soil and contaminant was $3.88E-4$ mol/L and CMC_{eff} values of soil/aqueous systems in the presence of diesel with concentration 0.25%, 0.50% and 1.00% (v/v) were $4.84E-4$ mol/L, $5.89E-4$ mol/L and $7.76E-4$ mol/L respectively.

In this investigation, the amount of surfactant sorbed onto soil at the surfactant concentration below the CMC was calculated and the relationship

between diesel concentrations and the amount of surfactant sorbed on the soil was developed. In the soil/aqueous system, the Freundlich isotherm and linear equation could be applied to all three types of the soil with 0.25%, 0.50% and 1.00% (v/v) diesel.

In this research, factors that may affect sorption of surfactant onto soil; such as pH, elevated temperature, and ionic strength have also been studied and experiment has shown that, all these factors have increased the sorption of surfactant onto soil. This in turn affect the micelle formation which play the important role in desorption of diesel.

Not only the CMC_{eff} value for each soil type is important but the amount of surfactant sorbed on each soil type is also crucial for utilizing surfactant to enhance soil remediation. The amount of surfactant sorbed on soil as the percent surfactant lost due to sorption on soil, the amount of surfactant in gram sorbed per gram of soil at any surfactant concentration, and also maximum amount of surfactant sorbed per gram of soil, Q_{max} , can be calculated. The amount of surfactant Triton X-100 sorbed onto soil with no contaminant present ranged from 9% to 15%. However, the amount of surfactant sorbed on the soils contaminated with Diesel ranged from 19.6% to 49.9%. These results indicate that the presence of organic contaminant may result in greater surfactant sorption onto soil, thereby further increasing

chemical costs in possible surfactant-enhanced subsurface remediation applications.

At surfactant concentrations higher than CMC, micelles are formed resulting in the micellar solubilization of organic contaminants from soil. The ratio of moles of organic contaminant solubilized to the moles of surfactant present as micelles is called the molar solubilization (MSR). Diesel solubility was seen to increase linearly with increasing surfactant concentration above CMC. The slope of the plots of contaminant solubilized and surfactant doses above the CMC were used to determine the molar solubilization ratio (MSR). The MSR value for diesel was 0.093 for the soil-water systems studied. The diesel concentration affects its MSR.

An alternative approach to quantify surfactant solubilization is the use of the micelle partition coefficient; K_m . Log K_m values calculated for diesel contaminated soils were about 4.63. The ratio of $\log K_m / \log K_{ow}$ was approximately 1.41.

The experiments in this study were batch mode to determine the amount of surfactant sorption on soil and the amount of contaminant solubilized by surfactant Triton X-100. Further studies using column tests and on a pilot scale needed before the full scale remediation process can be applied. Since the sorption of surfactant onto soil represents a loss of surfactant and the cost of surfactant is very significant in subsurface remediation, it is important to

minimize the amount of surfactant sorption onto soil. The targeted contaminated zone should be evaluated in detail before the application of surfactant-enhancements. Due to the cost of surfactant, surfactant recycling is also an important issue for further study. A study of optimum temperature and optimum pH for surfactant task in remediation is recommended. A study of surfactant toxicity and biodegradability is also recommended prior to full-scale application.

Overall, the results of this study suggest that the addition of aqueous surfactant solutions to contaminated soils may facilitate the removal of organic contaminants from soil. However, surfactant losses due to sorption onto soil appear significant and may increase due to presence of organic contaminants.

APPENDICES

Appendix A-1

Important Properties of Triton X- 100

Molecular formula	$C_{14}H_{22}O(C_2H_4O)_n$ (n=9-10)
Appearance	viscous colorless liquid
Density	1.07 g/cm ³
Melting Point	6°C
Boiling point	>200°C
Solubility in water	Soluble
Vapor Pressure	<1 mmHg at 20°C
Flash Point	251 °C

Appendix A-2

Important Properties of Diesel

Molecular formula	C_9-C_{23} including paraffins, naphthalenes, and aromatic compounds with average mass of 230gm/mol
Appearance	brownish yellow liquid
Density	0.85 gm/cm ³
Melting Point	-30 to -18
Boiling point	340°C (as an average)
Solubility in water	520 ppm
Vapor	0.40 mm Hg
Flash Point	53°C
log K _{ow}	3.3

* Flash point: The lowest temperature at which a flame will propagate through the vapor of a combustible material to the liquid surface

Appendix B-1

Surface Tension Reading, Average Surface Tension, Standard Deviation, and Coefficient of Variance at Different Mixing

Time

Mixing time	1 st reading	2 nd reading	3 rd reading	4 th reading	Average Surface Tension	Standard Deviation	Coefficient of Variance
1	44.3	44.4	44.7	44.6	44.5	0.18	0.41
2	44.1	44.4	44.1	44.2	44.2	0.14	0.32
4	45.1	44.8	44.9	44.8	44.9	0.14	0.31
6	44.4	44.9	44.9	45.0	44.8	0.27	0.60
12	45.3	44.9	45.1	43.9	44.8	0.62	1.39
24	44.7	44.3	44.1	44.5	44.4	0.26	0.58
48	44.9	44.3	44.8	44.8	44.7	0.14	0.41

Appendix B-2

Surface Tension of Triton X-100 at Different Concentration of Diesel

Diesel concentrati	surfactant concentratio	1 st	2 nd	3 rd	4 th	average	standard deviation	coefficient of variance
0% Diesel	0.000	64.1	62.7	63.8	62.2	63.2	0.90	1.42
	0.001	55.2	52.7	54.6	53.1	53.9	1.19	2.21
	0.005	42.8	44.9	44.7	44.8	44.3	1.00	2.26
	0.100	35.8	36.3	36.6	35.7	36.1	0.42	1.18
	0.500	35.2	35.3	35.9	34.4	35.2	0.62	1.75
	1.000	34.7	34.1	35.1	33.3	34.3	0.78	2.28
	2.000	35.6	36.1	36.4	35.5	35.9	0.42	1.18
0.25% Diesel	0.000	63.9	64.8	65.7	62.4	64.2	1.41	2.19
	0.001	63.2	60.5	63.7	61.8	62.3	1.44	2.32
	0.005	44.7	46.1	47.3	45.5	45.9	1.10	2.39
	0.100	38.2	35.2	38.6	36.4	37.1	1.59	4.28
	0.500	35.8	36.3	35.6	36.7	36.1	0.50	1.38
	1.000	35.1	34.8	33.6	33.3	34.2	0.88	2.58
	2.000	36.2	36.3	35.3	35.0	35.7	0.65	1.82
0.50% Diesel	0.000	66.1	64.8	67.2	65.1	65.8	1.09	1.65
	0.001	66.0	63.7	62.6	64.5	64.2	1.43	2.23
	0.005	61.9	60.2	65.4	61.7	62.3	2.20	3.53
	0.100	45.3	46.2	45.6	46.5	45.9	0.55	1.19
	0.500	36.8	38.1	37.4	36.1	37.1	0.85	2.30
	1.000	35.9	36.4	36.1	36.0	36.1	0.22	0.60
	2.000	34.7	34.1	34.0	34.0	34.2	0.34	0.98
1.00% Diesel	0.000	68.2	67.8	66.9	66.7	67.4	0.72	1.06
	0.001	65.1	64.3	63.8	63.6	64.2	0.67	1.04
	0.005	56.7	56.3	58.3	57.5	57.2	0.89	1.55
	0.100	37.9	38.1	38.1	38.3	38.1	0.16	0.43
	0.500	39.1	39.0	39.5	39.2	39.2	0.22	0.55
	1.000	37.7	38.1	38.0	37.4	37.8	0.32	0.84
	2.000	37.9	36.9	37.6	36.8	37.3	0.54	1.44

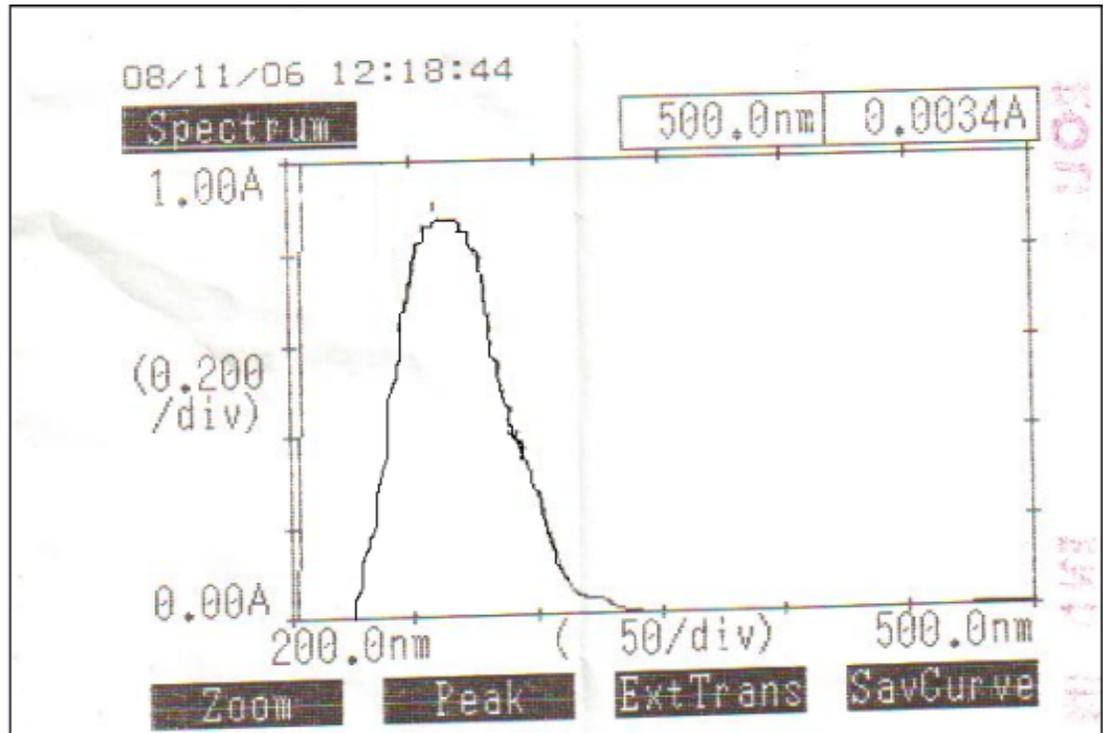
Appendix C-1

Diesel Absorbance in UV-Visible Spectrophotometer at 254 nm (for diluted solution)

Surfactant Concentration	0.25% Diesel	0.50% Diesel	1.00% Diesel
0.0005	~ 0.0000	0.0400	0.1200
0.0010	0.0240	0.0680	0.1480
0.0050	0.0320	0.1200	0.2080
0.1000	0.1600	0.2400	0.5600
0.5000	0.1920	0.2800	0.6000
1.0000	0.2000	0.2960	0.6400
2.0000	0.2400	0.3600	0.6800

Appendix C-2

A graph presents the absorbance of diesel at 254 nm



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جامعة النجاح الوطنية
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خصائص ادمصاص المادة نشطة السطح الغير الايونية TRITON X-100 في
التربة الملوثة بالديزل

اشراف
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اعداد
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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء من كلية
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2009

ب

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المخلص

تستخدم المواد نشطة الأسطح بطبيعة ألفتها المزدوجة نحو كل من المواد القطبية و غير القطبية، في

تحسين انتقال الملوثات غير القابلة للذوبان بالماء إلى المحاليل المائية. و ذلك من خلال خفض التوتر

السطحي بين هذه الملوثات و بين الماء عن طريق تكوين فقاعات غروية تحيط بهذه الملوثات و تعمل

على إذابتها. و عادة ما تصنف طبيعة الرغوة المكونة حسب شكلها و حجمها و المعتمدين عادة على

المحيط المائي لهما؛ كدرجة الحموضة و الحرارة و طبيعة المواد الكيماوية المذابة معها في الماء. و لكن

قد يؤدي إمصاص المواد نشطة الأسطح على المواد الصلبة كالتربة إلى خفض تركيزها بالماء إلى ما

دون التركيز المراد في تكوين الرغوة (CMC) مما يعيق تكون الرغوة الفعالة في عملية إذابة

الملوثات. لذا لا بد أن تؤخذ عملية الإمصاص هذه بعين الاعتبار عند دراسة التركيز اللازم من المواد

نشطة الأسطح لغرض إذابة الملوثات. و قد تم في هذا البحث دراسة تأثير الديزل كملوث عضوي على

السلوك الامصاصي ل (Triton X-100) و هي مادة نشطة السطح غير أيونية. و قد استخدم جهاز

قياس التوتر السطحي لدراسة هذا الامصاص. كما استخدمت المادة نشطة السطح غير الأيونية لدراسة

ج

تحسين تنقية التربة الملوثة بالديزل و ذلك عن طريق إذابته بالمحلول المائي. و قد استخدم جهاز

الامتصاص الطيفي للأشعة فوق البنفسجية و الضوء المرئي (UV-Vis Spectrophotometer) في

هذه الدراسة. و قد بينت النتائج أنه في حال وجود المادة نشطة السطح ما دون التركيز المكون للرغوة

(CMC)، فإن كمية المادة النشطة المدمصة على التربة تزداد بزيادة تركيزها في الماء و الديزل

المنزوع من التربة قليل مقارنة بتركيزه المضاف للتربة، بينما عندما ارتفع تركيز المادة النشطة إلى

التركيز المكون للرغوة فأعلى بدأ تأثيرها في نزع الديزل. تأثير عوامل أخرى كالحرارة و درجة

الحموضة و وجود مادة أيونية أيضاً تُرست من أجل معرفة إن كانت هذه العوامل تساعد في إزالة

الديزل أم تعيق و قد تبين أنها جميعها أعاققت عملية الإنتراع و لكن لكل سبب مختلف.