

ผลของเฟอโรซีนต่อการละลายไฮโดรคาร์บอนไฮโดรเจนในระบบไมโครอิมัลชัน



นางสาวศรณีย์ สิงห์ทอง

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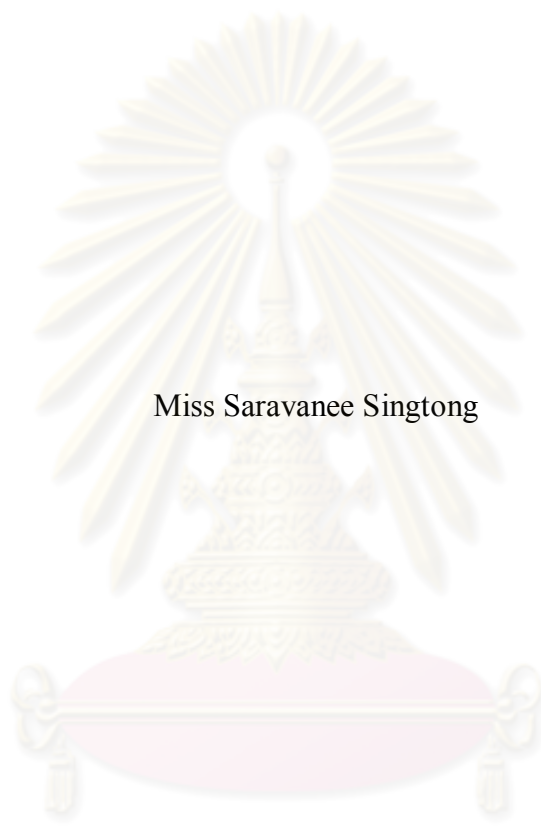
วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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EFFECT OF FERROCENE ON SOLUBILIZATION OF ALKANES IN  
MICROEMULSION SYSTEM



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ศรวณีย์ สิงห์ทอง: ผลของเฟอโรซีนต่อการละลายไฮโดรคาร์บอนไฮโดรเจนในระบบไมโครอิมัลชัน (EFFECT OF FERROCENE ON SOLUBILIZATION OF ALKANES IN MICROEMULSION SYSTEM) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: อาจารย์ ดร. จันทรา ทองคำเถา ที่ปรึกษาวิทยานิพนธ์ร่วม: ศาสตราจารย์ ดร. เดวิด เอ. สะบาตินี 80 หน้า.

เฟอโรซีนคือสารเติมแต่งเพื่อเพิ่มค่าออกเทนในน้ำมันแก๊สโซลีน ถึงแม้ว่าการปนเปื้อนของเฟอโรซีนในสิ่งแวดล้อมจะยังไม่เป็นที่ได้รับความสนใจก็ตาม แต่พบว่าสารนี้มักจะปนเปื้อนรวมอยู่กับน้ำมันแก๊สโซลีนในดิน เนื่องจากเฟอโรซีนคือสารโลหะอินทรีย์ ซึ่งอาจมีผลต่อพฤติกรรมของสารไฮโดรคาร์บอนไฮโดรเจนต่างๆ ที่การปนเปื้อนในสิ่งแวดล้อม และอาจเป็นข้อจำกัดต่อประสิทธิภาพการบำบัดสารไฮโดรคาร์บอนด้วยสารลดแรงตึงผิว ดังนั้นวัตถุประสงค์ของการศึกษาค้นคว้าครั้งนี้คือเพื่อประเมินผลกระทบของเฟอโรซีนต่อพฤติกรรมของไฮโดรคาร์บอนไฮโดรเจน และปริมาณความจุจำเพาะการไฮโดรคาร์บอนไฮโดรเจน ในขั้นตอนแรกได้มีการทดสอบเพื่อหาค่าจำนวนเทียบเท่าคาร์บอนสายตรงของเฟอโรซีนและพบว่ามีค่าเท่ากับ 8.386 หลังจากนั้นได้ทำการศึกษาพฤติกรรมของไฮโดรคาร์บอนไฮโดรเจนซึ่งเป็นตัวแทนของน้ำมันแก๊สโซลีน นอกจากนี้ได้ทำการศึกษาผลของเฟอโรซีนในไฮโดรคาร์บอนไฮโดรเจนชนิดต่างๆ ต่อความจุจำเพาะการไฮโดรคาร์บอนไฮโดรเจนและคอลัมน์ โดยระบบสารลดแรงตึงผิวที่เหมาะสมได้มาจากการศึกษาส่วนแรกคือ 2AMA: 2AOT ที่ 4 เปอร์เซ็นต์ (กรัมต่อกรัม) ซึ่งประสิทธิภาพการกำจัดไฮโดรคาร์บอนไฮโดรเจนชนิดต่างๆ และเฟอโรซีนในคอลัมน์อยู่ในช่วง 74 - 95 เปอร์เซ็นต์ พารามิเตอร์ในการศึกษาค้นคว้าครั้งนี้ ได้แก่ ชนิดของไฮโดรคาร์บอนไฮโดรเจน ความเข้มข้นของเฟอโรซีน และสารอิเล็กโทไลต์

สาขาวิชา การจัดการสิ่งแวดล้อม  
ปีการศึกษา 2552

ลายมือชื่อนิสิต.....ศรวณีย์ สิงห์ทอง.....  
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KEYWORDS : FERROCENE/ EQUIVALENT ALKYL CARBON NUMBER (EACN)/ SOLUBILIZATION/ SURFACTANT/ MICROEMULSION

SARAVANEE SINGTONG: EFFECT OF FERROCENE ON SOLUBILIZATION OF ALKANES IN MICROEMULSION SYSTEM. THESIS ADVISOR : CHANTRA TONGCUMPOU, Ph.D., THESIS CO-ADVISOR : PROF. DAVID A. SABATINI, Ph.D., 80pp.,

Ferrocene is a metallic additive that has been used to boost the octane number of gasoline. Even though ferrocene is not an environmental contaminant of high concern, it can be found in soil contaminated with gasoline. Due to its organometallic properties, ferrocene may affect the phase behavior of other alkanes, contaminating the environment and limit their removal using surfactant-enhanced aquifer remediation (SEAR). Therefore, the aim of this work is to investigate the effects of ferrocene on the solubilization behavior and capacity of alkanes in micellar surfactant solutions. The equivalent alkane carbon number (EACN) of ferrocene was first determined and found to be 8.386. Subsequently, the phase behaviors of alkanes (as representative of gasoline) in a microemulsion system were investigated. The solubilization capacity and column study of alkanes with and without ferrocene were performed in 2AMA: 2AOT at 4 %wt as suitable surfactant system selected from the phase study. The efficiency removals of alkanes and total Fe (ferrocene) in column study were obtained in range of 74-95%. In this study, different parameters were studied, namely the concentrations of ferrocene, electrolytes, and the types of alkanes.

Field of Study : Environmental Management

Student's Signature ศารทนต์ สิงทนต์

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# CHAPTER I

## INTRODUCTION

As a result of industrial accidents (spills, leaks, and leaking underground storage tanks) hydrophobic organic contaminants (HOCs) frequently enter the subsurface. These chemicals represent a long-term source for soil and aquifer contamination (Lee et al., 2001). Over one million underground storage tanks were identified to leak. In soil, a concentration of gasoline, diesel, and lubricating oil between 100 and 200 mg/L were introduced into the soil by leaking storage tanks (Rauckyte et al., 2005).

Nowadays, there has been an increasing interest in the use of ferrocene in gasoline and diesel. Two different additives, namely methylcyclopentadienyl manganese (MMT) and ferrocene have been proposed, although it appears that neither is as effective as lead in raising the Research Octane Number (RON); thus, metallic additives might also require refinery upgrading. The depth of analysis and availability of public data however is much less than that for methylcyclopentadienyl manganese (MMT). Octel, the manufacturer of ferrocene, has not reported octane-boosting data for ferrocene or recommended treatment rates (Graboski, 2003). Moreover, potential health effects of ferrocene have not been thoroughly investigated including toxicological information (MSDS No.C7046).

The contaminated site can be remediated by flushing the soil with water in a conventional pump-and-treat system (Palmer, 1992). Due to the limitations of pump-and-treat systems, research has focused on developing new techniques for expediting subsurface remediation, namely surfactant enhanced pump-and-treat remediation (Nivas et al., 1995). Therefore, the surfactant enhanced aquifer remediation (SEAR) using microemulsion technique has been applied over the past decade (Ouyang et al., 1996; Shiau et al., 1996; Dwarakanath et al., 1999; Harwell et al., 1999; Ouyang et al., 2000; Sabatini et al., 2000; Uchiyama et al., 2000; Wu et al., 2000; Wu et al., 2001; Acosta et al., 2003; Childs et al., 2004; Szekeres et al., 2005; Szekeres et al., 2006).

Even though the toxicity of ferrocene does not affect the human health and the environment, it might have an effect to remediate site by surfactant enhanced aquifer remediation (SEAR). Due to the fact that, criteria of the internal property of substance which is the equivalent alkane carbon number (EACN) as the equivalent alkyl carbon number changes, the behavior or solubilization of substance in micellar by microemulsion technique is different. The EACN is the amount of carbon atoms of the alkanes present in crude oil (Wade et al., 1977). Crude oil (gasoline) is a multicomponent hydrocarbon mixture and an EACN value is assigned to every hydrocarbon. Therefore, the EACN of the hydrocarbons can help to clarify the role of the molecular weight and the structure of the surfactants in forming a microemulsion system with oil.

In this study, ferrocene was mixed with alkanes at a similar ratio as found in gasoline (50, 100 mg/L) to compare the effects of ferrocene on solubilization and mobilization by using microemulsion technique.

### **1.1 Objectives of the study**

The three main objectives of this study were

1. To investigate whether surfactant systems are able to form microemulsions with alkanes and with and without ferrocene addition.
2. To evaluate the effects of ferrocene on the solubilization of alkanes in microemulsion systems.
3. To study the removal efficiency of alkanes in the presence of ferrocene using the microemulsion technique in column studies.

### **1.2 Hypotheses**

Addition of ferrocene in alkanes affect the Equivalent Alkane Carbon Number (EACN) and hence the phase behavior, solubilization, and treatment efficiency of microemulsion systems.



### 1.3 Scope of the study

The overall work can be categorized into four parts as presented in the following sections.

#### 1.3.1 Alkanes

Alkanes are the major components of gasoline, which can contain 500 different hydrocarbons consisting of 3 to 12 carbons. Ferrocene is mostly added to gasoline in order to increase the octane number; therefore, a mixture of decane, isooctane, and also of hexane is used, as they are the main components in gasoline, in order to investigate the solubilization behavior of a microemulsion system with and without ferrocene addition. Additionally, the ferrocene concentration was varied from 50 to 100 ppm and also the sodium chloride (NaCl) concentration to study the Winsor type of the microemulsion. In order to simulate the composition of gasoline the alkanes hexane, octane, and decane were used at varying concentrations.

#### 1.3.2 Phase behavior study

A phase behavior study of the microemulsion was performed to determine the EACN of ferrocene and to understand the phase behavior of surfactants and alkanes with and without ferrocene addition.

A suitable surfactant system for determining the EACN of ferrocene was selected considering the hydrophile-lipophile balance (HLB). The viscosity of the surfactant solution was acceptable and no precipitation was observed. In this part, the Winsor type of the microemulsion was Winsor type III (middle phase microemulsion). The EACN of ferrocene was studied using different solubilization parameters and the Salager's equation by using benzene, EACN=0; toluene, EACN=1; and xylene, EACN=2.

In order to understand the phase behavior of surfactants and alkanes with and without ferrocene addition, every Winsor type of the microemulsion was studied. The microemulsion should follow Winsor type I ( $O/W_m$  microemulsion or oil in water) and Winsor type III (middle phase microemulsion) in order to identify the supersolubilization region, which is closely located to the phase boundary between

type I and type III. Another possible phase is Winsor type II, which is a  $W_m/O$  or water in oil microemulsion. According to the HLB and EACN of the alkanes a suitable surfactant system for the studied substances with and without ferrocene addition was determined. The surfactant systems able to form microemulsions were used to determine the supersolubilization and optimum salinity ( $S^*$ ). For both studies (Investigation EACN of ferrocene and phase behavior study) only anionic surfactant (Dowfax 8390, AMA, and AOT) were used.

### **1.3.3. Solubilization study**

A solubilization study was conducted using a solubilized bath experiment. The conditions of the experiment were similar to the phase behavior study. The solubilization study was done under Winsor type I, supersolubilization, and Winsor type III microemulsion conditions.

### **1.3.4. Column study**

The surfactant systems obtained from the solubilization and phase behavior study were applied to flush a column containing alkanes with and without ferrocene at similar electrolyte concentration. A column experiment was performed using Ottawa sand as soil to evaluate the removal of organometallic oil in a contaminated aquifer. The aqueous surfactant solution was flushed through the column, and the effluent was collected and analyzed. The percentage of alkanes and ferrocene removal, efficiency removal, and mass balance was investigated. In this part only isooctane and decane were used as hexane is a volatile substance.

## CHAPTER II

# THEORETICAL BACKGROUND AND LITERATURE REVIEWS

### 2.1. Ferrocene

Nowadays, unleaded gasoline is becoming popular fuel in industrial and sold in general vehicle using. Lead is toxic substance, however it can have been composed of organometallic additive such as tetraethyl lead (TEL). It was used extensively to prevent knocking in fuel engine (gasoline) and increase the fuel's octane number. The other additives have been invented to increase octane number but not many additives can raise octane number as such high level as TEL.

Ferrocene is another metallic additive in gasoline and diesel that can have been used to boost octane. It is a coordination compound of iron and two molecules of cyclopentadiene as shown in Figure 2.1. The main utility of ferrocene is as a diesel additive for improving combustion and suppressing smoke (Environmental Australia department environmental and heritage, 2000). None of the studies identified differences in the toxicity of the exhausts derived from fuels with ferrocene addition of 30 ppm and without ferrocene. From an environmental perspective, iron oxide emissions are expected to be in the range of a normal engine wear, and ferrocene used at the recommended levels may not add significantly to the total levels of iron emitted (Graboski, 2003). Some properties of ferrocene are shown in Table 3.1.

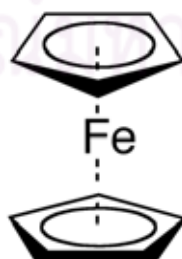


Figure 2.1 Structure ferrocene (<http://en.wikipedia.org/wiki/Ferrocene>, 2007).

## 2.2. Gasoline

Gasoline is made from crude oil. The crude oil pumped out of the ground is a black liquid called petroleum. This liquid contains hydrocarbons, and the carbon atoms in crude oil link together in chains of different lengths. The smaller molecule hydrocarbons that are usually a liquid at ambient temperatures are pentane, hexane, heptanes, octane, decane, and dodecane. When these six liquid hydrocarbons are put into a mixture together, the mixture is called gasoline. Some of the lighter liquids are chemically reformed to make them more suitable as a car fuel (from <http://science.howstuffworks.com/gasoline1.htm>, 2010).

## 2.3. Equivalent alkane carbon number (EACN)

The alkanes carbon number (ACN) is defined as oil hydrophobicity of linear *n*-alkanes with correspondence to its carbon number (i.e., ACN of hexane = 6). The mixture of different alkanes numbers (ACN) can be found to follow simple mole fraction averaging rules for microemulsion stability. For the non-alkanes such as benzene, a new

Term was introduced, namely the equivalent alkane carbon number or “EACN”, which is applicable for studies using surfactants. The oil EACN concept was initiated by Wade et al. (1977), where the EACN of the non-alkane was determined by comparing the optimum microemulsion formulation at the same physicochemical environment to those of *n*-alkanes. Equation for averaging EACN can have been expanded to any number of components and a general relationship base on mole fraction as equation 1:

$$EACN_{mix} = \sum_i X_i ACN_i \quad (1)$$

## 2.4. Salager's equation

Microemulsion formulation is largely a trial-and-error process. Empirical models can help to expedite this trial-and-error process. For systems containing hydrocarbons, anionic surfactants, alcohols, and salinity the following relationship named Salager equation (Equation 2) has been proven to be valid (Salager et al., 1979):

$$\ln S^* = K(EACN) + f(A) - \sigma + a_T(T - 25) \quad (2)$$

Where  $S^*$  is the optimum salinity of the microemulsion system, EACN is an equivalent alkane carbon number of oil,  $f(A)$  is a function of alcohol type and concentration,  $\sigma$  is the parameter indicating the characteristic of surfactant,  $a_T$  is a coefficient accounted for temperature effect. This equation can have been modified into a reduced form as shown in equation 3 if the system is applied at the same temperature using the same the surfactant type and concentration without alcohol addition.

$$\ln S^* = K(EACN) + c \quad (3)$$

## 2.5. Surfactants

Surfactants are surface active molecules that accumulate at interfaces. They are a substance consisting of a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail in its molecule structure. They are used into various products such as a motor oils, pharmaceuticals, detergents, and including to be an application in high-technology as electronic printing, magnetic recording. They able to act to reduce interfacial free energy. When placed into a water-oil or water-air systems, surfactants accumulate at the interface with their water-like moiety in the directed to the polar water phase and the oil-like moiety directed to the non-polar oil or less polar air phase (Rosen, 1989). Due to its amphiphilic structure, a surfactant can greatly reduce interfacial tension between water and oil, even though if present at very low concentration only (Harwell et al., 1999). Surfactants are classified according to the nature of the hydrophilic portion of the molecule as following:

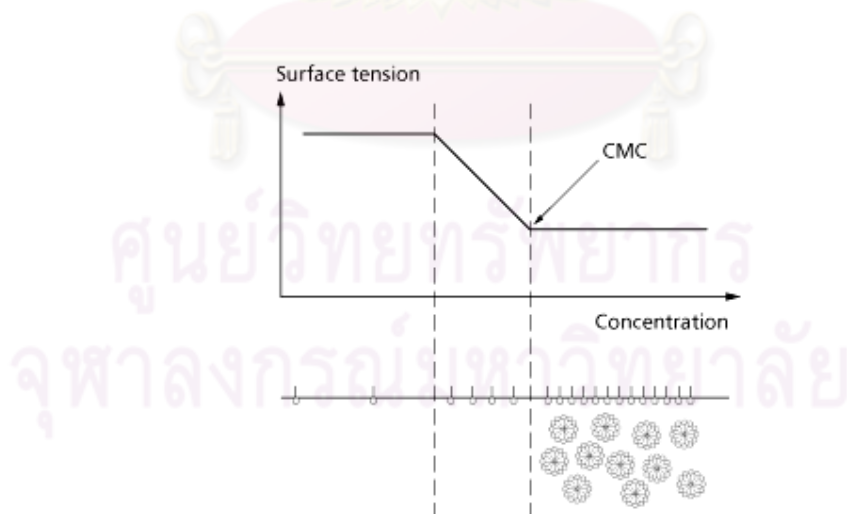
1. Anionic surfactant is surface-active portion of the molecule bears a negative charge such as  $\text{RCOO}^-\text{Na}^+$  (soap),  $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$  (alkylbenzene sulfonate).
2. Cationic surfactant is surface-active portion bears a positive charge such as  $\text{RNH}_3^+\text{Cl}^-$  (salt of a long-chain amine),  $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$  (long-chain amino acid).

3. Zwitterionic surfactant is both positive and negative charges may be present in the surface-active portion such as  $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid),  $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  (sulfobetaine).

4. Nonionic surfactant is surface-active portion bears no apparent ionic charge such as  $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$  (monoglyceride of long-chain fatty acid),  $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$  (polyoxyethylenated alkylphenol) (Rosen, 1989).

## 2.6. Micelles

At concentrations above the critical micelle concentration (CMC), surfactants form colloidal aggregates called micelles; this point is designated at the transition of region 2 to region 3 presented in figure 2.2 (Rosen, 2004). It is generally accepted that this rapid change in the property/concentration curve is due to the formation of aggregates of amphiphiles or micelles in solution. The particular arrangement of the amphiphilic compounds in a micelle is to be visualized as being such that the hydrophiles are in contact with water, whereas the lipophiles are collected together within the interiors of micelles to create small regions from which water is essentially excluded (Bourrel, 1988).



**Figure 2.2 Critical micelle concentration (CMC) (Yeh et al., 2002).**

Mixed micelle formation in mixtures of two surfactants is used to improve some properties of the system. CMC of surfactants mixture ( $C_{12}^M$ ) always change to be intermediate in value between those of the two components ( $C_1^M$ ,  $C_2^M$ ). If they interact



together,  $C_{12}^M$  is less than either  $C_1^M$  or  $C_2^M$  which is called synergism in mixed micelle formation. In case,  $C_{12}^M$  is larger than either  $C_1^M$  or  $C_2^M$  is called antagonism (negative synergism) in mixed micelle formation. The CMC of the mixture is given as equation 4:

$$\frac{1}{C_{12}^M} = \frac{\alpha}{f_1 C_1^M} + \frac{1-\alpha}{f_2 C_2^M} \quad (4)$$

Where  $\alpha$  is the mole fraction of surfactant 1 in the solution phase on a surfactant only basis (i.e., the mole fraction of surfactant 2 in the mixture is  $1-\alpha$ ) and  $f_1, f_2$  are the activity coefficients of surfactants 1 and 2, respectively, in the mixed micelle. When the mixture surfactants are not interaction together ( $f_1 = f_2 = 1$ ), equation become:

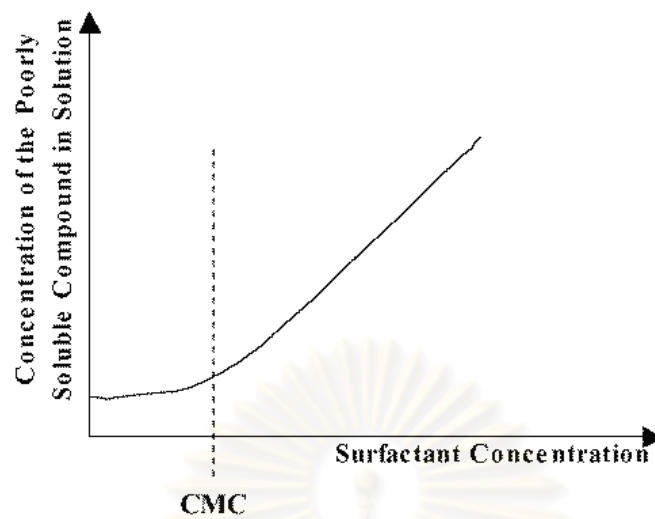
$$\frac{1}{C_{12}^M} = \frac{\alpha}{C_1^M} + \frac{1-\alpha}{C_2^M} \quad (5)$$

The CMC value of any mixture can then be calculated at any value of  $\alpha$  directly from the CMC values of the individual surfactants as equation 5:

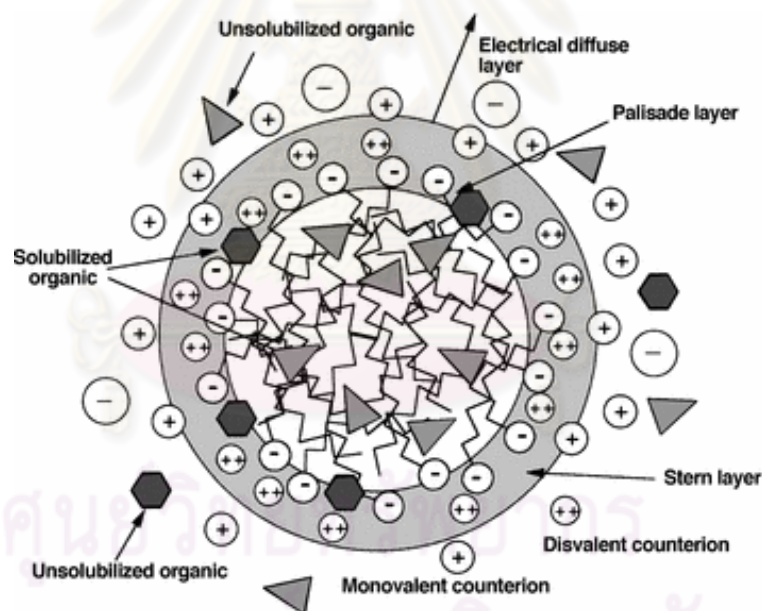
$$C_{12}^M = \frac{C_1^M C_2^M}{C_1^M (1-\alpha) + C_2^M \alpha} \quad (6)$$

## 2.7. Solubilization

Solubilization may have been defined as the spontaneous dissolving of a substance (solid, liquid, gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. The solubility of a normally solvent-insoluble material is plotted against the concentration of the surfactant solution that is solubilizing it. The solubility increases approximately linearly with the concentration of the surfactant. The critical concentration is the CMC of the surfactant as shown in figure 2.2 (Rosen, 2004). Solubilization occurs in such a way that contaminant droplets tend to be encased in surfactant micelles as shown in figure 2.4 (Ouyang et al., 1996).



**Figure 2.3** Plot of amount of material solubilized as a function of concentration of the surfactant in the bulk phase (Rangel-Yagui, 2005)



**Figure 2.4** Schematic of oil solubilized in anionic surfactant micelle (Lemordant, 2006)

Factors determining the extent of solubilization are the factors of the solubilization capacity or solubilizing power of the micelle. The extent that substance can have been solubilized into a particular micelle depends upon the portion of the micelle that is the locus of the solubilization. The volume of that portion depends upon the shape

of the micelle. Therefore, the amount solubilized in any location will also increase with increase in the volume of the micelle, and factors to determine it as follow:

### **2.7.1. Structure of the surfactant**

The solubilization capacity for hydrocarbons in the interior of the micelle in aqueous media can have been increased by increasing dissimilar between solvent and surfactant which is an increased in the chain length of the hydrophobic portion of the surfactant.

### **2.7.2. Structure of the solubilize**

Normally crystalline solids show less solubility in micelles than do liquids of similar structure. The extent of solubilization for aliphatic and alkylaryl hydrocarbons appeared to decrease with increased in the chain length and to increase with unsaturation or cyclization if only one ring was formed. The extent of solubilization for condensed aromatic hydrocarbons appeared to decrease with increase in the molecular size. Branched-chain compounds appeared to have approximately the same solubility as their normal chain isomers. Short-chain alkylaryl hydrocarbons may have been solubilized both at the micelle-water interface and in the core, with the proportion in the core increasing with increase in the concentration of the solubilize.

### **2.7.3. Effect of electrolyte**

The effect of neutral electrolyte addition on the ionic surfactant solution is to decrease the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing the CMC and increasing the aggregation number and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of the micelle. However, this may cause closer packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available there for solubilization of polar compounds. Therefore, this may be reasons for the observed reduction in the extent of solubilization of some polar compounds.

#### **2.7.4. Effect of monomeric organic additives**

The swell micelle from the solubilized hydrocarbon may have made it possible for the micelle to incorporate more polar material in the palisade layer. In opposite the solubilization of such polar material as long-chain alcohols, amines, mercaptans, and fatty acids into the micelles of a surfactant appeared to increase their solubilization of hydrocarbons. Therefore, the longer chain length of the polar compound and less hydrogen bonding appeared to increase the solubilization of hydrocarbons.

#### **2.7.5. Mixed anionic-nonionic micelles**

The solubilization of substance can have been increased by mixed micelles of anionic and nonionic surfactant as Yellow OB and POE. The interaction between the POE chain and the benzene sulfonate groups increased rather than the phenyl or sulfonate groups alone.

#### **2.7.6. Effect of temperature**

The increasing temperature for ionic surfactants results in an increase in the extent of solubilization for both polar and nonpolar solubilizates. Due to, it can increase thermal agitation increases the space available for solubilization in the micelle. In the other hand, the effect of increasing temperature for nonionic surfactant appears to depend on the nature of the solubilizate. Nonpolar materials, are solubilized in the inner core of the micelle, appear to show increased solubility as the temperature is raised.

#### **2.7.7. Hydrotropy**

When there was strong chain-chain and head-head interactions between surfactant molecules, either insoluble crystal formation or liquid-crystal formation may have occurred. From the rigid liquid-crystal structures is less space solubilization than flexible type micelle. The addition of certain nonsurfactant organic additives, which is called Hydrotropy, can reduce the tendency to form crystalline structures.

## 2.8. Microemulsion

Microemulsions are transparent dispersions containing two immiscible liquids with particles of 10-100 nm (0.01-0.1  $\mu\text{m}$ ) in diameter that are generally obtained upon mixing the ingredients gently. They differ markedly from both macro- and miniemulsions in this respect (Rosen, 2004). Figure 2.5 shows aqueous micelles at lower salt concentrations (as shown in number 1) and oil-phase inverse micelles at higher salt concentrations. If we change the salt concentration, the hydrophobic-lipophobic balance (HLB) of an ionic surfactant system will change. An increase in salt concentration in an ionic surfactant solution will eventually cause the surfactants to partition into the oil phase as shown in figure 2.5 (type II) (Sabatini, 2000). The multiphase microemulsion-containing systems are first described by Winsor. There are three possibilities for the type of phases depending on the compositions, temperature, and salinity. Two-phase systems, called Winsor I and Winsor II, correspond to an o/w microemulsion coexisting with excess water, respectively. A Winsor III system, as shown in figure 2.5 (number 2), is formed when the surfactant is concentrated in a middle phase, which coexists with oil and water (Watarai, 1997).

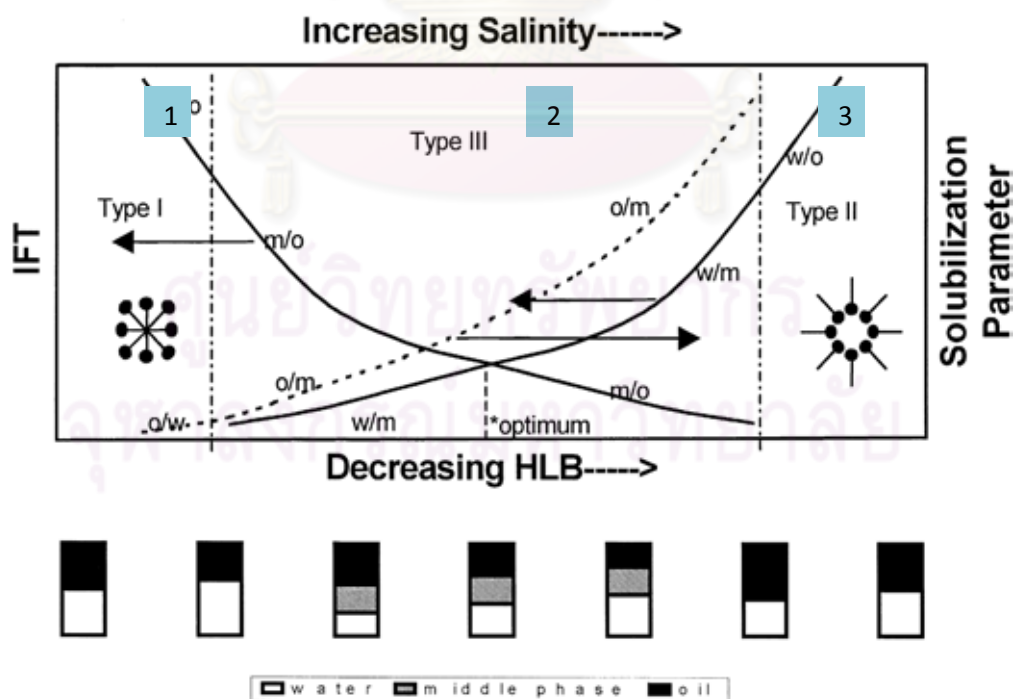


Figure 2.5 Winsor phase diagram (Sabatini et al., 2000)

## 2.9. Literature Reviews:

Edwards et al. (1991) investigated the solubilization of PAH in nonionic surfactant solution and determined the mole fraction micelle-phase/aqueous-phase partition coefficients. They reported that the partitioning of organic compounds between surfactant micelles and aqueous solution was characterized by a mole fraction with a linear function of  $\log K_m$  plotted against  $\log K_{ow}$  from the surfactant solution.

Baran, et al. (1994) found the behavior of chlorocarbons was parallels the ideal mixing rules for hydrocarbons; therefore, they studied and compared the optimum salinity of chlorocarbons. They investigated the polarity of chlorocarbon hydrocarbons as equivalent alkane carbon number (EACN) by plotting  $\ln S^*$  against EACN to obtain the salager's equation.

Walter et al. (1998) reported that the use of ferrocene as an additive at an amount of 1 to 100 ppm. Ferrocene has reduced the carbonaceous deposits resulting from combustion of heavy residual fuel oils in a low-speed, high compression, spontaneous-ignition internal combustion engine having a speed of 900 to 50 revolutions per minute. They suggested that an any additive content in excess of 100 ppm has reached a limit.

Dwarakanath et al. (1999) studied soil column experiments and found an anionic surfactants recovery rate of at least 99%. Firstly, they screened surfactant systems by using phase behavior experiments. Secondly, they selected the suitable surfactant system for subsequent column experiments. In summary, they recommended that good surfactants should possess a high contaminant solubilization, fast coalescence times, absence of liquid crystal phases and gels, and during column experiments they should not have a too high hydraulic gradient during and after surfactant flood.

Sabatini et al. (2000) illustrated the importance of system solubility enhancement, interfacial tension, viscosity and density in selecting a surfactant system for surfactant-enhanced remediation of contaminants. They recommended that the interfacial tension (IFT) should be 4 dyn/cm for avoiding mobilization, vertical migration, and surfactant gradient approach in column test that used increasing salt concentration to enhance the supersolubilization potential for decreasing vertical migration.



Wu et al. (2001) demonstrated that the more hydrophobic of oil has achieved desirable phase behavior with the more hydrophobic of surfactant system. They demonstrated that the surfactant systems like SDBS/IPA, AMA/IPA, and AOT/TWEEN 80 are able to effectively remediate these hydrophobic oils (EACN of 10-20). Highly hydrophobic oils (e.g., EACN>20) and highly viscous oil require combination approaches (surfactant plus alcohol/solvents and temperature) to achieve the desired phase behavior.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

# CHAPTER III

## METHODOLOGY

### 3.1. Materials

#### 3.1.1. Ferrocene contaminants and alkanes

Ferrocene (98%) was purchased from Sigma-Aldrich Co. (Germany). Alkanes (hexane, C-6, Unilab; octane, C-8, Univar; and decane, C-10) were purchased from Fluka were used as representative of gasoline. Benzene (Carlo Erba reagent), toluene (Carlo Erba reagent), and xylene (Scharlau Chemi) was used to determine the EACN of ferrocene. Some properties of alkanes, ferrocene, and aromatic hydrocarbons were shown in Table 3.1.

**Table 3.1 Alkanes properties and ferrocene**

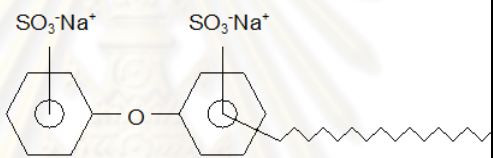
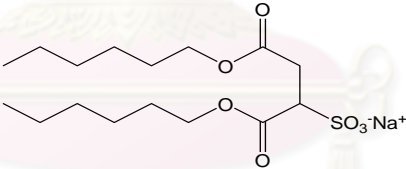
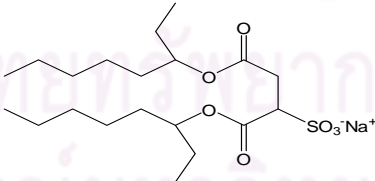
Parameter	Decane	Hexane	Octane	Ferrocene	Benzene	Toluene	Xylene
ACN/EACN	10	6	8	ND	0	1	2
MW(g/mol)	142.28	86.1766	114.23	186.4	78.11	92.13	106.16
Density (g/cm <sup>3</sup> )	0.73	0.664	0.7028	2.69	0.877	0.87	0.87
Log K <sub>ow</sub>	6	3.9	0	3.28	1.95-2.15	2.1-3	6.18 at 22 °C
Solubility (mg/L)	N	N	Very slightly soluble in cold water	N	Emulsion in water	Emulsion in water	Emulsion in water
Boiling point (°C)	174.5	69	125.6	249	80	110.6	138-142

*Note:* N means insoluble. ND means information.(cited from material safety data sheet (MSDS): science lab.com

### 3.1.2. Surfactants

Anionic surfactants were used in this research; sodium dihexyl sulfosuccinate (trade name of Aerosal MA or in short AMA with 80% active) and sodium dioctyl sulfosuccinate (trade name of Aerosal OT or in short AOT with 100% activity) were purchased from BDH Company (UK). Some properties of these surfactants were shown in Table 3.2.

**Table 3.2 Surfactants properties used in this study.**

Surfactants	Type	Structure	MW (g/mol)	HLB
Monoalkyl, diphenyloxide disulfonates (Dowfax 8390)	anionic		642	71.5
Sodium dihexyl sulfosuccinate (AMA)	anionic		388.45	16.6
Sodium dioctyl sulfosuccinate (AOT)	anionic		444.57	10.2

*Note:* HLB values for anionic surfactants were calculated based on the Davies method (Davies, 1959).

### 3.1.3. Electrolyte

NaCl with 99% purity purchased from Lab-Scan Ltd. (Ireland) was used for the salinity scan conducted in this research.

### 3.1.4. Synthetic soil

Ottawa sand or silica sand (20-30 mesh) with low an iron content was used as synthetic soil in this study and was purchased from Fisher Scientific Co., Ltd. (UK).

## 3.2. Methods

### 3.2.1. Characterization of the hydrophobicity of ferrocene

Ferrocene is an organometallic compound consisting of a central iron atom and two cyclopentadiene rings. It contains carbon in its aromatic structure. The hydrophobicity of ferrocene can be quantified as the EACN. The aim of this study was to investigate the EACN of ferrocene to select a suitable surfactant system in the phase behavior study.

Equal volumes of alkanes and aqueous surfactants were added into 1 mL tubes (0.5 mL each) possessing a cap. Firstly, in a tube containing the aqueous surfactant phase (containing a mixture of 3.6%wt AMA, 0.4%wt Dowfax 8390, and sodium chloride at various concentrations) equal volumes of *n*-hydrocarbons (benzene, toluene, and xylene) were added. The tubes were immediately sealed, gently shaken for 1 min, and equilibrated for 24 h at 25 °C. The experiment was performed in triplicates. The solubilization parameter (*SP*) was quantified by measuring the change of the volume of the oil and aqueous phase, which is indicated by changes of the solution height using a digimatic height gages (Model series 192, Mitutoyo). The *SP* of water (*SP<sub>w</sub>*) and oil (*SP<sub>o</sub>*) was plotted against %wt NaCl, and the *S\** was determined by the intercept. The same procedure was performed for all *n*-hydrocarbons. Then, the empirical linear relationship between *S\** and EACN was established. The EACN of the mixture for individual linear alkanes was quantified by

using the Salager's linear relation (Baran et. al., 1994). Ferrocene and benzene were mixed at a mole ratio of 0.2:0.8 and used for determining the EACN of ferrocene.

### 3.2.2. Phase behavior study

The phase behavior of microemulsions was studied by observing the transition from Winsor type I microemulsion (oil in water) to Winsor type III microemulsion (middle phase) to compare the behavior of alkanes with and without ferrocene addition. In this study, two systems of surfactants were considered:

- Mixed 2AMA :1AOT at 4%wt
- Mixed 1AMA :1AOT at 4%wt

The microemulsion formation phase study was conducted in 1 mL tubes with equal volumes of an aqueous surfactant solution and alkanes (hexane, octane, and decane) with and without ferrocene addition. A salinity scan using sodium chloride (NaCl) as electrolyte was performed to investigate the phase transition of the microemulsion systems. These tubes were sealed and gently shaken for 1 min. The samples were allowed to stand for 48 h at 25 °C to ensure that the solutions reach equilibrium. All experimental samples were performed in triplicates. The optimum salinity ( $S^*$ ) was determined from the plot of the solubilization parameter plotted against the NaCl concentration.

### 3.2.3. Solubilization study

The solubilization capacity of a suitable surfactant system for alkanes with and without ferrocene addition was studied at supersolubilization and Winsor type III conditions.

#### 3.2.3.1. Standard curve determination

The results of the phase behavior study were used to prepare a calibration curve for the mixed alkanes (octane and decane) and hexane over a concentration range of 50 to 2000 ppm in a mixed surfactants solution. Each sample was performed in duplicates and 0.1 mL sample solution was injected into a GC

equipped with a headspace auto sampler (Clarus 500, PerkinElmer Ltd.) at the following conditions: injector temperature was 200 °C, a column type HP-5 with 30 m x 0.32 mm ID was used with a film thickness of 0.25 µm, an oven temperature of 100-140 °C was applied, a flame ionization detector at 250 °C was used, and a flow rate of 14 psi utilized. The GC was coupled to a PerkinElmer Turbomatrix 40 headspace (HS) autosampler (Turbomatrix 40, PerkinElmer, PerkinElmer Ltd.) at the following conditions: a thermostating time of 30 min was used, an oven temperature of 80 °C was applied, the needle temperature was 100 °C, the transfer line temperature was 90 °C, a GC cycle time of 6 min, an injection time of 0.04 min, and withdrawal time of 0.2 min was applied.

### **3.2.3.2. Solubilization measurement**

The solubilization ability of alkanes with and without ferrocene at a concentration of 100 ppm was investigated by using 4 %wt mixed surfactants under Winsor type I, supersolubilization, and Winsor type III conditions. 2 mL of the alkane solution, 8 mL aqueous surfactant solution was added into a 50 mL separatory funnel. The funnel was immediately sealed and gently shaken for 1 min. Each sample was performed in duplicates. The vials were allowed to stand for 48 h to obtain equilibrium. 0.1 mL of the aqueous surfactant solution was collected and transferred into a Perkin vial, while 0.5 mL was transferred into vessel for digestion. The alkane concentration was measured with a GC-HS-FID under conditions similar to those of the standard curve determination. Ferrocene (organometallic compound mixed with alkanes) was determined by atomic absorption spectroscopy (AAS).

### **3.2.4. Column Experiment**

Column studies were conducted to compare the solubilization and mobility of alkanes with and without ferrocene Ottawa sand addition.

#### **3.2.4.1. Soil column preparation**

Column experiments were conducted with wet packed silica sand in glass columns (2.5 cm inner diameter) equipped with an adjustable flow adapter purchased from KONTES (Chromatography columns, KONTES CHROMAFLEX™).



The pore volume was evaluated by determining the volume of water replaced in the sand pores packed in the column. The initial volume of water was held in a separate container to be measured first. Then, a small amount of water and sand was gradually added into the column until the desired level of wet sand was reached. After packing the column, the volume of the remained water in the container was continuously measured in order to quantify the volume that is used, which represents the pore volume of the column. Degassed water was pumped upward into the column using a piston pump (Model QG6, Fluid Metering Inc.) at a flow rate of 0.40 mL/min (4.77 cm/h). The column was then flushed with 20 pore volumes of degassed water containing 0.01 Mol  $\text{Ca}(\text{NO}_3)_2$  at a flow rate of 0.40 mL/min in an upward direction to imitate groundwater conditions prior column soil contamination with alkanes and with and without ferrocene addition (adapted from Child et al., 2004).

#### **3.2.4.2. Alkane removal from column with and without ferrocene addition**

The selected surfactant system obtained from the phase behavior study was flushed into the column individually in an upward mode at a flow rate of 0.4 mL/min. A fraction collector (Model Frac 920, Amersham Bioscience) was used to collect the elution from the column every 0.25 pore volumes. Then, the removed alkanes (ferrocene mixed with alkanes) were determined solely analyzing the total iron ( $\text{Fe}_T$ ) concentration with an AAS. The characteristics of the effluent were observed to determine the  $\text{Fe}_T$  solubilization and the free phase oil as oil mobilization. The alkane removal efficiency from soil was calculated based on the amount of ferrocene solubilized and mobilized in the flushing solution.

#### **3.2.4.3. Alkane and ferrocene analysis**

##### **3.2.4.3.1. Total iron determination**

Iron (Fe) concentration was measured based on the total concentration of Fe that can have been solubilized into the surfactant micelles. Firstly, samples were digested in an Ethos Plus microwave system with high-pressure teflon vessels. Approximately 1 mL of samples was pipetted directly into the teflon vessel, and then

7 mL nitric acid and 1 mL hydrogen peroxide was added and homogenously mixed. In a three-step program the solution was heated within 10 min up to 220 °C (1000 W) and the temperature was hold for 13 min. After that, the vessels were vent for 30 min to cool down. The digested samples were measured for total iron concentration by AAS. All experiments were performed in duplicate.

#### **3.2.4.2.2. Alkane determination**

Alkanes (octane and decane) dissolved in a surfactant solution were quantified using a similar standard compared to this of the standard curve determination. The alkanes were determined by GC-HS equipped with a similar headspace auto sampler as used for the standard curve determination.

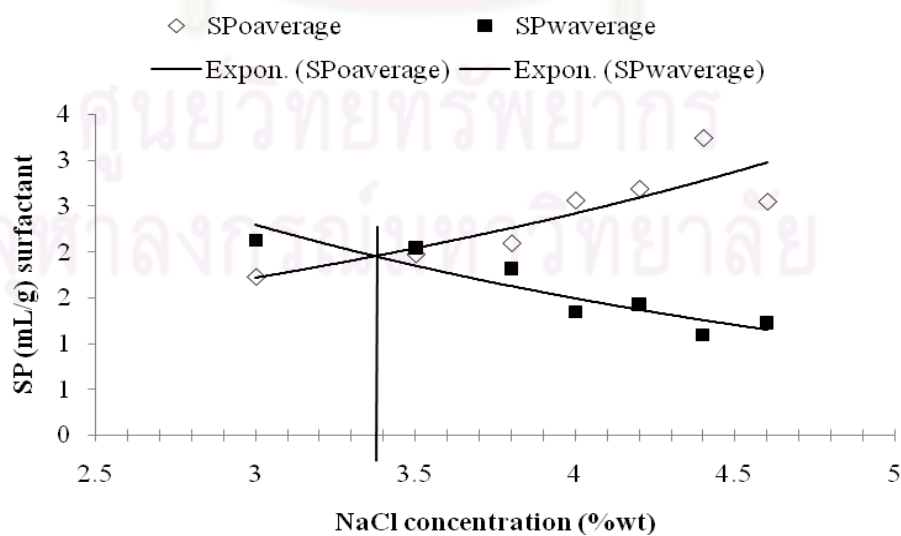


# CHAPTER IV

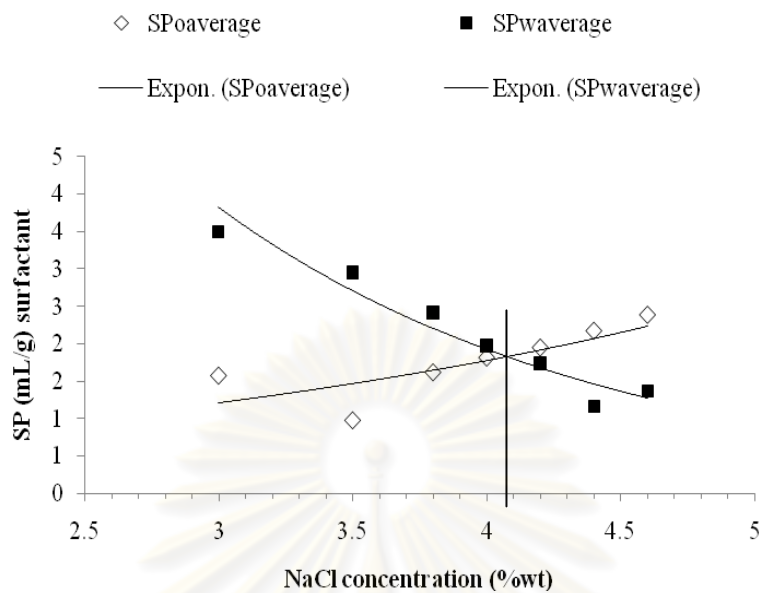
## RESULTS AND DISCUSSION

### 4.1 Characterization of the hydrophobicity of ferrocene

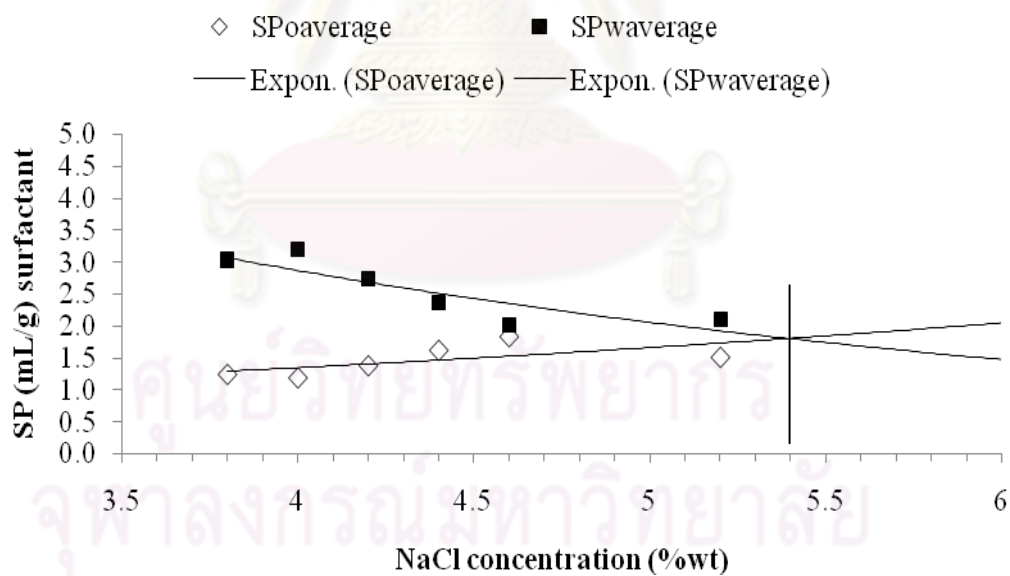
As described in Chapter III, in order to determine EACN of ferrocene, the EACN curve is needed to be constructed by using Salager equation for the known alkane carbon number (ACN) oils. For this section, a mixture of AMA and Dowfax 8390 at a ratio of 3.6:0.4 by weight and a total concentration of 4%wt was used to form microemulsion with benzene (EACN=0), toluene (EACN=1), and xylene (EACN=2) (Ysambertt et al.; 1997, Sumit et al.; 2009, Cayias et al.; 1976) to obtain the  $S^*$  of each oil as shown in Figure 4.1-4.3. The optimum salinity ( $S^*$ ) values were obtained from the plot of the  $SP_w$  and  $SP_o$  against the NaCl concentrations. Whereas  $SP_w$  and  $SP_o$  were calculated by volumes of the phase change and the phase transition, respectively (see Appendix A). The  $S^*$  values of benzene, toluene, and xylene were quantified as 3.38, 4.095, and 5.4 %wt respectively. Regarding to the  $S^*$  values of the three hydrocarbons, the highest EACN the oil possess the highest the  $S^*$ , this agreed to the rule of thumb that higher hydrophobic oil desires higher salt concentration for phase transition (Rosen, 2004).



**Figure 4.1** The optimum salinity( $S^*$ ) of benzene in AMA/Dowfax 8390 surfactant system.



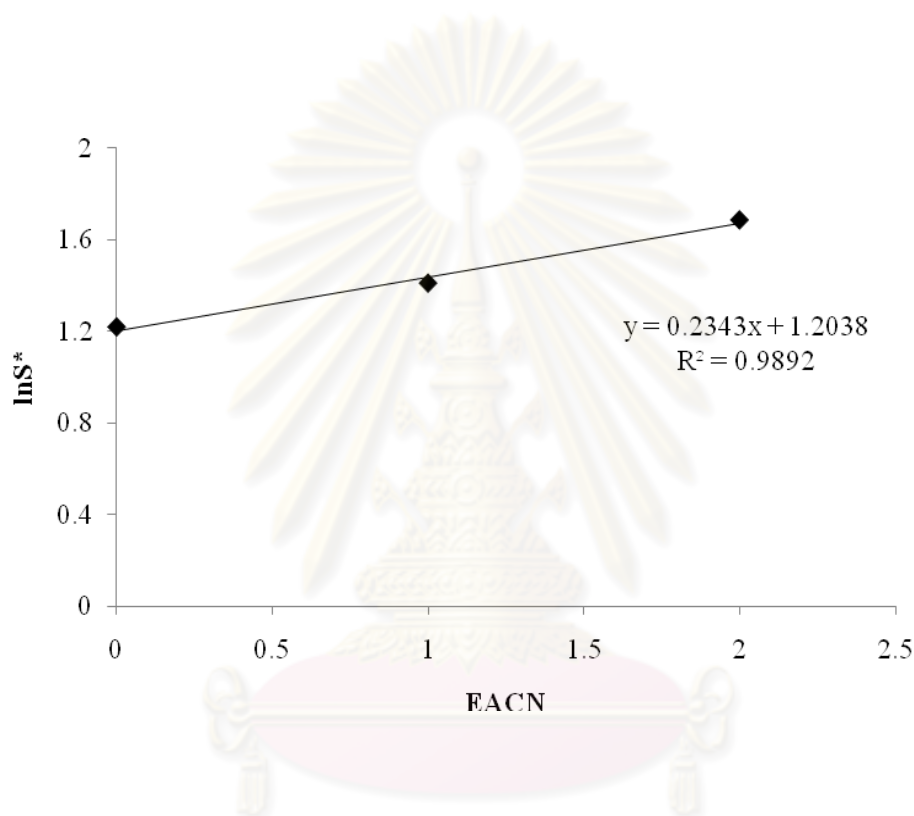
**Figure 4.2** The optimum salinity( $S^*$ ) of toluene in AMA/Dowfax 8390 surfactant system.



**Figure 4.3** The optimum salinity( $S^*$ ) of xylene in AMA/Dowfax 8390 surfactant system.

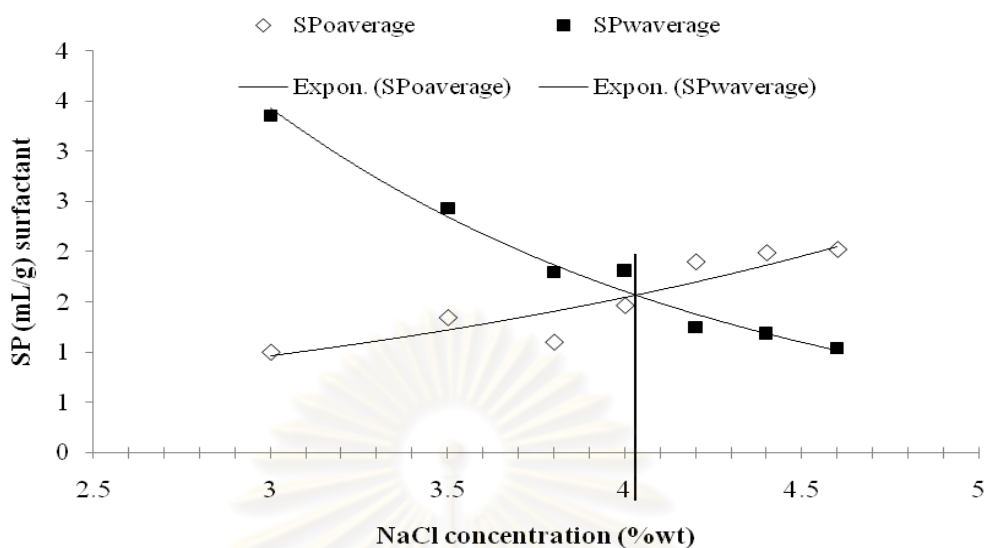
The natural logarithm of  $S^*$  was plotted against the oils' EACN as shown in Figure. 4.4. Thus, the empirical equation between  $\ln S^*$  and EACN was obtained as:

$$\ln S^* = 0.234EACN + 1.2038$$



**Figure 4.4 The empirical relationship between  $\ln S^*$  and the oils' EACNs.**

In order to determine the EACN of ferrocene, which is the one metallic additive, ferrocene was mixed with benzene at a molar ratio of 0.2:0.8 and conducted salt scan with the same surfactant system (AMA and Dowfax 8390 at a ratio of 3.6:0.4). The microemulsion and phase transition were observed and volume change measured in order to determine  $S^*$  of the systems with ferrocene. From the  $S^*$  value as shown in Figure 4.5, the EACN of ferrocene can thus be calculated by mixing rule and found to be 8.386.



**Figure 4.5 The  $S^*$  of ferrocene mixed in benzene at a molar ratio of 0.2:0.8 in an AMA/Dowfax 8390 system**

#### 4.2. Phase behavior study

In this section aim is to investigate the suitable surfactant systems to form microemulsion with alkanes with and without ferrocene (50 and 100 ppm) and understand their performance in bath experiment. Two surfactant systems were selected to investigate the suitable system based on their HLB of the system which can be indicated oil soluble surfactant. Surfactants can have been performed microemulsion with hexane, octane, and decane (Anuradee Witthayapanyanon et al., 2008).

Preliminary experiments were performed and the mixture of AMA-AOT was found to be capable of forming a microemulsion (Winsor type I) with our studied oils. The suitable ratio of AMA-AOT was 2:2 by weight and a total concentration of 4%wt resulted in an oil-in-water microemulsion, whereas the formation of a microemulsion using an AMA-AOT ratio of 2:1 by weight and a total concentration of 4%wt could not be observed. Therefore, the system of AMA-AOT of 2:2 was selected for further study.



The suitable surfactant system for this study is ratio of AMA-AOT of 2:2 systems. Table 4.1 summarizes the phase behavior of the AOT-AMA system with three different alkanes both with and without ferrocene. Even though the ratio of ferrocene (50 and 100 ppm) mixed to the alkanes may not significantly alter EACN values of the mixed oil based on mixing rule calculation, the results shows obviously that the hydrophobicity of ferrocene affects the phase behavior of the system. The ACN of hexane is 6 and that of octane is 8, which are lower than the EACN of ferrocene of 8.386, so in accordance with the mixing rule, when ferrocene was added to these oils, it increased their ACN values. As a result, higher ferrocene concentrations produced higher  $S^*$  values in the systems containing hexane or octane. On the other hand, since decane possesses an ACN of 10, the addition of ferrocene decreased the ACN of the new mixed oil; thus, lower  $S^*$  values were observed at higher ferrocene concentrations.

The current study found that  $S^*$  in each alkanes with and without ferrocene relation with their own phase behavior. Supersolubilization and Winsor type III of decane with and without ferrocene required the highest electrolyte than octane and hexane respectively. It relates with Winsor diagram (Figure 2.5) that type of microemulsion (phase) change with increasing electrolyte and relates with their own EACN (see Appendix B).

**Table 4.1 Phase behavior and the optimum salinity ( $S^*$ ) of the AMA-AOT at 4%wt (ratio 2:2) surfactant system with each alkane both with and without ferrocene at different salinities**

Oil	Phase behavior of the microemulsion										$S^*$
	NaCl (%wt)										
	1.2	1.3	1.5	1.6	1.7	1.8	2.0	2.2	2.6	3.0	
Hexane	SPS	III	III	III	III	III	III	N	N	N	2.03
Hexane + ferrocene 50 ppm	SPS	III	III	III	III	III	III	N	N	N	2.30
Hexane + ferrocene 100 ppm	I	SPS	III	III	III	III	III	III	III	III	2.34
Octane	N	N	I	SPS	III	III	III	III	III	III	2.78
Octane + ferrocene 50 ppm	N	N	I	SPS	III	III	III	III	III	III	2.93
Octane + ferrocene 100 ppm	N	N	I	I	SPS	III	III	III	III	III	3.07
Decane	N	N	N	N	N	N	I	SPS	III	III	5.00
Decane + ferrocene 50 ppm	N	N	N	N	N	N	SPS	III	III	III	4.89
Decane + ferrocene 100 ppm	N	N	N	N	N	N	SPS	III	III	III	4.82

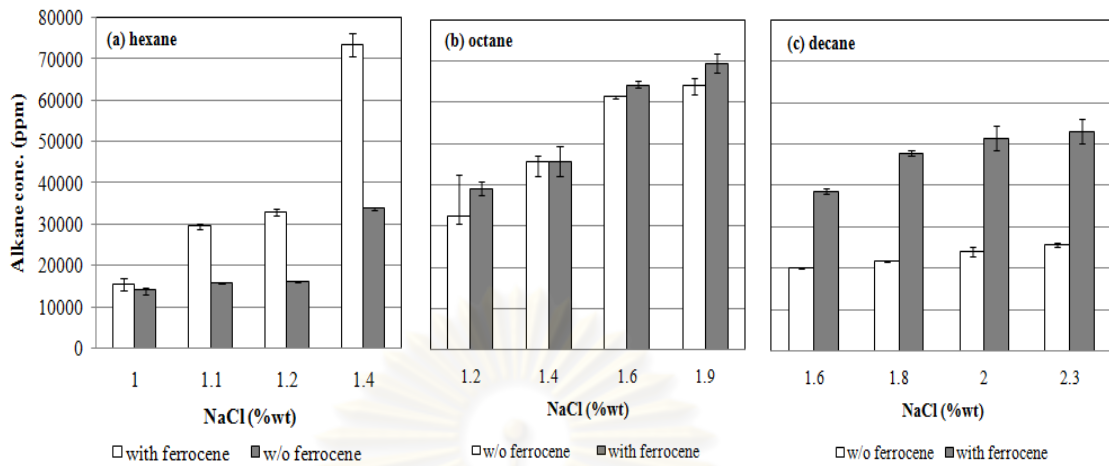
*Note:*  $S^*$  is the optimum salinity; I and III refer to the type of microemulsion; SPS refers to supersolubilization, where the microemulsion occurs at the point close to the transition from Type I to Type III; and N is an appearance that cannot be defined as microemulsion.

### 4.3 Solubilization study

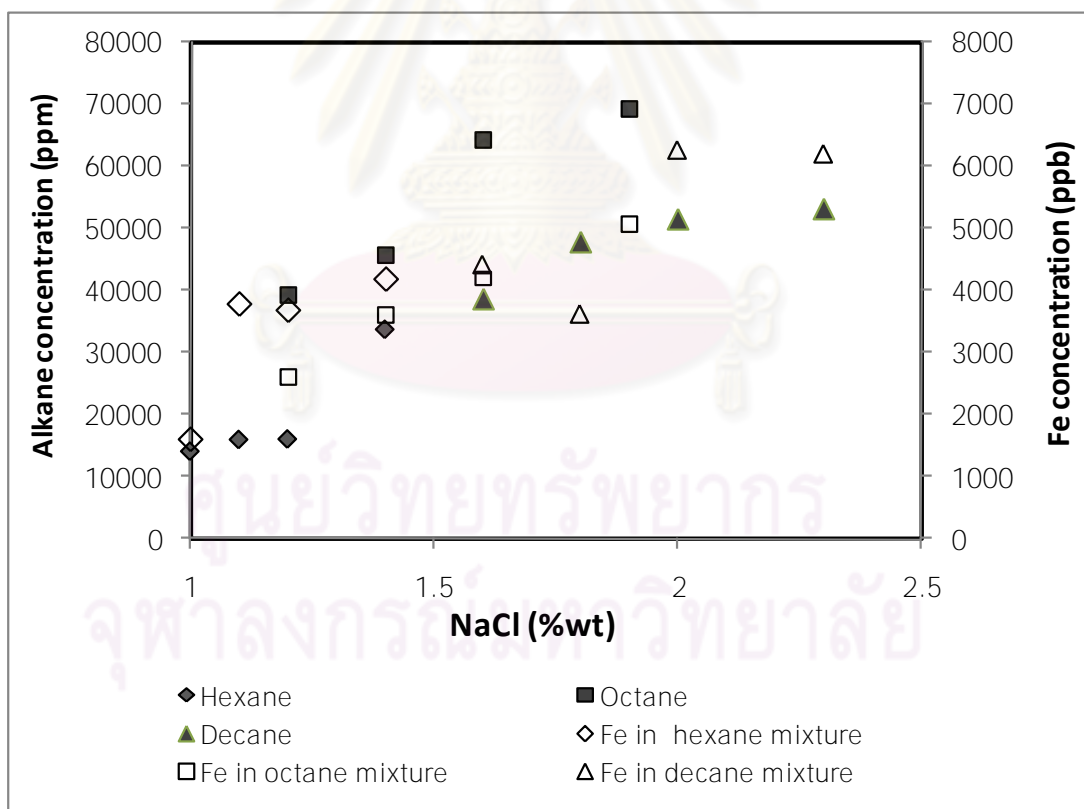
Solubilization study was carried out to evaluate the solubilization capacity in each alkane with and without ferrocene. They were performed covered the range of salinities that Winsor type I to III were generated Excess amount of alkanes

with and without ferrocene were mixed with suitable surfactant solution (from previous study). After equilibrium of solution was reached, the supernatant solution was analyzed for alkane and total Fe. The results are as shown in Figures 4.6 and 4.7 for the concentration of alkanes in the system of with and without ferrocene; and comparison of alkanes and ferrocene concentration as Fe in system of various salinity, respectively (see Appendix C).

From Figure 4.6, the results show the same trend for all cases (all alkanes concentration in the systems of with and without ferrocene) that the increasing salinity of the systems, the solubilization of the alkanes increase. However, only hexane solubilization that found to be decreased when ferrocene is added to the system while an increasing of octane and decane solubilization occur in the system of mixing with ferrocene. In each supersolubilization condition of alkane (at NaCl 1.2 %wt, hexane; 1.6 %wt, octane; 2 %wt, decane), the highest solubilization of octane was found for both the systems with and without ferrocene while hexane with ferrocene was found lowest. For the Winsor type III condition (1.4, 1.9, and 2.3 %wt NaCl for hexane, octane, and decane, respectively.), hexane was found to solubilized highest while the lowest solubilization was decane. Among the 3 alkanes, hexane has shortened ACN, implied to be lower hydrophobicity. It can probably be expected that the system of 2 %wt of AMA and 2 %wt of AOT is more suitable to form middle phase with hexane rather than higher hydrophobic oil like decane. This is confirmed by the result that once ferrocene was added, EACN of mixed decane and ferrocene was reduced, hence the solubilization of decane was decreased. It is interesting to point here that for the case of octane that having the ACN closest to those of ferrocene (8 and 8.386 for octane and ferrocene, respectively), the solubilization show slightly increasing.



**Figure 4.6 Solubilization of alkanes in the systems of without and with ferrocene at 100 ppm at various salinity**



**Figure 4.7 Solubilization of alkanes and ferrocene (as Fe) in the systems of without and with ferrocene at 100 ppm at various salinity**

Another important finding was that the solubilization of total iron (Fe) correspond the solubilization of alkanes which increased with increase electrolyte and changed type of microemulsion (see Figure 4.7). It was also shown that ferrocene can solubilized in micellar. In addition, the same trend of solubilization of alkanes and ferrocene (as Fe) are found in all cases. This may indirectly indicate that ferrocene is miscible well the three alkanes and ratio of solubilization of solubilized mixture oil still similar to the initial ratio. From this result, it can be expected that the flushing surfactant solution for remediation contaminated alkane will remove contaminated ferrocene in the same time. The column study in the next part will evaluate this expectation.

#### **4.4. Column study**

The column study was conducted to imitate the actual subsurface remediation. The selected surfactant system (2AMA: 2AOT at 4 %wt) from solubilization study at the formula supersolubilization (1.6 and 2.0 % NaCl for octane and decane, respectively) were used in the column experiments with decane and octane with and without ferrocene. In addition, the formulation of the same surfactant at 1.6% NaCl was flushed the columns saturated with octane with and without ferrocene were also study for comparison. Ottawa sand was used as media for packing columns. Each of contaminated oil was saturated in the packed column. Then, the surfactant solution was flushed to remove the contaminated oil. The effectiveness of removal were analyzed as total, solubilized, mobilized, and mass balance of alkanes and total Fe as summarized in Tables 4.2-4.3 ( see Appendix D).

##### **4.4.1 Removal alkanes**

The result shows that by flushing surfactant solution, alkanes can be removed in the range of 85 to 92%. As a consequent, the surfactant flushing approach can be considered to be a procedure for remediate the contaminant containing organometallic (alkanes mixed with ferrocene).

Figures 4.8-4.13 show the solubilization and mobilization of alkanes as linear line and dashed line respectively. As expected, the surfactant solution initially

mobilized a portion of the trapped alkanes which migrated vertically downward through the column. The maximum solubilized of alkanes occurred after mobilized. The effectiveness of oil removal by surfactant solution is primarily attributable to a high ability of the solution to dramatically lower the interfacial tension between alkanes (for both system with and without ferrocene) with water, creating oil-surfactant-water micelles, and producing oil-in-water microemulsion (Ouyang et al., 1996).

The solubilized at 2 %wt NaCl as supersolubilization condition of decane for both systems of with and without ferrocene were found to be slightly different that mobilization of the decane without ferrocene (Figure 4.8) the mobilized oil came out in the first PV while those of the system of decane with ferrocene the mobilized oil came out from the column after second PV of flushing and slightly lower than the system without ferrocene (Figure 4.8). These differences can be explained in part by the proximity of their EACN. On the other hand, the solubilized and mobilized of octane with ferrocene by the surfactant solution at 1.6 %wt NaCl (supersolubilization condition) was found higher than those of the with octane only. However, both octane and decane from the column experiment were agreed with the results of the solubilization study. Moreover, for the column of octane with and without ferrocene flushing with the surfactant at 2 %wt NaCl (formulation forming Winsor type III microemulsion) showed that almost oil removal, higher than 95% of the total were from mobilization (see Figures 4.13-4.14 and Table 4.3). It is not surprising because middle phase provides very low interfacial tension, hence the oil mobilize was spontaneously occur before the oil will be solubilize in micelle. As a consequence, several studies suggest that middle phase microemulsion recommend avoiding because of vertical migration (high mobilization) (Sabatini et al., 2000). However, in this present study, since the mixture oils, octane and decane with ferrocene, at the low proportion of ferrocene (100 ppm), the oils are still LNAPL, thus vertical migration may not be crucial concern. From results of this study confirm the previous works that The supersolubilization condition as Winsor type I was increasing the solubilization and reducing mobilization in the same time (James et al., 1998)



**Table 4.2 Column flushing test alkanes results in 2AMA:2AOT at 4 %wt surfactant system**

Parameter	alkanes					
	octane @ NaCl 1.6%wt	octane+ ferrocene @ NaCl 1.6%wt	octane @ NaCl 2%wt	octane+ ferrocene @ NaCl 2%wt	decane @ NaCl 2%wt	decane+ ferrocene @ NaCl 2%wt
Pore volume(mL)	32.77	32.98	29.01	30.21	31.46	31.52
Residual saturation (%)	16.54	15.79	15.84	15.83	19.64	22.12
Removal efficiency (%)						
- solubilization	7.9	8.4	0.01	0.02	9.07	9
- mobilization	78.38	82.63	84.76	87.15	83.73	76.56
Total removal (%)	86.28	91.04	84.77	87.17	92.8	85.56
Mass balance (%)	86.28	91.67	84.77	87.36	92.92	90.5

**Table 4.3 Column flushing test total Fe results in 2AMA:2AOT at 4 %wt surfactant system**

Parameter	Total Fe		
	octane+ ferrocene @ NaCl 1.6%wt	octane+ ferrocene @ NaCl 2%wt	decane+ ferrocene @ NaCl 2%wt
Pore volume(mL)	32.98	30.21	31.52
Initial total Fe(ppb)	519.72	477.12	666.263
Residual saturation (%)	0.0006395	0.0005378	0.0007847
Removal efficiency (%)			
-solubilization	8.05	0.47	8.23
- mobilization	85.27	85.59	68.972
Total removal (%)	93.32	86.07	77.2
Mass balance (%)	101.3759	107.5883	97.49

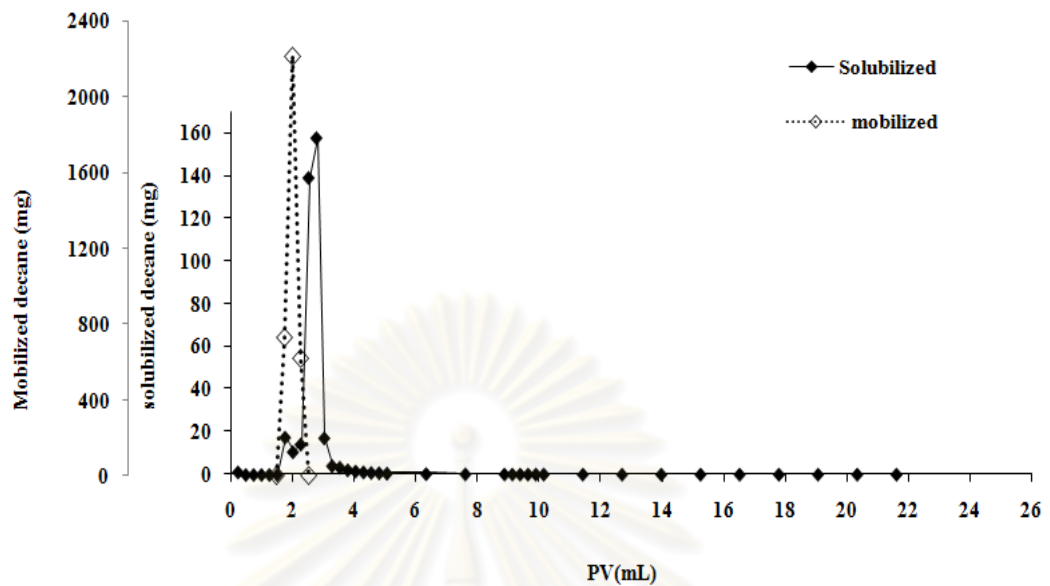


Figure 4.8 Mass of solubilization and mobilization decane removal by pore volume (mL) of 2AMA:2AOT at 4 %wt surfactant system at NaCl 2 %wt flushing through the column contaminated with decane only

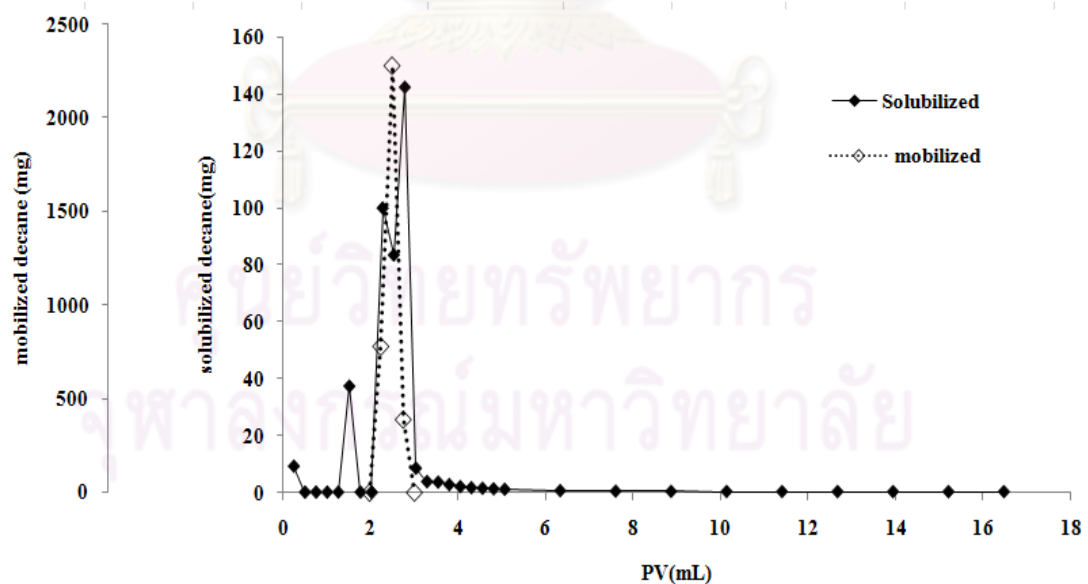


Figure 4.9 Mass of solubilization and mobilization decane removal by pore volume (mL) of 2AMA:2AOT at 4 %wt surfactant system at NaCl 2 %wt flushing through the column contaminated with decane and ferrocene

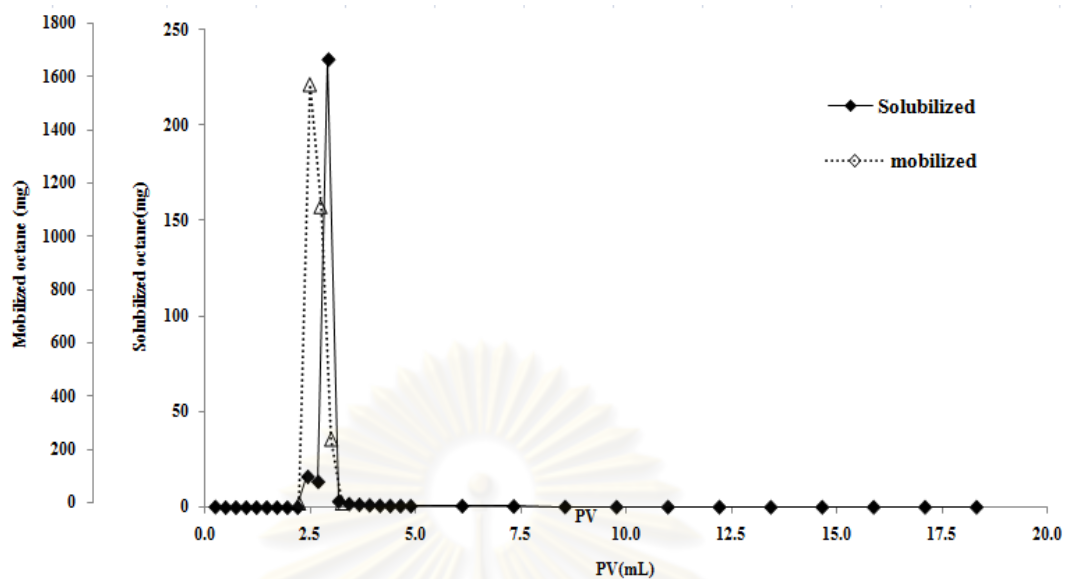


Figure 4.10 Mass of solubilization and mobilization octane removal by pore volume (mL) of 2AMA:2AOT at 4 %wt surfactant system at NaCl 1.6 %wt flushing through the column contaminated with octane only

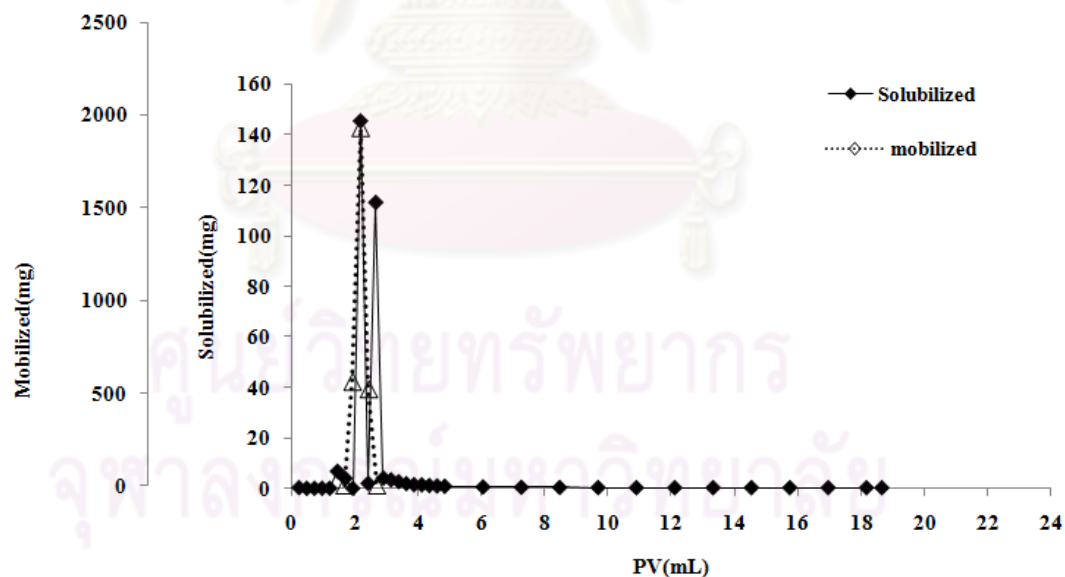


Figure 4.11 Mass of solubilization and mobilization decane removal by pore volume (mL) of 2AMA:2AOT at 4 %wt surfactant system at NaCl 1.6 %wt flushing through the column contaminated with octane and ferrocene

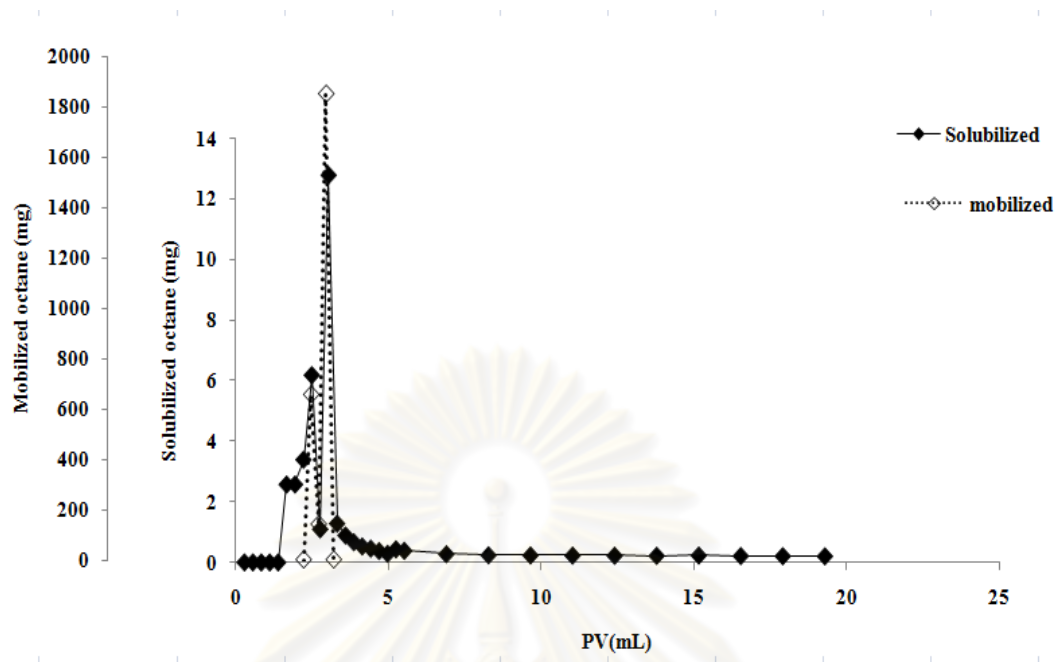


Figure 4.12 Mass of solubilization and mobilization octane removal by pore volume (mL) of 2AMA:2AOT at 4 %wt surfactant system at NaCl 2.0 %wt flushing through the column contaminated with octane only

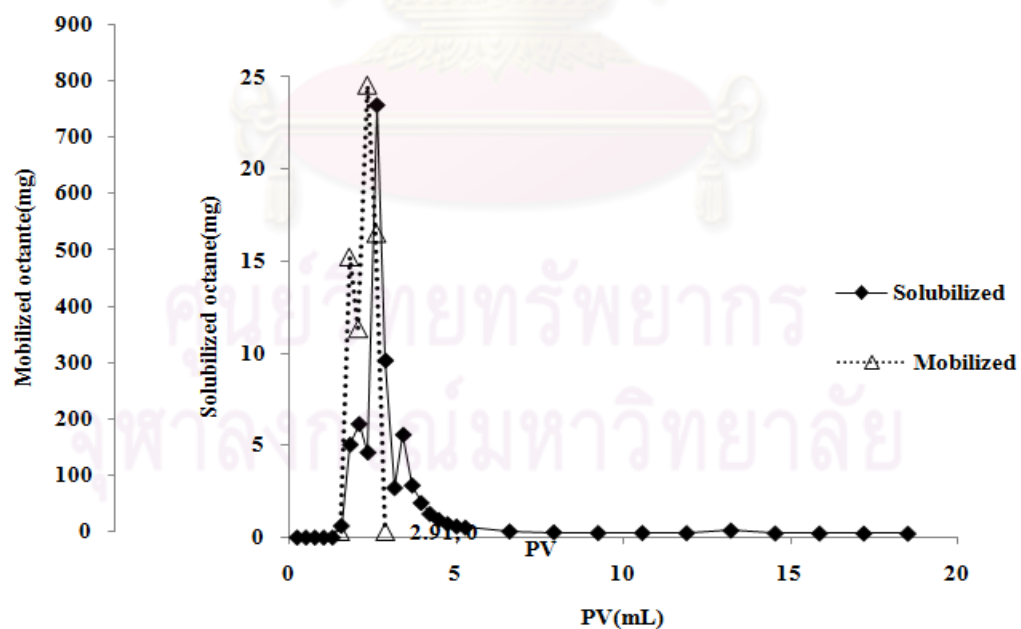


Figure 4.13 Mass of solubilization and mobilization octane removal by pore volume (mL) of 2AMA:2AOT at 4 %wt surfactant system at NaCl 2.0 %wt flushing through the column contaminated with octane and ferrocene

#### 4.4.2 Removal of ferrocene

In the same column experiments described in 4.4.2, ferrocene removal by the surfactant solution was evaluated by analysis of total Fe to indicate the ferrocene removal as shown in Figure 4.14-4.16 and Table 4.3. It should be noted here that in this study, mobilized oil is assumed to have the same proportion of ferrocene as an initial (100 ppm of ferrocene), thus the different efficiency of alkanes and ferrocene removal was based on solubilization phenomena of the two compounds. From Figures 4.14 to 4.16, the results show obviously that for the system of octane with ferrocene either flushing at 1.6 or 2.0 %NaCl, ferrocene solubilized along with octane in the first 1 to 3 PVs while the case of decane, ferrocene was found to be solubilized less than decane and used surfactant up to almost 20 PVs to complete performance. As compared the solubilization between alkanes (octane and decane) and ferrocene (as total Fe), the same trend was for all cases that the system of octane with ferrocene flushing by the surfactant solution with 2% NaCl yield the lowest solubilization for both octane and ferrocene. The observation corresponds to the results found in the solubilization study.

Conclusively, the experimental result suggests that the presence of ferrocene in octane and decane affects total oil removal efficiency depending on EACN of the alkane as well as the surfactant use for flushing. In addition, both solubilization and column study indicate that ferrocene can be removed by the technique of surfactant flushing for alkane removal. As a consequence, ferrocene may not be a major concern as a contaminant as compared to other organometallic compounds.

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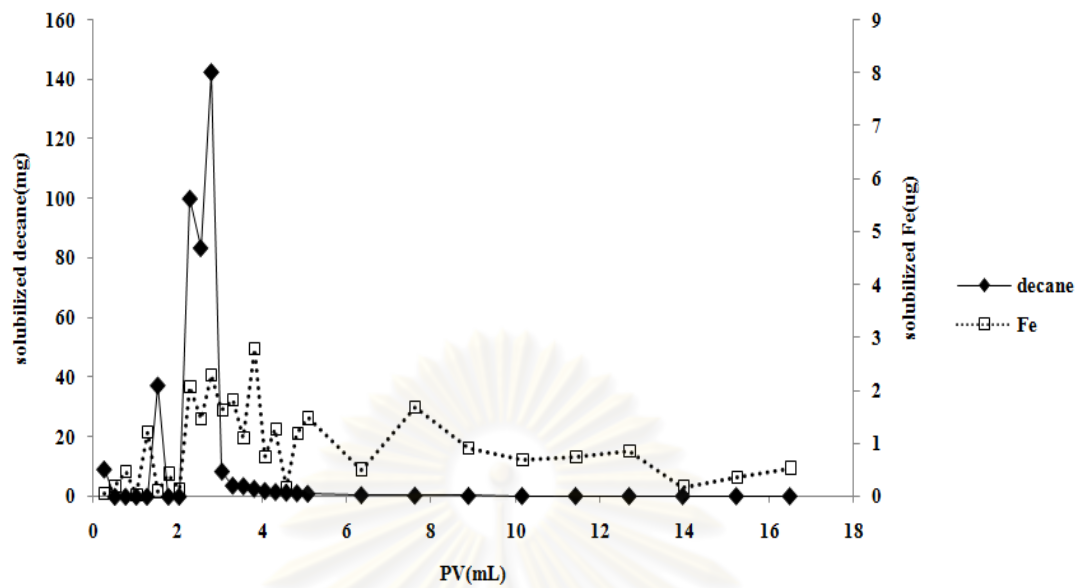


Figure 4.14 Plots between mass of decane with ferrocene and total Fe solubilization, mobilization and pore volume (mL) in 2AMA:2AOT at 4 %wt surfactant system at NaCl 2 %wt

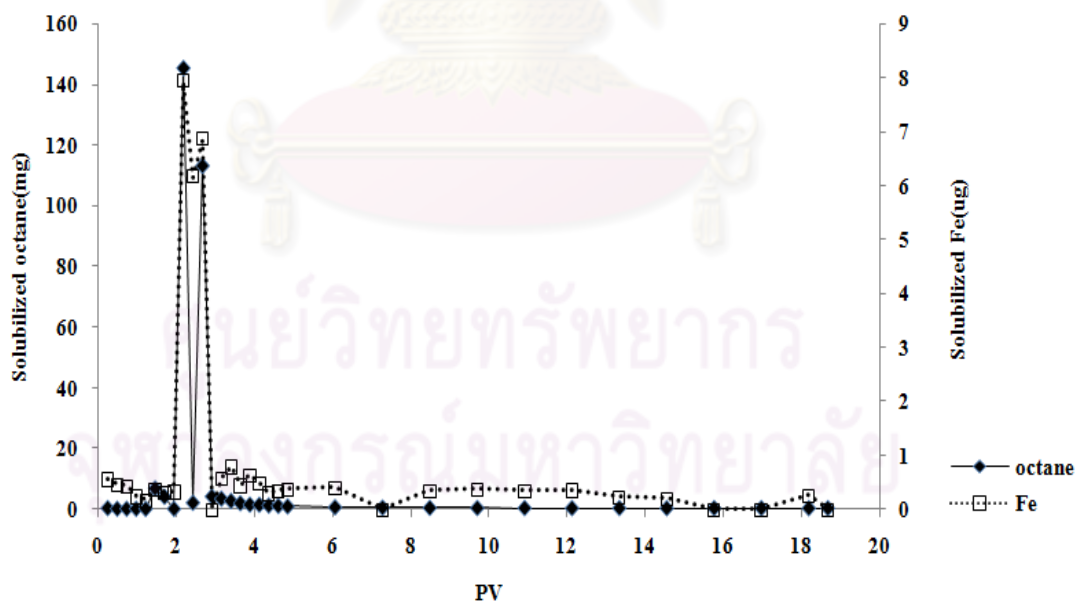


Figure 4.15 Plots between mass of octane with ferrocene and total Fe solubilization, mobilization and pore volume (mL) in 2AMA:2AOT at 4 %wt surfactant system at NaCl 1.6 %wt



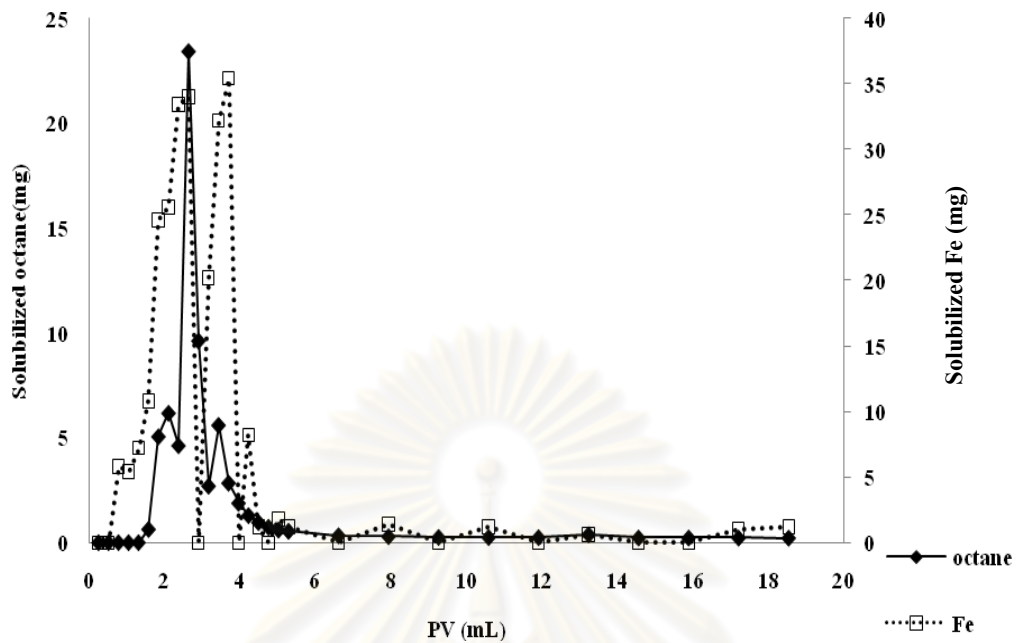


Figure 4.16 Plots between mass of octane with ferrocene and total Fe solubilization, mobilization and pore volume (mL) in 2AMA:2AOT at 4 %wt surfactant system at NaCl 2%wt

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# CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Conclusion

As described in Chapter III, in order to determine EACN of ferrocene, the EACN curve is needed to be constructed by using Seleger equation for the known alkane carbon number (ACN) oils. For this section, a mixture of AMA and Dowfax 8390 at a ratio of 3.6:0.4 by weight and a total concentration of 4%wt was used to form microemulsion with benzene (EACN=0), toluene (EACN=1), and xylene (EACN=2) (Ysambertt et al.; 1997, Sumit et al.; 2009, Cayias et al.; 1976) to obtain the  $S^*$  of each oil as shown in Figure 4.1-4.3. The optimum salinity ( $S^*$ ) values were obtained from the plot of the  $SP_w$  and  $SP_o$  against the NaCl concentrations. Whereas  $SP_w$  and  $SP_o$  were calculated by volumes of the phase change and the phase transition, respectively (see Appendix A). The  $S^*$  values of benzene, toluene, and xylene were quantified as 3.38, 4.095, and 5.4 %wt respectively. Regarding to the  $S^*$  values of the three hydrocarbons, the highest EACN the oil possess the highest the  $S^*$ , this agreed to the rule of thumb that higher hydrophobic oil desires higher salt concentration for phase transition (Rosen, 2004).

The ferrocene addition found affect on optimum salinity and solubilization. Since EACN of ferrocene is 8.386, the optimum salinity of hexane and octane found increased once ferrocene addition is increased. On the other hand for denane, the opposite trend found since decane has higher ACN (10).

For solubilization of alkanes in the same surfactant solution, hexane and decane show opposite result while octane found insignificant different for the system with or without ferrocene. In addition, another finding on solubilization is that ferrocene (as total Fe) solubilization found to be the same trend as alkanes. This indicates that to remove contaminated alkanes in the presence of ferrocene, ferrocene will also be removed as well. Final part of this work is column experiments; only octane and decane with and without ferrocene were selected for the study. The formulation of surfactant used for column study was at supersolubilization (1.6% and

2% NaCl for octane and decane, respectively). In addition, for octane the formulation at 2% NaCl (type III microemulsion) was also carried out for comparison study. In case of octane, both formulation at 1.6% and 2% NaCl in the surfactant solution, addition of ferrocene increased solubilization of octane while in case of decane, addition of ferrocene decrease decane solubilization. For ferrocene solubilization, the system at SPS (1.6% NaCl) of octane yield the highest solubilization of ferrocene (93.32 % removal) while the system with decane, solubilization of ferrocene found to be the lowest (77.2 % removal). In summary, the surfactant solubilization capacity of alkanes with and without ferrocene occurred different on phase behavior, solubilization, and column study. They were shown that ferrocene affect alkanes on solubilization by microemulsion technique.

## **5.2 Recommendations**

In recent years, surfactant has been used in cooperation pump and treats to removal NAPL, which contaminate in subsurface. The surfactant flooding after prior pump and treat is to help the mobilization and solubilization chemical trapped in aquifer (Intera Inc. and Naval Facilities Engineering Service Center, 2003). The microemulsion formation is application of surfactant and its formation depends on property of substance (EACN).

Gasoline which is mixture of hydrocarbon with various additives as organometallic should find the suitable surfactant system before apply to use in remediation. The findings of this study are confirmed that ferrocene (additive) effect to solubilization of alkanes (represent in gasoline) by microemulsion technique.

Furthermore, the other additive mixed with alkanes and ferrocene mixed in gasoline or diesel should be further studied for their effect on solubilization by microemulsion technique.

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## **APPENDICES**

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## APPENDIX A

### Experiment data of section 4.1 characterization of the hydrophobicity of ferrocene

Table A-1 Solubilization parameter (*SP*) of benzene with ferrocene 20 %wt in 9AMA: 1Dowfax surfactant system at 20 %wt

SP <sub>w1</sub>	SP <sub>w2</sub>	SP <sub>w3</sub>	SP <sub>o1</sub>	SP <sub>o2</sub>	SP <sub>o3</sub>	NaCl (%wt)	SP <sub>oaverage</sub>	SD	SP <sub>waverage</sub>	SD
2.96	3.9	3.2	0.74	0.79	1.47	3	1	0.49	3.35	0.41
1.77	3.09	2.44	1.8	0.74	1.49	3.5	1.34	0.66	2.43	0.55
1.75	1.25	2.39	0.81	1.62	0.87	3.8	1.1	0.57	1.80	0.45
1.35	1.77	2.31	1.71	1.68	1	4	1.46	0.48	1.81	0.40
1.13	1.07	1.53	2.03	2.05	1.61	4.2	1.90	0.25	1.24	0.25
1.11	1.25	1.19	1.9	2.08	1.98	4.4	1.99	0.07	1.18	0.09
1.02	1.05	1.04	2.15	1.81	2.1	4.6	2.02	0.02	1.04	0.18

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**Table A-2 Solubilization parameter (*SP*) of benzene in 9AMA: 1Dowfax surfactant system at 20 %wt**

SP <sub>w1</sub>	SP <sub>w2</sub>	SP <sub>w3</sub>	SP <sub>o1</sub>	SP <sub>o2</sub>	SP <sub>o3</sub>	NaCl (%wt)	SP <sub>oaverage</sub>	SD	SP <sub>waverage</sub>	SD
1.927	2.32	2.1	1.523	1.84	1.81	3	1.72	0.20	2.12	0.18
2.097	2.28	1.73	1.813	1.85	2.25	3.5	1.97	0.28	2.04	0.24
1.777	1.86	1.8	1.833	2.25	2.19	3.8	2.09	0.04	1.81	0.23
0.857	1.02	2.16	2.783	3.03	1.86	4	2.56	0.71	1.35	0.62
1.337	1.6	1.33	2.733	2.29	3.03	4.2	2.68	0.15	1.42	0.37
1.317	1.17	0.8	3.253	3.01	3.45	4.4	3.24	0.27	1.10	0.22
0.837	1.87	0.97	2.553	1.94	3.14	4.6	2.54	0.56	1.23	0.60

**Table A-3 Solubilization parameter (*SP*) of toluene in 9AMA: 1Dowfax surfactant system at 20 %wt**

SP <sub>w1</sub>	SP <sub>w2</sub>	SP <sub>w3</sub>	SP <sub>o1</sub>	SP <sub>o2</sub>	SP <sub>o3</sub>	NaCl (%wt)	SP <sub>oaverage</sub>	SD	SP <sub>waverage</sub>	SD
3.487	-	-	1.573	-	-	3	0.52	-	1.16	-
2.327	3.14	3.38	1.013	1.11	0.81	3.5	0.98	0.55	2.95	0.15
2.327	2.1	2.82	1.853	1.81	1.19	3.8	1.62	0.37	2.42	0.37
1.327	2.07	2.54	2.303	1.78	1.36	4	1.81	0.61	1.98	0.47
1.447	2.06	1.72	2.303	1.59	1.95	4.2	1.95	0.31	1.74	0.36
0.957	1.69	0.87	2.713	1.86	1.94	4.4	2.17	0.45	1.17	0.47
1.007	1.58	1.52	2.653	2.26	2.24	4.6	2.38	0.31	1.37	0.23

**Table A-4 Solubilization parameter (*SP*) of xylene in 9AMA: 1Dowfax surfactant system at 20 %wt**

SP <sub>w1</sub>	SP <sub>w2</sub>	SP <sub>w3</sub>	SP <sub>o1</sub>	SP <sub>o2</sub>	SP <sub>o3</sub>	NaCl (%wt)	SP <sub>oaverage</sub>	SD	SP <sub>waverage</sub>	SD
3.027	-	-	1.593	-	0.89	3.8	0.83	-	1.01	0.80
2.737	3.25	3.58	1.523	0.75	1.29	4	1.19	0.42	3.19	0.40
2.207	2.83	3.15	1.453	1.3	1.38	4.2	1.38	0.48	2.73	0.08
1.957	2.29	2.83	1.483	1.53	1.84	4.4	1.62	0.44	2.36	0.19
1.477	1.84	2.7	2.233	1.74	1.52	4.6	1.83	0.63	2.01	0.37
1.923	2.303	2.063	1.407	1.057	2.063	5.2	1.51	0.19	2.10	0.51

**Table A-5 Relationship between  $\ln S^*$  vs oils' EACN of two surfactant systems**

Oil	EACN	$\ln S^*$	$S^*$
benzene	0	1.2179	3.38
toluene	1	1.4098	4.095
xylene	2	1.6864	5.4
<b>Equation</b>	$\ln S^* = 0.2343EACN + 1.2038$		



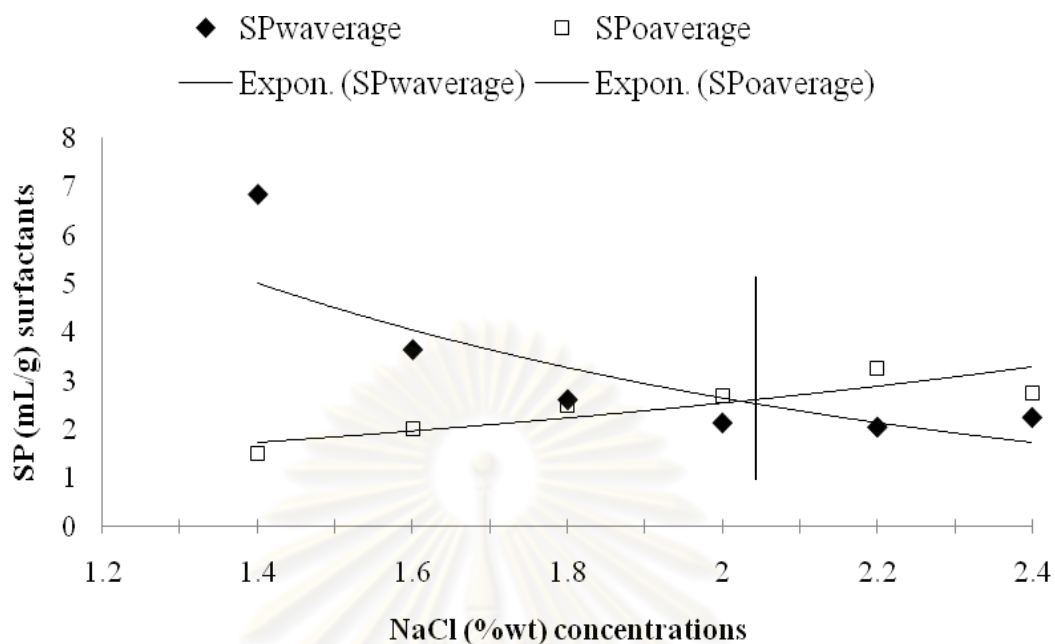
## APPENDIX B

### Experiment data of section 4.2 phase behavior study

**Table B-1 Solubilization parameter (*SP*) of hexane only in AOT/AMA surfactant system at 4 %wt**

$SP_{w_1}$	$SP_{w_2}$	$SP_{w_3}$	$SP_{o_1}$	$SP_{o_2}$	$SP_{o_3}$	NaCl (%WT)	$SP_{w_{average}}$	SD	$SP_{o_{average}}$	SD
-	6.78	6.91	-	1.35	1.66	1.4	6.845	0.09	1.505	0.22
3.27	3.79	3.88	2.373	1.89	1.75	1.6	3.647	0.33	2.004	0.33
2.707	2.55	2.59	2.493	2.36	2.62	1.8	2.616	0.08	2.491	0.13
1.907	2.23	2.28	2.853	2.63	2.6	2	2.139	0.20	2.694	0.14
2.007	2.19	1.96	3.963	2.79	2.99	2.2	2.052	0.12	3.248	0.63
-	2.25	2.24	-	2.6	2.88	2.4	2.25	0.01	2.74	0.20

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**Figure B-1** The  $S^*$  of hexane only in AOT/AMA surfactant system at 4 %wt

**Table B-2** Solubilization parameter ( $SP$ ) of hexane mixed with ferrocene 50 ppm in AOT/AMA surfactant system at 4 %wt

$SP_{w_1}$	$SP_{w_2}$	$SP_{w_3}$	$SP_{o_1}$	$SP_{o_2}$	$SP_{o_3}$	NaCl (%WT)	$SP_{w_{average}}$	SD	$SP_{o_{average}}$	SD
7.447	6.85	6.03	1.873	1.52	1.24	1.4	6.776	0.71	1.544	0.32
3.317	5.77	5.41	2.043	1.112	0.98	1.6	4.832	1.32	1.378	0.58
2.467	5.68	5.12	2.483	1.04	0.74	1.8	4.422	1.72	1.421	0.93
1.087	3.95	2.89	4.133	0.98	1.46	2	2.642	1.45	2.191	1.70
1.857	2.72	2.95	4.113	1.58	1.28	2.2	2.509	0.58	2.324	1.56
-	2.55	2.5	-	1.24	1.24	2.4	2.525	0.04	1.240	0.00
-	2.05	2.31	-	1.6	1.24	2.6	2.180	0.18	1.420	0.25

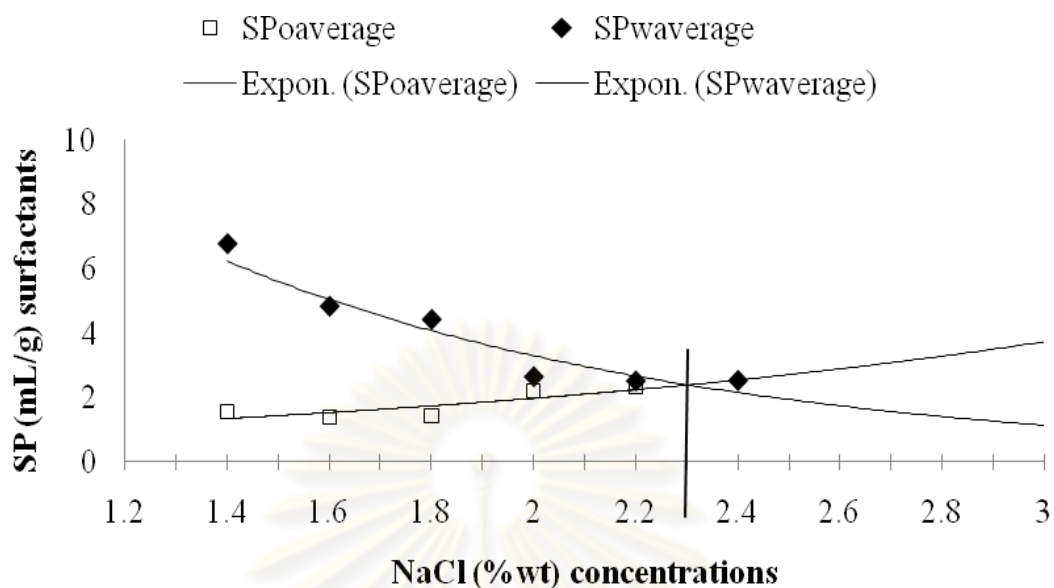
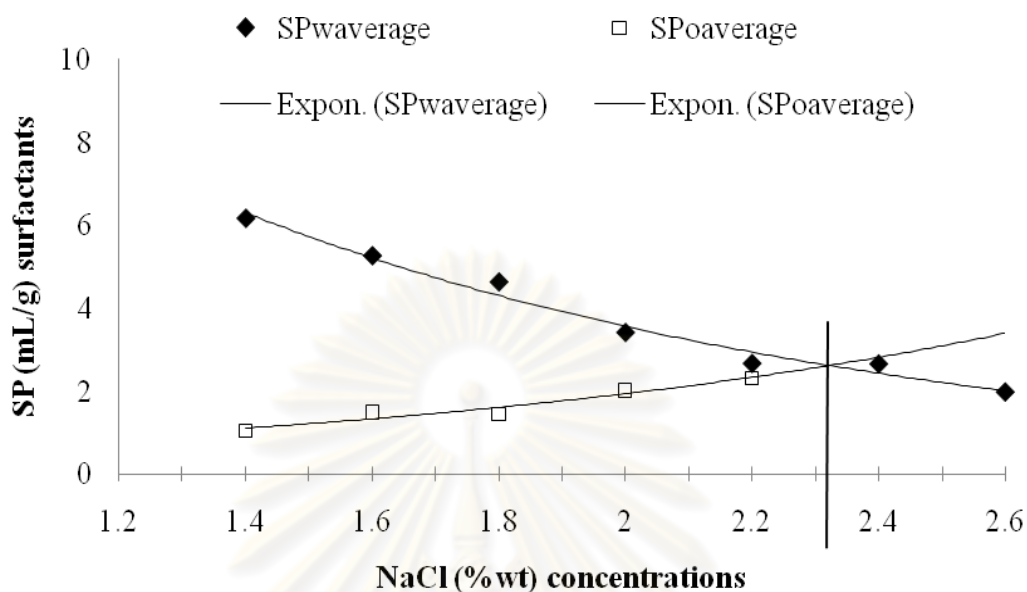


Figure B-2 The  $S^*$  of hexane mixed with ferrocene 50 ppm in AOT/AMA surfactant system at 4 %wt

Table B-3 Solubilization parameter ( $SP$ ) of hexane mixed with ferrocene 100 ppm in AOT/AMA surfactant system at 4 %wt

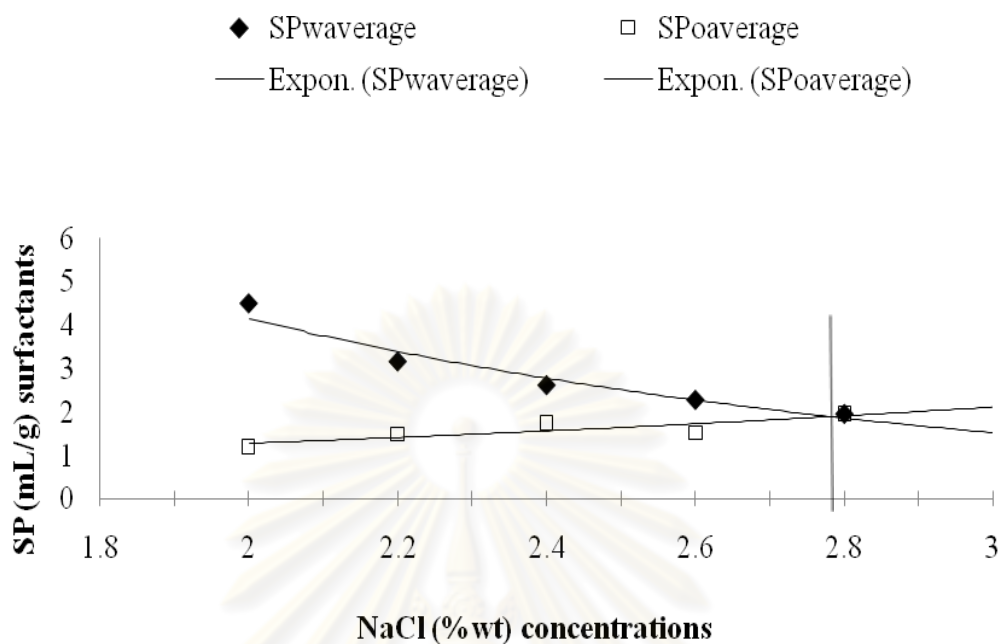
$SPw_1$	$SPw_2$	$SPw_3$	$SPo_1$	$SPo_2$	$SPo_3$	NaCl (%WT)	$SPw_{average}$	SD	$SPo_{average}$	SD
6.517	5.86	6.16	1.623	0.84	0.69	1.4	6.179	0.33	1.051	0.50
4.157	5.73	5.94	2.533	1.13	0.83	1.6	5.276	0.97	1.498	0.91
2.497	6.76	4.67	2.483	1.07	0.81	1.8	4.642	2.13	1.454	0.90
2.707	4.04	3.52	4.133	0.86	1.07	2	3.422	0.67	2.021	1.83
2.237	3.17	2.62	4.113	1.31	1.5	2.2	2.676	0.47	2.308	1.57
-	2.3	3.03	-	1.38	0.62	2.4	2.665	0.52	1.000	0.54
-	2	1.97	-	1.53	1.59	2.6	1.985	0.02	1.560	0.04



**Figure B-3** The  $S^*$  of hexane mixed with ferrocene 100 ppm in AOT/AMA surfactant system at 4 %wt

**Table B-4** Solubilization parameter ( $SP$ ) of octane only in AOT/AMA surfactant system at 4 %wt

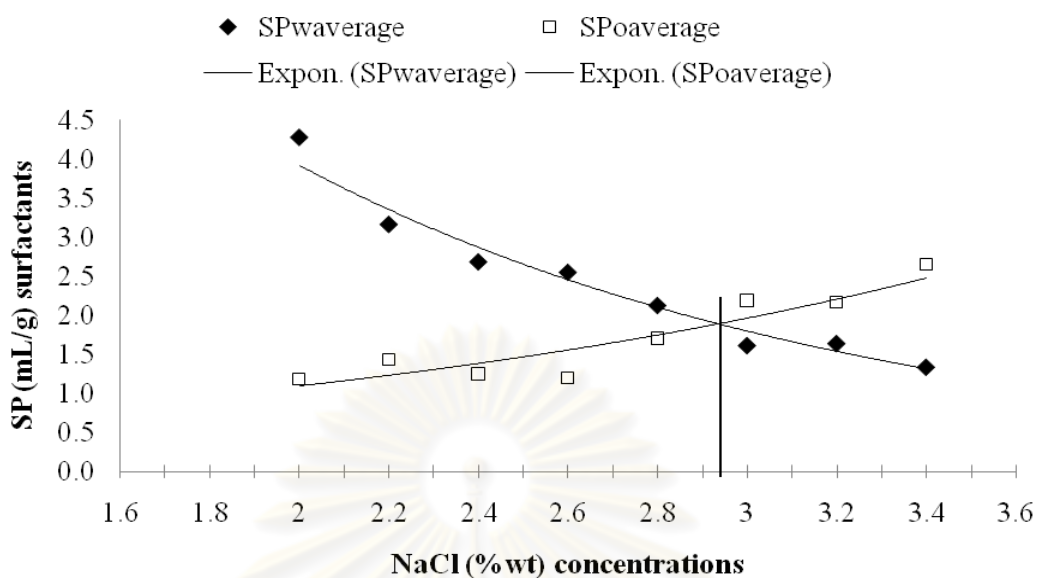
$SP_{w_1}$	$SP_{w_2}$	$SP_{w_3}$	$SP_{o_1}$	$SP_{o_2}$	$SP_{o_3}$	NaCl (%WT)	$SP_{w_{average}}$	SD	$SP_{o_{average}}$	SD
4.417	4.803	4.243	1.433	1.257	0.897	2	4.488	0.29	1.196	0.27
3.197	3.263	2.993	1.493	1.387	1.567	2.2	3.151	0.14	1.482	0.09
2.947	2.463	2.413	1.673	1.747	1.807	2.4	2.608	0.29	1.742	0.07
2.507	2.243	2.053	1.023	1.757	1.757	2.6	2.268	0.23	1.512	0.42
2.333	1.653	1.853	1.447	2.467	1.967	2.8	1.946	0.35	1.960	0.51



**Figure B-4** The  $S^*$  of octane only in AOT/AMA surfactant system at 4 %wt

**Table B-5** Solubilization parameter ( $SP$ ) of octane mixed with ferrocene 50 ppm in AOT/AMA surfactant system at 4 %wt

$SP_{w_1}$	$SP_{w_2}$	$SP_{w_3}$	$SP_{o_1}$	$SP_{o_2}$	$SP_{o_3}$	NaCl (% WT)	$SP_{w_{average}}$	SD	$SP_{o_{average}}$	SD
4.317	4.333	4.203	1.343	1.287	0.937	2	4.284	0.07	1.189	0.22
3.147	3.483	2.883	1.413	1.127	1.777	2.2	3.171	0.30	1.439	0.33
2.667	2.703	2.703	0.903	1.597	1.247	2.4	2.691	0.02	1.249	0.35
2.357	2.733	2.583	1.133	1.137	1.337	2.6	2.558	0.19	1.202	0.12
2.243	2.253	1.903	1.377	1.637	2.107	2.8	2.133	0.20	1.707	0.37
1.723	1.903	1.233	1.897	1.907	2.777	3	1.620	0.35	2.194	0.51
1.723	1.563	1.653	2.087	2.267	2.157	3.2	1.646	0.08	2.170	0.09
-	1.183	1.503	-	2.907	2.397	3.4	1.343	0.23	2.652	0.36

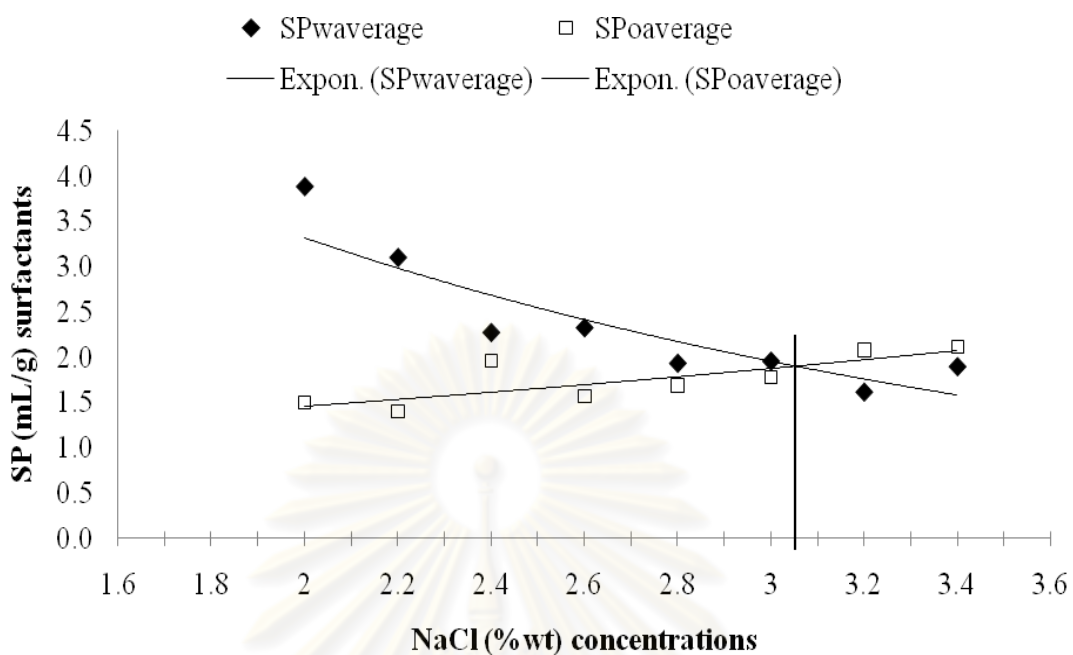


**Figure B-5** The  $S^*$  of octane mixed with ferrocene 50 ppm in AOT/AMA surfactant system at 4 %wt

**Table B-6** Solubilization parameter ( $SP$ ) of octane mixed with ferrocene 100 ppm in AOT/AMA surfactant system at 4 %wt

$SP_{w_1}$	$SP_{w_2}$	$SP_{w_3}$	$SP_{o_1}$	$SP_{o_2}$	$SP_{o_3}$	NaCl (%WT)	$SP_{w_{average}}$	SD	$SP_{o_{average}}$	SD
3.537	3.873	4.243	1.643	1.547	1.297	2	3.884	0.35	1.496	0.18
3.487	2.833	2.993	1.153	1.707	1.337	2.2	3.104	0.34	1.399	0.28
1.587	2.833	2.413	2.643	1.447	1.777	2.4	2.278	0.63	1.956	0.62
2.627	2.313	2.053	0.923	1.737	2.037	2.6	2.331	0.29	1.566	0.58
2.053	1.913	1.853	1.527	1.937	1.577	2.8	1.940	0.10	1.680	0.22
2.113	1.983	1.793	1.497	1.657	2.177	3	1.963	0.16	1.777	0.36
1.603	1.673	1.593	2.127	2.067	2.027	3.2	1.623	0.04	2.074	0.05
-	1.913	1.893	-	1.957	2.257	3.4	1.903	0.01	2.107	0.21

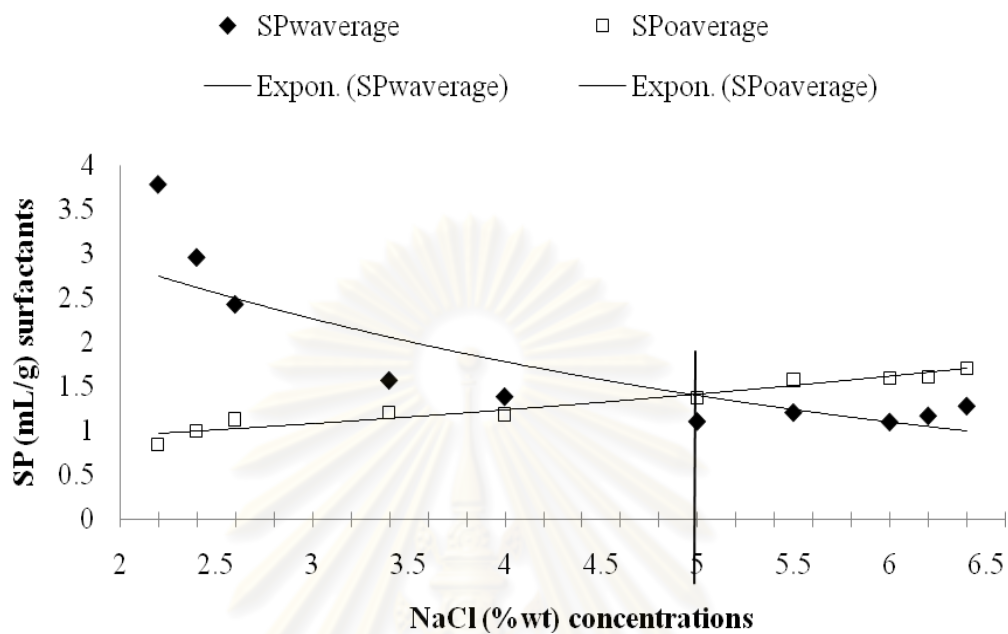




**Figure B-6 The  $S^*$  of octane mixed with ferrocene 100 ppm in AOT/AMA surfactant system at 4 %wt**

**Table B-7 Solubilization parameter (SP) of decane only in AOT/AMA surfactant system at 4 %wt**

SPw <sub>1</sub>	SPw <sub>2</sub>	SPw <sub>3</sub>	SPo <sub>1</sub>	SPo <sub>2</sub>	SPo <sub>3</sub>	NaCl (%WT)	SPw <sub>average</sub>	SD	SPo <sub>average</sub>	SD
2.187	4.31	4.85	1.153	0.54	0.86	2.2	3.782	1.41	0.851	0.31
3.187	2.85	2.84	0.017	1.42	1.56	2.4	2.959	0.20	0.999	0.85
2.897	2.4	1.99	0.743	1.14	1.52	2.6	2.429	0.45	1.134	0.39
1.46	1.81	1.44	1.21	0.85	1.56	3.4	1.570	0.21	1.207	0.36
1.43	1.27	1.46	1.25	1.19	1.12	4	1.387	0.10	1.187	0.07
1.5	0.89	0.93	0.86	1.6	1.66	5	1.107	0.34	1.373	0.45
0.91	1.15	1.56	1.83	1.78	1.11	5.5	1.207	0.33	1.573	0.40
1.35	1	0.95	1.27	1.66	1.87	6	1.100	0.22	1.600	0.30
1.03	0.89	1.59	1.95	1.95	0.94	6.2	1.170	0.37	1.613	0.58
1.24	1.32	-	1.78	1.63	-	6.4	1.280	0.06	1.705	0.11

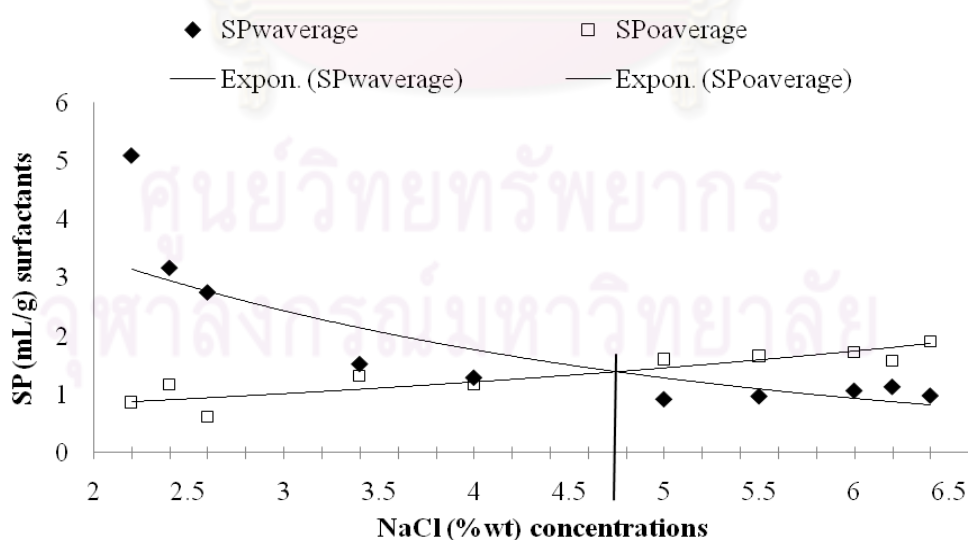


**Figure B-7 The  $S^*$  of decane only in AOT/AMA surfactant system at 4 %wt**

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**Table B-8 Solubilization parameter ( $SP$ ) of decane mixed with ferrocene 50 ppm in AOT/AMA surfactant system at 4 %wt**

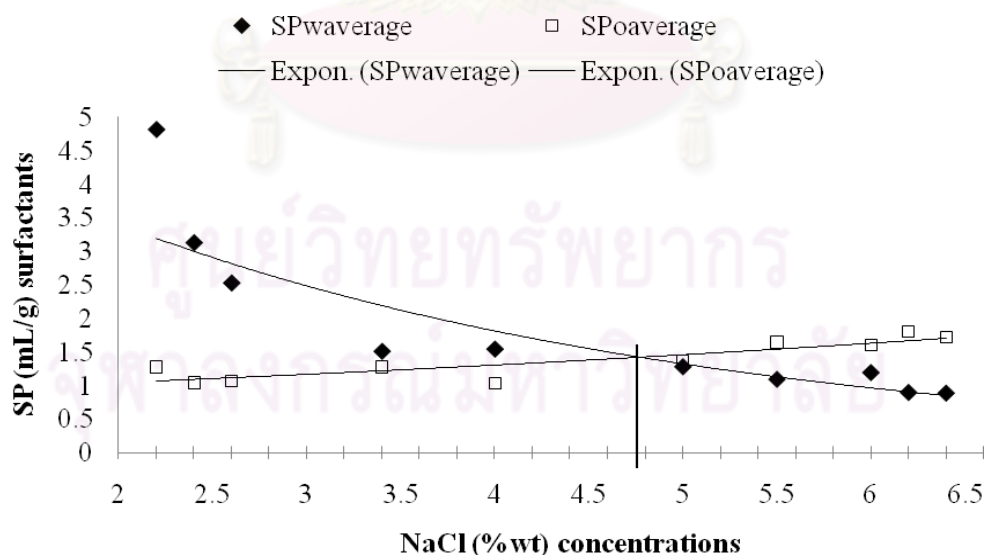
$SP_{w_1}$	$SP_{w_2}$	$SP_{w_3}$	$SP_{o_1}$	$SP_{o_2}$	$SP_{o_3}$	NaCl (%WT)	$SP_{w_{average}}$	SD	$SP_{o_{average}}$	SD
6.307	4.72	4.25	0.033	1.11	1.45	2.2	5.092	1.08	0.864	0.74
3.257	3.12	3.12	0.573	1.49	1.45	2.4	3.166	0.08	1.171	0.52
3.087	2.08	3.07	0.063	1.35	0.44	2.6	2.746	0.58	0.618	0.66
1.44	1.72	1.39	1.32	1.21	1.43	3.4	1.517	0.18	1.320	0.11
1.12	1.52	1.21	1.36	0.94	1.24	4	1.283	0.21	1.180	0.22
0.82	0.94	0.98	1.71	1.53	1.59	5	0.913	0.08	1.610	0.09
0.64	0.73	1.52	1.8	1.97	1.21	5.5	0.963	0.48	1.660	0.40
0.62	0.9	1.66	2.12	1.87	1.21	6	1.060	0.54	1.733	0.47
1.04	1.56	0.78	1.65	1.14	1.95	6.2	1.127	0.40	1.580	0.41
0.88	1.07	-	2.02	1.8	-	6.4	0.975	0.13	1.910	0.16



**Figure B-8 The  $S^*$  of decane mixed with ferrocene 50 ppm in AOT/AMA surfactant system at 4 %wt**

**Table B-9 Solubilization parameter (SP) of decane mixed with ferrocene 100 ppm in AOT/AMA surfactant system at 4 %wt**

SPw <sub>1</sub>	SPw <sub>2</sub>	SPw <sub>3</sub>	SPo <sub>1</sub>	SPo <sub>2</sub>	SPo <sub>3</sub>	NaCl (%WT)	SPw <sub>average</sub>	SD	SPo <sub>average</sub>	SD
4.627	4.15	5.7	1.203	1.45	1.19	2.2	4.826	0.79	1.281	0.15
3.227	3.1	3.09	0.703	1.23	1.21	2.4	3.139	0.08	1.048	0.30
2.887	1.87	2.86	0.823	1.68	0.71	2.6	2.539	0.58	1.071	0.53
1.76	1.09	1.71	0.95	1.73	1.16	3.4	1.520	0.37	1.280	0.40
1.76	1.49	1.41	0.79	1.19	1.14	4	1.553	0.18	1.040	0.22
1.14	1.09	1.64	1.5	1.49	1.1	5	1.290	0.30	1.363	0.23
1.16	1.01	1.14	1.65	1.64	1.65	5.5	1.103	0.08	1.647	0.01
1.07	1	1.54	1.77	1.82	1.24	6	1.203	0.29	1.610	0.32
0.57	0.67	1.48	2.1	2.09	1.22	6.2	0.907	0.50	1.803	0.51
0.56	0.82	1.31	2.14	1.92	1.12	6.4	0.897	0.38	1.727	0.54



**Figure B-9 The S\* of decane mixed with ferrocene 100 ppm in AOT/AMA surfactant system at 4 %wt**

## APPENDIX C

### Experiment data of section 4.3 solubilization study

Table C-1 Standard curve of hexane measured by GC-HS

concentration (mg/L)	area				
	1	2	3	SD	average
10000	5341150	5355794	5287693	35847	5328212
1000	238616	233535	232164	3399	234771.7
500	114910	117260	-	1662	116085
100	17787	19318	19795	1049	18966.67
50	11658	9165	9467	1361	10096.67
10	7125	7143	-	13	7134

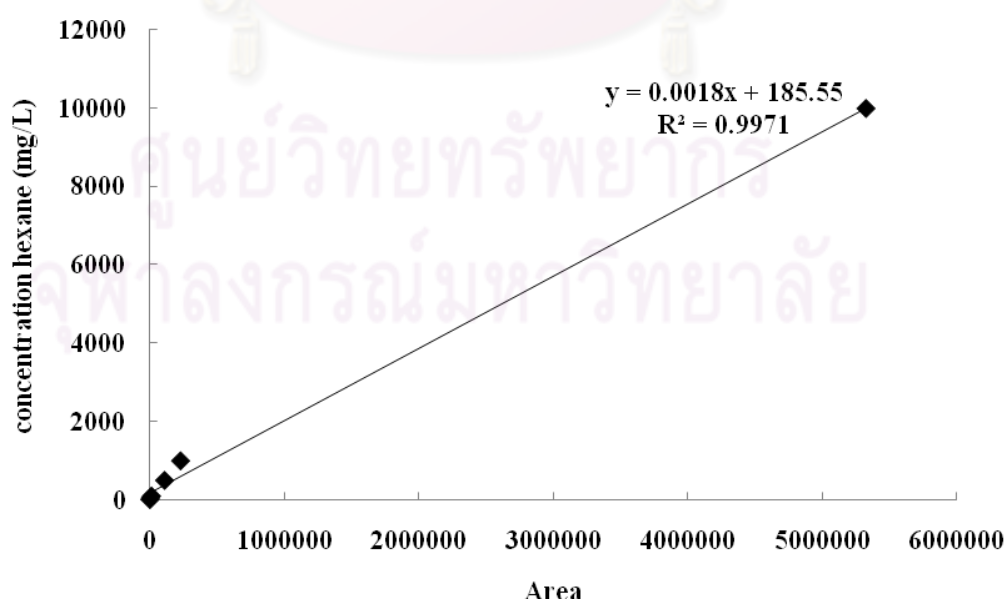


Figure C-1 Standard curve of hexane measured by GC-HS

Table C-2 Standard curve of octane measured by GC-HS

Concentration (ppm)	Area			
	1	2	average	SD
3000	2518311.40	2484524.38	2501417.89	23891
2000	1725978.94	1625557.41	1675768.18	71008.7
1000	796568.31	818148.6	807358.46	15259.6
500	352301.42	348121.87	350211.65	2955.39
100	37249.41	37969.26	37609.34	509.011
50	20351.33	18652.98	19502.16	1200.91
10	5555.03	6115.48	5835.26	396.298
5	4461	-	4461.00	-
3	2551.97	2993.24	2772.61	312.025
1	1479.1	1520.6	1499.85	29.3449

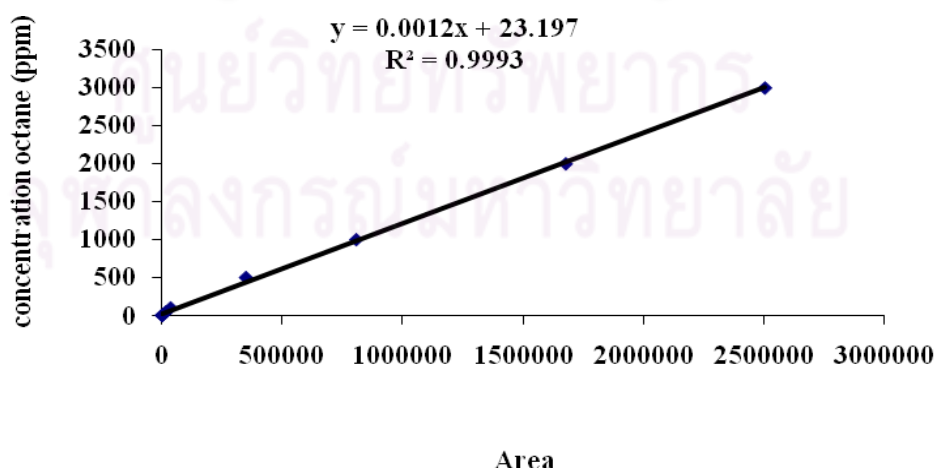


Figure C-2 Standard curve of octane measured by GC-HS



Table C-3 Standard curve of decane measured by GC-HS

Concentration (ppm)	area			
	1	2	Average	SD
3000	2718772.62	2660796.60	2689784.61	40995.2
2000	1869524.31	1762145.53	1815834.92	75928.3
1000	869676.57	897164.53	883420.55	19436.9
500	418802.54	410125.75	414464.15	6135.42
100	38837.76	39980.14	39408.95	807.785
50	18938.72	18119	18528.86	579.63
10	3901.85	3852.55	3877.20	34.8604
5	3267.34	-	3267.34	-
3	2605.65	2871.03	2738.34	187.652
1	-	1102.52	1102.52	-

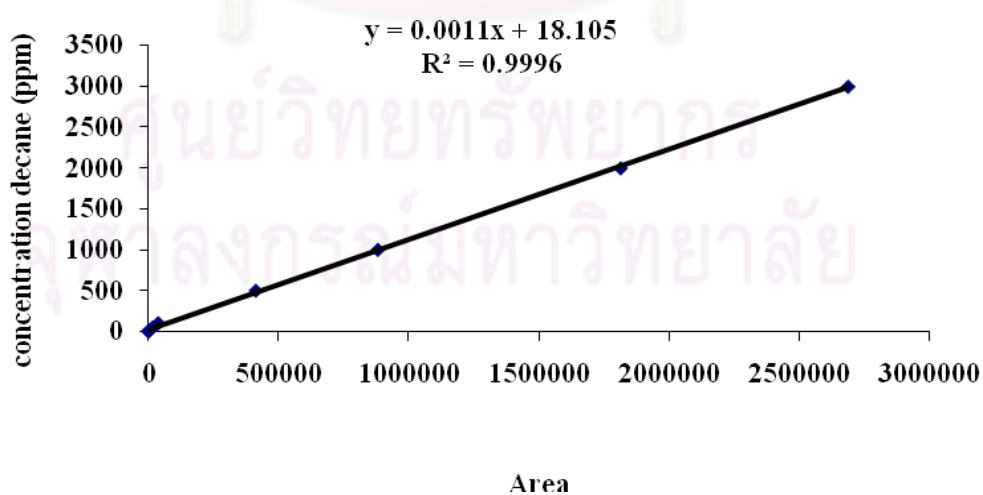


Figure C-2 Standard curve of decane measured by GC-HS

**Table C-3 Solubilization capacity for alkanes and Fe (total iron) at the AMA-AOT at 4%wt (ratio 2:2) surfactant system in various concentration electrolytes (NaCl)**

Alkanes system	NaCl (%wt)	Type system	Solubilization	
			Alkane (ppm)	Total Fe (ppb)
Hexane 1	1	I	15549.15	N
Hexane 2	1.1	sps	29543.4	N
Hexane 3	1.2	sps	33043.7	N
Hexane 4	1.4	III	73493.83	N
Hexane mixed F100ppm 1	1	I	14025.27	1600
Hexane mixed F100ppm 2	1.1	sps	15924.3	3775
Hexane mixed F100ppm 3	1.2	sps	16004.7	3675
Hexane mixed F100ppm 4	1.4	III	33757.33	4175
Octane 1	1.2	I	32416.5	N
Octane 2	1.4	I	45753.83	N
Octane 3	1.6	sps	61620.75	N
Octane 4	1.9	III	64219.5	N

*Note:* I and III refer to the type of microemulsion; SPS refers to supersolubilization, where the microemulsion occurs at the point close to the transition from Type I to Type III; and N is an appearance that did not analyzed.

**Table C-3 (continue) Solubilization capacity for alkanes and Fe (total iron) at the AMA-AOT at 4%wt (ratio 2:2) surfactant system in various concentration electrolytes (NaCl)**

Alkanes system	NaCl (%wt)	Type system	Solubilization	
			Alkane (ppm)	Total Fe (ppb)
Octane mixed F100ppm 1	1.2	I	39169.8	2613.96
Octane mixed F100ppm 2	1.4	I	45780.25	3603.95
Octane mixed F100ppm 3	1.6	sps	64290	4198.95
Octane mixed F100ppm 4	1.9	III	69336	5073.96
Decane 1	1.6	I	20065.88	N
Decane 2	1.8	sps	21691.61	N
Decane 3	2	sps	23985.7	N
Decane 4	2.3	III	25705.8	N
Decane mixed F100ppm 1	1.6	I	38533.5	4416.45
Decane mixed F100ppm 2	1.8	sps	47718.45	3616.45
Decane mixed F100ppm 3	2	sps	51401.75	6271.45
Decane mixed F100ppm 4	2.3	III	53048.96	6208.95

*Note:* I and III refer to the type of microemulsion; SPS refers to supersolubilization, where the microemulsion occurs at the point close to the transition from Type I to Type III; and N is an appearance that did not analyzed.

## APPENDIX D

### Experimental Data of Section 4.4 Column study

#### Terms Notification

- (i) **The volume of alkanes entrapment (Pabute, 2005)**

$$A = x - (y + z)$$

where A = Volume of residual alkanes in the column (mL)

x = Volume of alkanes before the contamination procedure (total oil introduced to the column) (mL)

y = Volume of alkanes after the contamination procedure (exiting column during alkanes flooding) (mL)

z = Volume of the free phase of alkanes leaving the column during water flushing (mL)

- (ii) **%Residual saturation ( $S_N$ )**

$$S_N = (A / B) \times 100$$

where A = Volume of residual alkanes in the column (mL)

B = Volume of pore space (mL)

**(iii) %Efficiency**

$$\text{Efficiency} = (S+M) \times 100$$

where S = mass solubilization of alkanes (mg)

M = mass mobilization of alkanes (mg)

**(iv) %Mass balance**

$$\text{Mass balance} = [(S+M+E)/A] \times 100$$

where S = mass solubilization of alkanes (mg)

M = mass mobilization of alkanes (mg)

E = mass extraction of alkanes (mg)

A = mass of residual alkanes in column (mg)



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**Table D-1 decane only concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	PV	Solubilization of decane			Mobilize
		mg/L	mg	Accumulate mass (mg)	
No.1	0.25	151.28	1.21	0	-
No.2	0.51	0	0.00	0.61	-
No.3	0.76	0	0.00	0.61	-
No.4	1.02	0	0.00	0.61	-
No.5	1.27	0	0.00	0.61	-
No.6	1.53	0	0.00	0.61	-
No.7	1.78	2184.96	17.48	9.34	*
No.8	2.03	1333.45	10.67	23.42	*
No.9	2.29	1777.94	14.22	35.86	*
No.10	2.54	17372.2	138.98	112.46	-
No.11	2.8	19703.4	157.63	260.77	-
No.12	3.05	2144.63	17.16	348.16	-
No.13	3.31	521.74	4.17	358.82	-
No.14	3.56	424.3	3.39	362.61	-
No.15	3.81	277.43	2.22	365.42	-
No.16	4.07	201.72	1.61	367.33	-
No.17	4.32	150.43	1.20	368.74	-
No.18	4.58	116.39	0.93	369.81	-
No.19	4.83	98.36	0.79	370.67	-
No.20	5.09	74.84	0.60	371.36	-
No.25	6.36	48.77	0.39	373.83	-



**Table D-1 (continue) decane only concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	PV	Solubilization of decane			Mobilize
		mg/L	mg	Accumulate mass (mg)	
No.30	7.63	38.11	0.30	375.57	-
No.35	8.9	30.48	0.24	376.94	-
No.36	9.15	29.44	0.24	377.18	-
No.37	9.41	29.1	0.23	377.42	-
No.38	9.66	28.29	0.23	377.65	-
No.39	9.92	26.57	0.21	377.86	-
No.40	10.17	27.06	0.22	378.08	-
No.45	11.44	25.16	0.20	379.12	-
No.50	12.71	23.72	0.19	380.10	-
No.55	13.99	22.05	0.18	381.02	-
No.60	15.26	21.2	0.17	381.88	-
No.65	16.53	20.61	0.16	382.72	-
No.70	17.8	21.86	0.17	383.57	-
No.75	19.07	21.09	0.17	384.43	-
No.80	20.34	20.99	0.17	385.27	-
No.85	21.61	20.45	0.16	386.10	-

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**Table D-2 decane mixed with ferrocene 100 ppm concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	Solubilized decane				Mobilized
	PV	mg/L	mg	Accumulate mass (mg)	
No.1	0.25	1138.60	9.11	0	-
No.2	0.51	0	0.00	4.554	-
No.3	0.76	0	0.00	4.554	-
No.4	1.02	0	0.00	4.554	-
No.5	1.27	0	0.00	4.554	-
No.6	1.52	4657.37	37.26	23.184	-
No.7	1.78	0	0.00	41.813	-
No.8	2.03	0	0.00	41.813	-
No.9	2.28	12488.4	99.91	91.767	*
No.10	2.54	10419.9	83.36	183.4	*
No.11	2.79	17793.5	142.35	296.253	*
No.12	3.05	1051.43	8.41	371.633	-
No.13	3.30	459.96	3.68	377.679	-
No.14	3.55	441.34	3.53	381.284	-
No.15	3.81	331.05	2.65	384.373	-
No.16	4.06	239.74	1.92	386.657	-
No.17	4.31	196.29	1.57	388.401	-
No.18	4.57	168.06	1.34	389.858	-
No.19	4.82	146.28	1.17	391.116	-
No.20	5.08	124.56	1.00	392.199	-
No.25	6.35	64.01	0.51	395.97	-
No.30	7.61	44.08	0.35	398.132	-
No.35	8.88	33.15	0.27	399.677	-
No.40	10.15	29.25	0.23	400.925	-
No.45	11.42	25.81	0.21	402.026	-
No.50	12.69	23.52	0.19	403.013	-
No.55	13.96	22.00	0.18	403.923	-
No.60	15.23	21.33	0.17	404.79	-
No.65	16.50	20.71	0.17	405.631	-

**Table D-3 ferrocene mixed in decane concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	Solubilized ferrocene				Mobilized
	PV	$\mu\text{g/L}$	$\mu\text{g}$	Accumulate mass (ug)	
No.1	0.25	4.05	0.0324	0	-
No.2	0.51	21.55	0.1724	0.10	-
No.3	0.76	57.2	0.4576	0.42	-
No.4	1.02	1.85	0.0148	0.65	-
No.5	1.27	149.45	1.1956	1.26	-
No.6	1.52	10.4	0.0832	1.90	-
No.7	1.78	51.45	0.4116	2.15	-
No.8	2.03	14.2	0.1136	2.41	-
No.9	2.28	258.825	2.0706	3.50	*
No.10	2.54	182.6	1.4608	5.27	*
No.11	2.79	285.325	2.2826	7.14	*
No.12	3.05	203.2	1.6256	9.09	-
No.13	3.30	226.725	1.8138	10.81	-
No.14	3.55	136.525	1.0922	12.26	-
No.15	3.81	348.075	2.7846	14.20	-
No.16	4.06	90.775	0.7262	15.96	-
No.17	4.31	158.6	1.2688	16.96	-
No.18	4.57	17.625	0.1410	17.66	-
No.19	4.82	147.275	1.1782	18.32	-
No.20	5.08	183.975	1.4718	19.65	-
No.25	6.35	62.35	0.4988	24.57	-
No.30	7.61	210.2	1.6816	30.02	-
No.35	8.88	111.7	0.8936	36.46	-
No.40	10.15	84.25	0.6740	40.38	-
No.45	11.42	91	0.7280	43.88	-
No.50	12.69	105.425	0.8434	47.81	-
No.55	13.96	20.15	0.1612	50.32	-
No.60	15.23	44.05	0.3524	51.61	-
No.65	16.50	65.1	0.5208	53.79	-

**Table D-4 octane only concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 1.6 wt% NaCl**

No.	Solubilized octane				Mobilized
	PV	mg/L	mg	Accumulate mass (mg)	
No.1	0.24	40.95	0.33	0	-
No.2	0.49	0	0	0.1638	-
No.3	0.73	0	0	0.1638	-
No.4	0.98	0	0	0.1638	-
No.5	1.22	0	0	0.1638	-
No.6	1.46	0	0	0.1638	-
No.7	1.71	0	0	0.1638	-
No.8	1.95	0	0	0.1638	-
No.9	2.20	0	0	0.1638	-
No.10	2.44	2010.39	16.08	8.2053	*
No.11	2.69	1677.14	13.42	22.9555	*
No.12	2.93	29271.36	234.17	146.7494	*
No.13	3.17	398.34	3.19	265.4282	-
No.14	3.42	230.64	1.85	267.9441	-
No.15	3.66	187.52	1.50	269.6168	-
No.16	3.91	150.93	1.21	270.9706	-
No.17	4.15	120.58	0.96	272.0567	-
No.18	4.39	108.53	0.87	272.9731	-
No.19	4.64	103.75	0.83	273.8222	-
No.20	4.88	96.88	0.78	274.6248	-
No.25	6.10	96.68	0.77	278.4959	-
No.30	7.32	77.34	0.62	281.9763	-
No.35	8.54	43.71	0.35	284.3973	-
No.40	9.77	36.42	0.29	285.9998	-
No.45	10.99	33.77	0.27	287.4034	-
No.50	12.21	35.34	0.28	288.7856	-
No.55	13.43	28.62	0.23	290.0650	-
No.60	14.65	28.65	0.23	291.2105	-
No.65	15.87	27.42	0.22	292.3320	-
No.70	17.09	26.70	0.21	293.4143	-
No.74	18.31	26.48	0.21	294.4779	-

**Table D-5 octane mixed with ferrocene 100 ppm concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 1.6 wt% NaCl**

No.	Solubilized octane				Mobilized
	PV	mg/L	mg	Accumulate mass (mg)	
No.1	0.24	32.0158	0.2561	0	-
No.2	0.49	0	0	0.1281	-
No.3	0.73	0	0	0.1281	-
No.4	0.97	0	0	0.1281	-
No.5	1.21	0	0	0.1281	-
No.6	1.46	840.2974	6.7224	3.4893	-
No.7	1.70	495.853	3.9668	8.8339	-
No.8	1.94	0	0.0000	10.8173	-
No.9	2.18	18190	145.5200	83.5773	*
No.10	2.43	247.738	1.9819	157.3282	*
No.11	2.67	14158.13	113.2650	214.9517	*
No.12	2.91	506.17	4.0494	273.6089	-
No.13	3.15	420.4798	3.3638	277.3155	-
No.14	3.40	326.3362	2.6107	280.3027	-
No.15	3.64	227.959	1.8237	282.5199	-
No.16	3.88	173.6386	1.3891	284.1263	-
No.17	4.12	164.5906	1.3167	285.4792	-
No.18	4.37	134.1946	1.0736	286.6744	-
No.19	4.61	117.307	0.9385	287.6804	-
No.20	4.85	99.9454	0.7996	288.5494	-
No.25	6.06	66.6262	0.5330	291.8808	-

**Table D-5 (continue) octane mixed with ferrocene 100 ppm concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 1.6 wt% NaCl**

No.	Solubilized octane				Mobilized
	PV	mg/L	mg	Accumulate mass (mg)	
No.30	7.28	47.3098	0.3785	294.1595	-
No.35	8.49	39.4834	0.3159	295.8954	-
No.40	9.70	35.461	0.2837	297.3943	-
No.45	10.92	31.513	0.2521	298.7338	-
No.50	12.13	31.1026	0.2488	299.9861	-
No.55	13.34	28.6318	0.2291	301.1808	-
No.60	14.55	28.5826	0.2287	302.3250	-
No.65	15.77	27.6274	0.2210	303.4492	-
No.70	16.98	27.1594	0.2173	304.5450	-
No.75	18.19	26.743	0.2139	305.6230	-
No.77	18.68	27.1654	0.2173	306.0543	-

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**Table D-6 ferrocene mixed in octane concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 1.6 wt% NaCl**

No.	Solubilized ferrocene				Mobilized
	PV	µg/L	µg	Accumulate mass (µg)	
No.1	0.24	70.48	0.56	0	-
No.2	0.49	56.78	0.45	0.5090	-
No.3	0.73	53.65	0.43	0.9507	-
No.4	0.97	29.73	0.24	1.2842	-
No.5	1.21	20.43	0.16	1.4848	-
No.6	1.46	47.38	0.38	1.7561	-
No.7	1.70	39.75	0.32	2.1046	-
No.8	1.94	41.13	0.33	2.4281	-
No.9	2.18	991.30	7.93	6.5578	*
No.10	2.43	770.25	6.16	13.6040	*
No.11	2.67	858.00	6.86	20.1170	*
No.12	2.91	0	0.00	23.5490	-
No.13	3.15	71.80	0.57	23.8362	-
No.14	3.40	98.75	0.79	24.5184	-
No.15	3.64	54.93	0.44	25.1331	-
No.16	3.88	79.43	0.64	25.6705	-
No.17	4.12	60.83	0.49	26.2315	-
No.18	4.37	37.00	0.30	26.6228	-
No.19	4.61	43.75	0.35	26.9458	-
No.20	4.85	46.98	0.38	27.3087	-
No.25	6.06	49.48	0.40	29.2377	-



**Table D-6 (continue) ferrocene mixed in octane concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 1.6 wt% NaCl**

No.	Solubilized ferrocene				Mobilized
	PV	µg/L	µg	Accumulate mass (µg)	
No.30	7.28	0	0	30.2272	-
No.35	8.49	43.44	0.35	31.0959	-
No.40	9.70	47.50	0.38	32.9147	-
No.45	10.92	41.95	0.34	34.7037	-
No.50	12.13	44.08	0.35	36.4242	-
No.55	13.34	27.60	0.22	37.8578	-
No.60	14.55	25.80	0.21	38.9259	-
No.65	15.77	0.00	0.00	39.4419	-
No.70	16.98	0.00	0.00	39.4419	-
No.75	18.19	32.20	0.26	40.0859	-

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**Table D-7 octane only concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	Solubilized octane				Mobilized
	PV	mg/L	mg	Accumulate mass (mg)	
No.1	0.28	0	0	0	-
No.2	0.55	0	0	0	-
No.3	0.83	0	0	0	-
No.4	1.10	0	0	0	-
No.5	1.38	0	0	0	-
No.6	1.65	322.07	2.58	0.0103	-
No.7	1.93	322.07	2.58	0.0309	-
No.8	2.21	424.46	3.40	0.0548	-
No.9	2.48	774.01	6.19	0.0932	*
No.10	2.76	137.26	1.10	0.1223	*
No.11	3.03	1600.39	12.80	0.1779	*
No.12	3.31	160.39	1.28	0.2343	-
No.13	3.58	111.37	0.89	0.2430	-
No.14	3.86	83.6	0.67	0.2492	-
No.15	4.14	65.96	0.53	0.2540	-
No.16	4.41	57.32	0.46	0.2579	-
No.17	4.69	47.16	0.38	0.2613	-
No.18	4.96	35.54	0.28	0.2639	-
No.19	5.24	54.19	0.43	0.2668	-
No.20	5.52	48.09	0.38	0.2701	-
No.25	6.89	33.96	0.27	0.2832	-
No.30	8.27	29.68	0.24	0.2934	-
No.35	9.65	28.72	0.23	0.3027	-
No.40	11.03	28.23	0.23	0.3118	-
No.45	12.41	27.87	0.22	0.3208	-
No.50	13.79	27.41	0.22	0.3297	-
No.55	15.17	28.46	0.23	0.3386	-
No.60	16.55	26.59	0.21	0.3474	-
No.65	17.92	25.84	0.21	0.3558	-
No.70	19.30	25.42	0.20	0.3640	-

**Table D-8 octane mixed with ferrocene 100 ppm concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	Solubilized octane				Mobilized
	PV	mg/L	mg	Accumulate mass (mg)	
No.1	0.26	0	0	0	-
No.2	0.53	0	0	0	-
No.3	0.79	0	0	0	-
No.4	1.06	0	0	0	-
No.5	1.32	0	0	0	-
No.6	1.59	78.73	0.63	0.0025	-
No.7	1.85	631.55	5.05	0.0252	*
No.8	2.12	771.5	6.17	0.0701	*
No.9	2.38	577.75	4.62	0.1133	*
No.10	2.65	2929.4	23.44	0.2256	*
No.11	2.91	1203.22	9.63	0.3578	-
No.12	3.18	336.56	2.69	0.4071	-
No.13	3.44	699.37	5.59	0.4402	-
No.14	3.71	354.52	2.84	0.4739	-
No.15	3.97	235.04	1.88	0.4928	-
No.16	4.24	160.98	1.29	0.5055	-
No.17	4.50	119.5	0.96	0.5145	-
No.18	4.77	91.5778	0.73	0.5212	-
No.19	5.03	75.02	0.60	0.5265	-
No.20	5.30	67.47	0.54	0.5311	-
No.25	6.62	40.89	0.33	0.5484	-
No.30	7.94	35.02	0.28	0.5606	-
No.35	9.27	30.94	0.25	0.5711	-
No.40	10.59	30.64	0.25	0.5810	-
No.45	11.92	29.93	0.24	0.5907	-
No.50	13.24	47.26	0.38	0.6030	-
No.55	14.56	27.75	0.22	0.6150	-
No.60	15.89	27.69	0.22	0.6239	-
No.65	17.21	27.05	0.22	0.6327	-
No.70	18.59	26.4	0.21	0.6412	-

**Table D-9 ferrocene mixed in octane concentration and weight at different pore volumes of column study flushing with 4 wt% of AMA/AOT and 2 wt% NaCl**

No.	Solubilized octane				Mobilized
	PV	µg/L	µg	Accumulate mass (µg)	
No.1	0.26	0	0	0	-
No.2	0.53	0	0	0.00	-
No.3	0.79	725	5.8	0.02	-
No.4	1.06	675	5.4	0.07	-
No.5	1.32	900	7.2	0.12	-
No.6	1.59	1350	10.8	0.19	-
No.7	1.85	3075	24.6	0.33	*
No.8	2.12	3200	25.6	0.53	*
No.9	2.38	4175	33.4	0.77	*
No.10	2.65	4250	34	1.04	*
No.11	2.91	0	0	1.17	-
No.12	3.18	2525	20.2	1.26	-
No.13	3.44	4025	32.2	1.46	-
No.14	3.71	4425	35.4	1.74	-
No.15	3.97	0	0	1.88	-
No.16	4.24	1025	8.2	1.91	-
No.17	4.50	150	1.2	1.95	-
No.18	4.77	0	0	1.95	-
No.19	5.03	225	1.8	1.96	-
No.20	5.30	150	1.2	1.97	-
No.25	6.62	0	0	2.00	-
No.30	7.94	175	1.4	2.02	-
No.35	9.27	0	0	2.05	-
No.40	10.59	150	1.2	2.08	-
No.45	11.92	0	0	2.10	-
No.50	13.24	75	0.6	2.11	-
No.55	14.56	0	0	2.12	-
No.60	15.89	0	0	2.12	-
No.65	17.21	125	1	2.14	-
No.70	18.53	150	1.2	2.19	-

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