CHAPTER I

INTRODUCTION

Tetraethyl lead (TEL) is an organometallic substance that was extensively used as an additive to prevent knocking in fuel engine. Since it has high toxicity and posed harmful effect to human and environment, the United States Environmental Protection Agency (US EPA) has initiated an approach to phase out this poisonous substance since 1973. However, it is still used in aviation fuel and racing cars (Ouyang et al., 1996). Their contaminations are shown in many sites such as the abandon gas stations, production and storage sites, where an effective remediation technique should be applied to remedy these areas. Therefore, the surfactant enhanced aquifer remediation (SEAR) using microemulsion technique has been applied over the past decade (Ouyang et al., 1996, 2002; Shiau et al., 1996; Dwarakanath et al., 1999; Harwell et al., 1999; Sabatini et al., 2000; Uchiyama et al., 2000; Wu et al., 2000, 2001; Acosta et al., 2003a,b; Childs et al., 2004; Szekeres et al., 2005, 2006). Due to the high stability of microemulsion solution, and the harmonization between the small droplets size dispersing in aqueous phase and soil pores size, the displacement of microemulsion solution though aquifer or soil can minimize the clogging in remediation process (Ouyang et al., 1996, 2002). To investigate the remediation of TEL from contaminated site using microemulsion technique, the TEL surrogate is needed to identify and use instead of TEL due to its harmfulness.

Dibutyltin dichloride (DBTDC) shows high potential to be used as the TEL surrogate as considering four dominant criteria: 1) being an organomatallic substance, 2) analogy in physical and chemical properties, 3) less poisonous as compared to TEL, and 4) able to mix well with other oils to obtain similar equivalent alkane carbon number (EACN) to TEL. The DBTDC is an organotin commonly used as the stabilizers in polyvinyl chloride (PVC) products such as packaging, bottles, pipes, mouldings, etc. manufacturing processes; and the catalyst in many chemical reactions; for instance, electrodeposition, silicones, and polyurethanes processes resulting in an extensive distribution and contamination in the environment (Risk &

Policy Analysts Limited, 2002). Organotins can be accumulated in the food chain and possesses potential effects on human health (Dopp et al., 2007). According to their physical and chemical properties (see Table 2.1), DBTDC possesses low water solubility and high specific gravity similar to TEL. However, DBTDC is in the solid form where TEL is in liquid form. Regarding to toxicity, DBTDC (LD_{50}= 50 mg/kg) is less toxic than TEL (LD_{50}= 12.3 mg/kg) which is very attractive to be used as TEL surrogate.

Due to the fact that, the first three criteria are the intrinsic properties of the substance, EACN identification of TEL and finding a surrogate of TEL based on a similarity of EACN (the last criteria) is a major task of this study.

The alkane carbon number (ACN) is defined as the degree of hydrophobicity of linear *n*-alkane with correspondence to its carbon number (i.e., ACN of hexane = 6). For the non-alkane oils such as benzene, the new wording was designated so-called the equivalent alkane carbon number or "EACN". The oil EACN concept was initiated by Cayias and co-workers (Cayias et al., 1976), where the EACN of the non-alkane oils can be determined by comparing the optimum microemulsion formulation at the same physicochemical environment to those of *n*-alkanes. Baran and co-workers (Baran et al., 1994) demonstrated the method to determine the EACN of chlorinated hydrocarbons such as tetrachloroethylene (PCE), 1,2-dichlorobenzene (DCE), and trichloroethylene (TCE). However, the EACN discovery for organometallic compound (i.e., TEL) is rare at the moment. Understanding the oil EACN is useful for designing the surfactant systems that suit for solubilizing that oil (Wu et al., 2000, 2001). Consequently, this research was one of the very first works demonstrating the EACN of organometallic compound. The EACN of TEL and its oil surrogate could be obtained based on the surfactant microemulsion formation coupled with the Salager's equation (Salager et al., 1979).

The second part of this work demonstrated the surfactant ability to form microemulsion with oil surrogate in order to achieve the supersolubilization condition. The supersolubilization is the region located in Winsor type I microemulsion but closed to the boundary of Winsor transition from type I-III. Although the interfacial tension (IFT) in this region is not as low as at the optimum condition showed in Winsor type III, the obtained solubilization capability is adequate for remediation process. In addition, the surfactant microemulsion solution at supersolubilization condition has been utilized in many surfactant field studies (Wu et al., 2000; Sabatini et al., 2000; Acosta et al., 2003b; Childs et al., 2004) due to its advantage in terms of preventing a downward migration problem when dealing with Dense nonaqueous phase liquids (DNAPLs) remediation such as TEL or chlorinated hydrocarbons. Three types of surfactants including an anionic, nonionic and extended anionic surfactants were used to form the microemulsion solution with oil surrogate. Three surfactant systems that produced the highest oil solubilization were selected to apply for flushing the synthetic soil in the column study.

To summarize an overall work, a surrogate for TEL was investigated based on the Salager's concept. Then, the surfactant solutions that able to form microemulsion with the TEL surrogate were investigated and only promising systems were tested to identify 3 surfactant systems that provide the highest solubilization of the TEL surrogate. These 3 surfactant solutions were used to flush the TEL surrogate contaminated soil in column studied instead of the gradient approach.

The ultimate objectives of this work were to find the surrogate substance to be used instead of TEL and to investigate the surfactant systems which can form microemulsion with the TEL surrogate. The application of this research was shown by flushing the suitable surfactant system for removal of TEL surrogate from soil in column study.

1.1 Objectives of the study

The objectives of this work were categorized into three topics as follows:

1. To find the surrogate substance which can be used for the tetraethyl lead (TEL) in experimental work due to its extremely high toxicity.

2. To investigate the surfactant systems which can form microemulsion with the TEL surrogate and to determine their phase behavior.

3. To apply the selected surfactant system to remove the TEL surrogate from soil in column experiment.

1.2 Hypotheses

1. Salager's Equation can be applied to this study in order to characterize the hydrophobicity of TEL.

2. The mixed oils that have similar Equivalent Alkane Carbon Number (EACN) to TEL can be used as a TEL surrogate to form microemulsion system.

3. The higher oil solubilization in the microemulsion system, the higher oil removal efficiency will be in column study.

1.3 Scope of study

The overall works can be categorized into four parts as shown in the list below:

1.3.1. TEL surrogate investigation

- **Investigation for a surrogate for TEL using Salager's Approach**

In order to find the surrogate which can be used instead of TEL, Salager's approach, which is based on the correlation between equivalent alkane carbon number (EACN) and optimum salinity (S*), was applied. Various compounds with known EACN were used in this study. The correlation between EACN and S* equations using known EACN oil/surfactant system was determined. A greater detail of Salager's approach was provided in chapter 2. The same procedure was applied with TEL and the S* of TEL/surfactant was obtained. As a consequence, the EACN of TEL was achieved. Further finding was the proportion of DBTDC in solvent which have the same S* of TEL, in other word, mixture DBTDC at proportion that presented the EACN same as TEL

1.3.2. Phase behavior study

Phase behavior of microemulsion was performed to understand the behavior of surfactant and the surrogate oil. These experiments were used to categorize the surfactant formulations that do not show the surfactant precipitation.

The desired behavior is O/W_m microemulsion (oil in water or Winsor type I microemulsion) to middle phase microemulsion (Winsor type III microemulsion) in order to identify the supersolubilization region. The supersolubilization region located in type I but closed to the phase boundary between type I and type III. To obtain surfactant microemulsion formation with TEL surrogate, the approach for surfactant system selection was based on hydrophile-lipophile balance (HLB) and EACN of surfactant(s) and the surrogate oil. In this study, three types of surfactant were considered:

- Anionic surfactants : Dowfax 8390, AMA and AOT
- Nonionic surfactant : Tween 80
- Extended anionic surfactant : Alfoterra 167-7PO

Salinity scan using sodium chloride (NaCl) as an electrolyte was done to investigate the phase transition of microemulsion systems. Some promising surfactant systems were used to determine the supersolubilization and optimum salinity (S^*) by measuring IFT using the spinning drop tensiometer.

1.3.3. Solubilization study

The solubilization capacity of each surfactant system for TEL surrogate at supersolubilization region was studied. A comparison between single and mixed surfactant systems in term of solubilization capacity were carried out.

1.3.4. Column study

- **TEL surrogate removal study**

Three selected surfactant systems obtained from solubilization part were applied to flush a column containing TEL surrogate contaminated soil. In this work, silica (Ottawa) sand was used as soil. The TEL surrogate was contaminated onto soil at a saturation condition, where the water was flushed until only residue oil left in the packed column. The residue oil trapped in soil due to a capillary force. The surfactant aqueous solution was then flushed through the column where the effluent solution was collected and analyzed. The percentage of TEL surrogate removal was investigated.