CHAPTER IV

RESULTS AND DISCUSSION

4.1 EACN determination of TEL

In this section, we aimed to establish an empirical correlation between the optimum salinity (S^*) and oils' EACN using *n*-alkane series based on Salager's equation (Eq.9). Both surfactant mixtures, AOT/Tween80 and AOT/AMA, are found able to form microemulsion with alkanes in the range from ACN = 5 (pentane) to ACN = 10 (decane). The system of AOT/Tween80 was formulated with 3 *n*-alkanes including hexane (ACN = 6), octane (ACN = 8), and decane (ACN = 10). Volume of phase change and phase transition could be observed and thus to obtain the optimum salinity for each oil, the plots between *SP* of water phase (SP_w) and of oil phase (SP_o) versus NaCl concentration (wt%) in the system of AOT/Tween80 with hexane was drawn. The S^* of each oil can be obtained from the intersection point between SP_w and SP_o. From this procedure, the optimum salinity of the three alkanes can be obtained as shown in Figure 4.1-4.3. The S^* of hexane, octane, and decane were determined as 2.04, 2.84, and 3.76, respectively (see Appendix A).

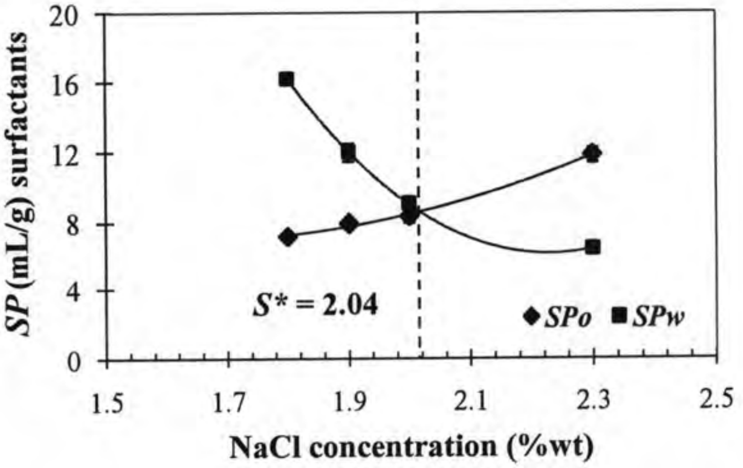

Figure 4.1 The optimum salinity (S^*) of hexane in AOT/Tween80 surfactant system

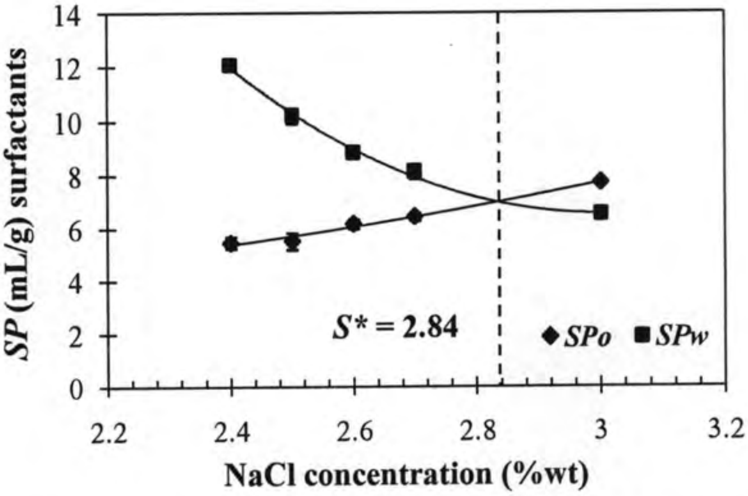

Figure 4.2 The optimum salinity (S^*) of octane in AOT/Tween80 surfactant system

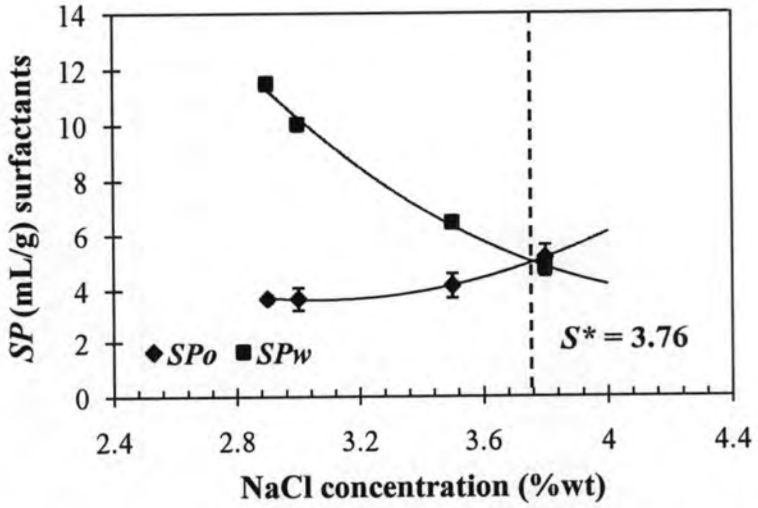

Figure 4.3 The optimum salinity (S^*) of decane in AOT/Tween80 surfactant system

For a system of AOT/AMA, the optimum salinities with 3 *n*-alkane oils: pentane, hexane, and octane were also achieved by the same procedures. Figure 4.4-4.6 showed the S^* values of pentane, hexane, and octane which were 1.49, 1.85, and 2.94, respectively.

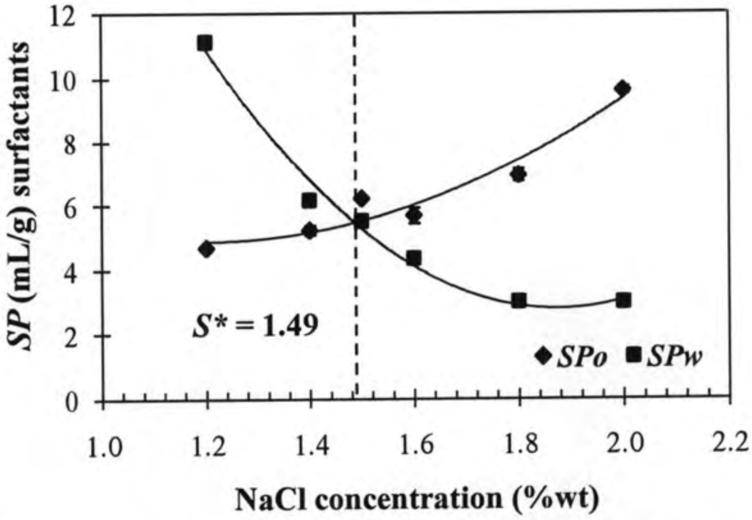

Figure 4.4 The optimum salinity (S^*) of pentane in AOT/AMA surfactant system

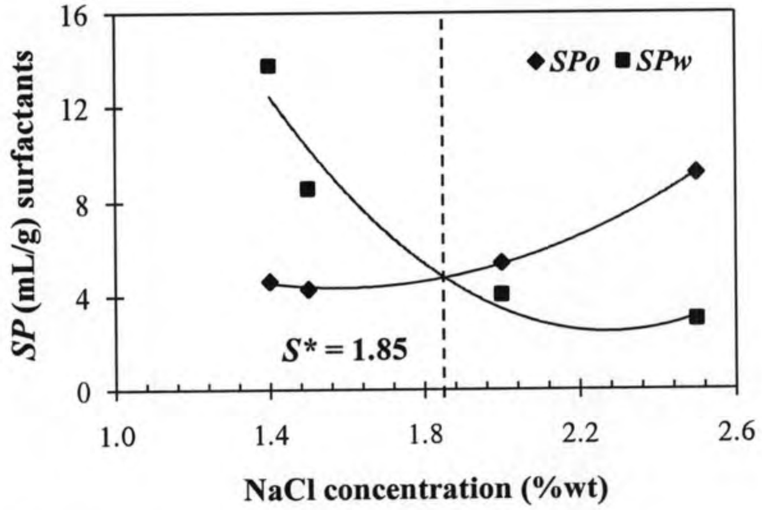

Figure 4.5 The optimum salinity (S^*) of hexane in AOT/AMA surfactant system

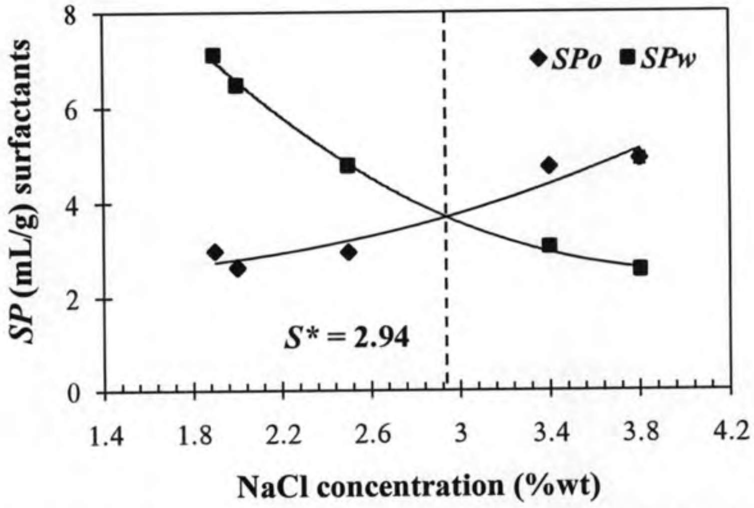

Figure 4.6 The Optimum salinity (S^*) of octane in AOT/AMA surfactant system

The natural logarithm of S^* was plotted against oils' EACN as shown in Figure 4.7. The empirical equation between ln S^* and EACN for AOT/Tween80 system was $\ln S^* = 0.1529$ EACN - 0.1959 (Eq.12) with $R^2 = 0.9978$. And the empirical equation obtained from AOT/AMA system was $\ln S^* = 0.2273$ EACN - 0.7419 (Eq.13) with $R^2 = 0.9997$.

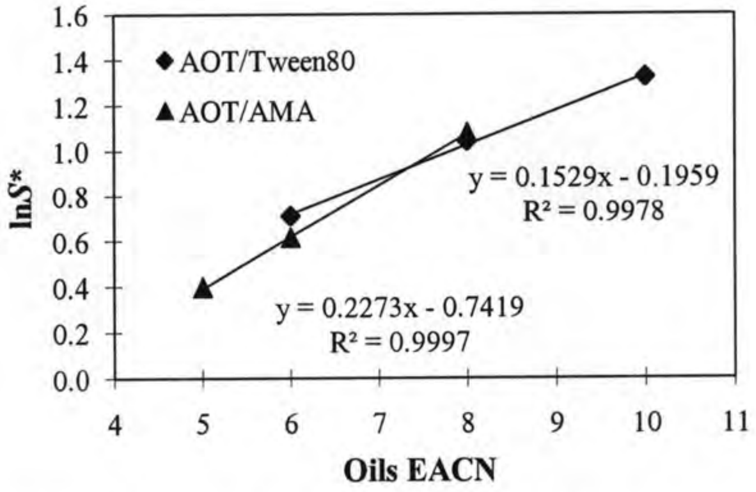

Figure 4.7 Relationship between lnS^* and oils' EACN of two surfactant systems

In order to quantify the EACN of TEL which is the main pollutant of this research, the TEL with high purity was mixed with hexane at molar ratio of 0.2: 0.8. The mixed oils solution was used to form microemulsion with both surfactant systems and obtained $S^*_{\mathrm{m,\ AOT/Tween80}} = 2.06$ and $S^*_{\mathrm{m,\ AOT/AMA}} = 1.97$ as shown in Figure 4.8 and 4.9. Finally, the EACN of pure TEL was found to be in the range of 6.04 to 7.23 using the Salager's equation.

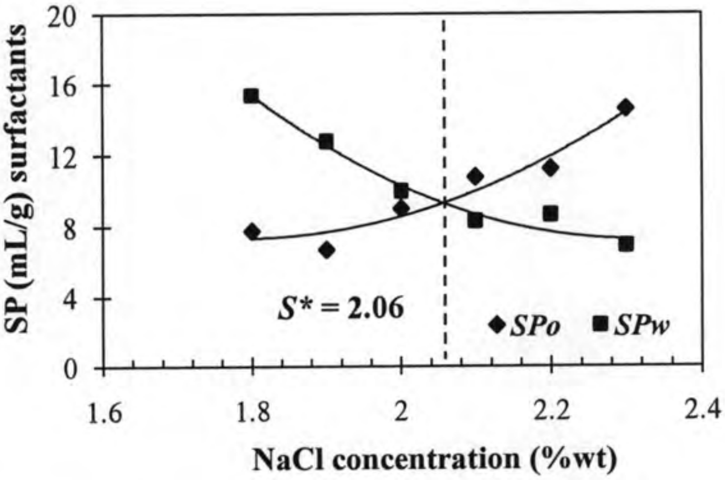

Figure 4.8 The Optimum salinity (*S) of TEL in hexane at molar ratio of 0.2: 0.8 in AOT/Tween80 surfactant system**

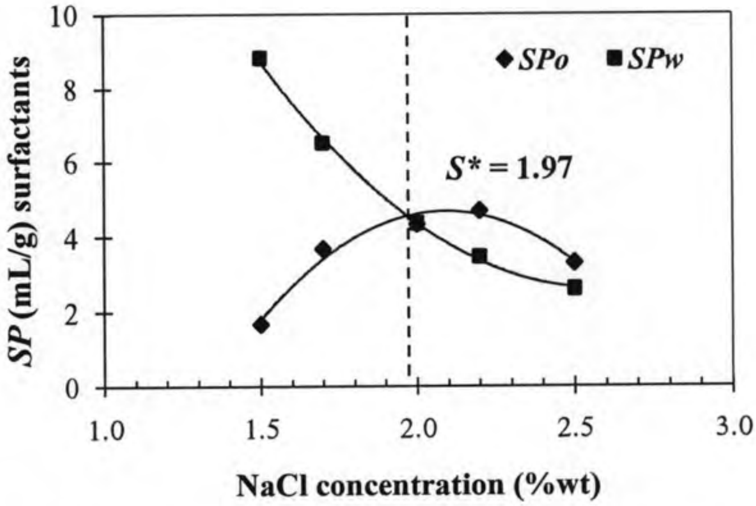

Figure 4.9 The optimum salinity (*S) of TEL in hexane at molar ratio of 0.2: 0.8 in AOT/AMA surfactant system**

4.2 DBTDC preparation as TEL surrogate

From the previous experiment, the EACN of TEL was successfully determined. The subsequent step was to find the TEL surrogate that has similar EACN to TEL. In this study, DBTDC, which is a chlorinated organotin, was proposed to be used as TEL surrogate. It has high polarity, low hydrophobicity and thus very low EACN. Therefore, it required oil with high hydrophobicity to mix with and to suppress its polarity. Thus, the EACN of the mixed oil can be equivalent to that of TEL. In this case, the EACN mixing rule (Eq.10) was used to calculate the EACN of oil mixture. To obtain oil surrogate with EACN in range of 6.04 to 7.23 (TEL's EACN), the same surfactant systems were used. Initially, several organic solvents were preliminary examined to adjust the EACN of mixed oils and to dissolve DBTDC since it was in a solid form. Oil used for mixing with DBTDC are *n*-alkane series with high ACN such as octane, decane, dodecane (ACN =12), and etc. due to the fact that alkanes normally be able to form microemulsion with a wide range of surfactant systems and the EACN of the mixed oils can be directly calculated that made a system to a lot less complicated. From this experiment, it was found that only octane and decane could mix with DBTDC and formulate microemulsion system whereas a phase separation occurred when mixed with dodecane.

Unexpectedly, AOT/Tween80 surfactant mixture, which used to form microemulsion successfully with TEL, could not be able to form microemulsion with the mixture of DBTDC with either octane or decane. This may be because of complexity of mixed oil comprising of rather high hydrophobic oil (octane or decane) and high polarity oil (DBTDC), thus the oils may be separated and solubilized in the preferred surfactant. Consequently, the solution was not an isotropic phase and microemulsion could not be formed. Fortunately, the AOT/AMA system (both anionic surfactants) was able to form microemulsion with the mixed oils and hence, the EACN of DBTDC mixed with octane and decane can be determined as depicted in Table 4.1.

In AOT/AMA system, DBTDC was firstly dissolved in octane at molar ratio of 0.050:0.950 in order to determine the S^*_m of oil mixture. That ratio was randomly selected as a base oil mixture ratio for testing since the EACN value of DBTDC was not yet known. Similarly to section 4.1, the S^*_m of oil mixture could be obtained from the intersection point between SP_w and SP_o, thus we found the S^*_m = 1.24 as shown in Table 4.1. The S^*_m value was then calculated to attain the EACN of oil mixture and solely DBTDC by using the empirical equation for AOT/AMA system (Eq. 13) and EACN mixing rule (Eq.10), respectively. Therefore, we got the EACN of oil mixture equal to 4.21 which was far away from the EACN of TEL. From the new piece of information about the EACN of DBTDC ($\text{EACN}_{\text{DBTDC}} \sim -67.69$), this value was very useful since it can be used to calculate a certain molar ratio that gave the EACN of oil mixture closed to that of TEL, by coupling with Eq. 13. The determining of TEL surrogate was set up again by varied molar ratio of DBTDC and octane based on that calculation until we got the certain EACN in range of TEL, which was also proven by the experiments (see Appendix B). Ultimately, we could find the oil mixtures of DBTDC in octane at molar ratio of 0.011:0.989 that offered the S* of 2.23 (see Figure 4.10). As a consequence, the EACN of mixture was found to be 6.79, which was closed to that of TEL.

Table 4.1 Observation of n-alkanes mixed with DBTDC in AOT/AMA surfactant system

Solvent mixed with DBTDC (ACN)	Molar Ratio[a] DBTDC : Solvents	Optimum salinity of mixed oil[b] (S^*_m)	EACN	
			Mixed oils[c]	DBTDC[d]
Octane (8)	0.011 : 0.989	2.23	6.79	-101.79
	0.050 : 0.950	1.24	4.21	-67.69
Decane (10)	0.035 : 0.965	2.75	7.71	-55.30
	0.038 : 0.962	2.44	7.19	-63.99
	0.042 : 0.958	1.64	5.44	-98.56
	0.050 : 0.950	1.33	4.52	-99.63
Dodecane (12)	Omit to study due to phase separation			

Note: [a] All molar ratios were obtained from the experiments.

[b] S^*_m were obtained from the S^*_m determining of oil mixture's experiments.

[c] EACN of mixed oils were obtained based on the calculation of Eq. 13.

[d] EACN of DBTDC were obtained based on the calculation of EACN mixing rule (Eq.10).

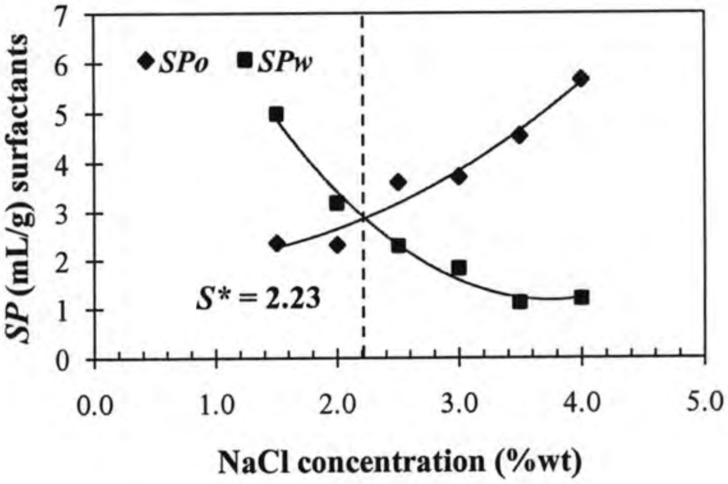

Figure 4.10 The Optimum salinity of DBTDC in octane at molar ratio of 0.011: 0.989 in AOT/AMA surfactant system

The same procedure was applied to the mixed system of DBTDC and decane and the results were showed in Figure 4.11 and Table 4.1. As a consequence, the oil mixture of DBTDC in decane at molar ratio of 0.038:0.962 was found to offer an EACN closed to that of TEL, which was 7.19.

In this study, DBTDC mixed with decane at molar ratio of 0.038:0.962 was selected to be used as the TEL surrogate since this mixture contains a higher amount of organometallic compounds as compared to another one.

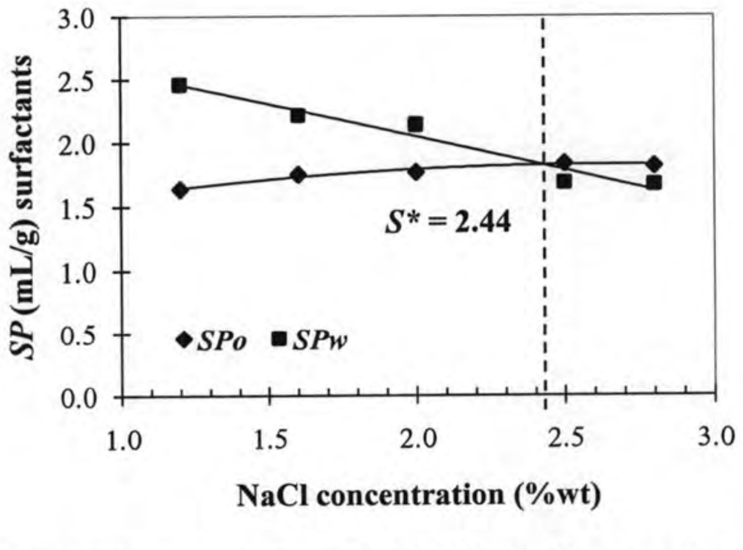

Figure 4.11 The Optimum salinity of DBTDC in decane at molar ratio of 0.038:0.962 in AOT/AMA surfactant system

4.3 Phase behavior study

This part aimed to demonstrate the ability of surfactant solution to solubilized surrogate oil (DBTDC mixed with decane at molar ratio of 0.038:0.962). Three types of surfactants (anionic, nonionic and extended anionic surfactants) were used in this study and can be categorized into single and mixed surfactants systems as shown in Table 4.2. These surfactants systems were used to form microemulsion with the mixed oils in order to determine if they can yield the supersolubilization condition, which is the Winsor type I microemulsion where the highest oil solubilization occurs (Sabatini et al., 2000).

For single surfactant systems, only AMA 4wt% was effectively formed microemulsion with TEL surrogate oil and provided the supersolubilization condition in the presence of NaCl at 2.5wt%. The mixed surfactants systems of AMA/Dowfax8390 and AMA/Tween80 could also form the microemulsion with surrogate oil and provided the supersolubilization condition at NaCl of 4.3 and 3.0wt%, respectively. To evaluate the salt addition with Winsor Phase Diagram (see Fig 2.2), the AMA/Dowfax8390 system was found to require the highest NaCl concentration to form microemulsion at supersolubilization condition thus, indicating that AMA/Dowfax8390 system has the highest hydrophilicity (the highest HLB) among surfactant systems studied here. This indication could be supported by approximating the values of HLB of those systems. According to the HLB values summarized in Table 3.1, the HLB values of three surfactant systems based on Eq. 5 were calculated where HLB_{AMA} = 16.6, $HLB_{AMA/Dowfax8390}$ = 22.09 and $HLB_{AMA/Tween80}$ = 15.8. Due to the fact that the Dowfax8390 anionic surfactant has very high HLB (~71.5), the addition of Dowfax as a second surfactant can raise the overall HLB of system if compare to pure AMA and AMA/Tween80 systems. Thus, this finding could support the result obtained here. On the other hand, the addition of a nonionic surfactant with moderate HLB (Tween80) similar to that of AMA as a second surfactant cannot alter the overall HLB of system much.

Table 4.2 Observation on phase behavior of various surfactant systems investigated in this study

Surfactant System (wt%)	NaCl (wt%)	Winsor Type
Single surfactant		
4% AMA	2.5	I_{sp}
	2.6	III
4% Dowfax8390	-*	-
4% Tween80	-	-
4% Alfoterra167-7PO	-	-
Mixed surfactants		
3.6% AMA/0.4% Dowfax 8390	4.3	I_{sp}
	4.4	III
2% AMA/2% Tween80	3.0	I_{sp}
	3.1	III
0.8% Dowfax8390/3.2% Tween80	-	-

Note: This experiment was conducted at room temperature (24-28 °C) where:

* indicates that microemulsion could not form.

I_{sp} indicates the Winsor type I with the supersolubilization condition could be investigated.

4.4 Solubilization study

Three promising surfactants systems obtained from previous part were used to determine the solubilization capacity of these surfactants for TEL surrogate at the supersolubilization condition (see Table 4.3). The surfactant solutions at their supersolubilization condition were prepared and an excess amount of TEL surrogate was mixed. After equilibrium solubilization was reached, the supernatant solution was analyzed for the concentrations of total tin and decane separately in order to investigate whether a preferential solubilization of each component in the mixed oil occurs or all components go together when solubilization takes place. The results showed that the system of AMA/Dowfax8390, anionic-anionic surfactants, yielded the highest solubilization capacity for both DBTDC and decane, whereas the system of AMA/Tween80, anionic-nonionic surfactants, yielded the lowest solubilization capacity as shown in Table 4.3.

The interaction occurring in pure and mixed surfactant along with the locus of solubilization of surrogate oil in surfactant(s) micelles could be used to explain what might happen during solubilization process. Fundamentally, the solubilization regions of oil(s) depend on the molecular structure and polarity of that oil (Szekeres et al., 2005). Non-polar oils are solubilized in the micelle core region whereas semi-polar and polar oils preferably solubilized at the palisade and surface regions, respectively (see Figure 2.1). According to this fundamental, the oil having high polarity such as DBTDC in this case tends to solubilize in the palisade layer or surface region, unlike decane that tends to solubilize in the core of micelle, which provides the hydrophobicity environment.

Table 4.3 Solubilization capacity for TEL surrogate of each surfactant(s) system

Surfactant Systems	**Solubilization of TEL surrogate (mg)**		**Molar ratio of Tinn : Decane**
	Tin	**Decane**	
TEL surrogate oil preparation at initial ratio DBTDC : Decane = 0.038 : 0.962			0.038 : 0.962
Surfactant Systems			
4% AMA/2.5% NaCl	7.46	57.51	0.063 : 0.404
3.6% AMA/0.4% Dowfax8390/4.3% NaCl	7.66	78.11	0.065 : 0.549
2% AMA/2% Tween80/3.0% NaCl	7.02	23.86	0.059 : 0.168

In term of surfactant interaction, in general, the mixed surfactant can show either synergistic or antagonistic effect. Vora and his co-workers (Vora et al., 1999) observed an antagonism behavior of similarly charges of mixed surfactants: Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) due to a steric hindrance. However, within the same work, they also observed the synergism of anionic-anionic surfactants mixture: SDS combining with mono- and bivalent metal dodecyl sulfates. In our study, it was found that the mixed anionic-anionic surfactant system of AMA/Dowfax showed a synergistic effect where the mixed surfactant aggregates open up a space between anionic-anionic heads, pertaining to the fact that Dowfax is a twin heads surfactant. Thus, this orientation facilitates tin and decane to solubilize at palisade layer and the inner core of micelle which are their favorable, respectively.

For anionic-nonionic surfactants system (AMA/Tween80), the antagonistic effect was found as shown by the least amount of tin and decane solubilization even comparing to a system of pure AMA. It was stipulated that the addition of nonionic surfactant could help screening the repulsion forces between AMA molecules. Thus, the packing of surfactants molecules was tighten until a partitioning of tin and decane molecules was obstructed and become less favorable. Therefore, the solubilization in AMA/Tween80 is less than that of mixed anionic-anionic surfactants mixture (AMA/Dowfax) and pure anionic surfactant (AMA only), respectively.

Even though these three surfactant systems could form microemulsion well and exhibited their solubilization performance onto surrogate oil, an unexpected outcome was discovered. Table 4.3 (last column) illustrated an inconsistency of tin and decane ratio after solubilized into surfactants micelles of each surfactant system compared with an initial ratio of surrogate oil (see Table 4.3). It was found that tin is more favorable to solubilize into these three surfactant systems than decane as shown by the molar ratio of compound solubilized as compared to its initial ratio, where the mole of total tin solubilized increased and the mole of solubilized decane decreased.

Although, it was found out that two components in oil mixtures behave differently upon solubilizing in the surfactant aggregates, the study on organometallic compound removal by these surfactant systems was worth preceded in the column study.

4.5 Column study

Based on the solubilization study in batch experiments, AMA, AMA/Dowfax8390 and AMA/Tween80, the screened surfactant systems were proven to have a capacity to solubilize the surrogate oil with differing degrees. The column study was conducted to imitate the actual subsurface remediation, the TEL surrogate were contaminated in Ottawa sand in a packed column where those surfactants solutions were used to flush the column. The effectiveness of these surfactant treatments were showed in terms of %TEL surrogate removal as total, solubilization, and mobilization as summarized in Table 4.4 and Figure 4.12-4.14. The pore volume (PV) of each column was determined and found that the pore volume of three columns were about 30 mL. In addition, the residual saturation of surrogate oil in the column was investigated and found in range of 12-17%. It should be noted that the total tin concentration was only analyzed and used as a representative of TEL surrogate oil mixtures to observe the behavior of organometallic compound removal by surfactant microemulsion solutions.

Table 4.4 Column flushing test results using various surfactant microemulsion formulations at supersolubilization condition

	Surfactant Systems		
	4% AMA/ 2.5% NaCl	**3.6% AMA / 0.4% Dowfax8390/ 4.3% NaCl**	**2% AMA / 2% Tween80/ 3.0% NaCl**
Pore volume (mL)	30.8	29.8	30.4
Residual saturation (%)	15	12	17
Removal efficiency (%)			
- **Solubilization**	55.7	64.5	62.1
- **Mobilization**	35.7	21.6	36.4
Total removal (%)	91.4	86.1	98.5

Figure 4.12 illustrated the plots between mass of solubilized tin normalized by initial mass of tin presented in the column at the same pore volume using three surfactant systems at their supersolubilization condition. Similar to Figure 4.12, Figure 4.13 was the plots between accumulation mass of solubilized tin normalized by initial mass of tin presented in the column at the same pore volume using three surfactant systems at their supersolubilization condition. The reason why

the normalization of data was used because the residual saturation achieved from each column set up was slightly different from batch to batch as shown in the range of 12-17%. Thus, the total amount of tin presented in each column was not equal. Consequently, normalization of the data by total mass of tin in the column would mitigate the bias in comparing the TEL surrogate removal efficiency by each surfactant microemulsion solution.

Since the surfactant flushing into the column was done in an upward direction, the mobilization of oil, which can be noticed by the presence of free oil phase in the collected effluent solution, was initially observed at 0.5 PVs and completed at around 3 PVs. Then, the solubilization was gradually attained up to around 40 PVs until the level of solubilized TEL surrogate remained almost constant with the relative standard deviation (RSD) less than 5%. All of these surfactants microemulsion solutions were successfully found to remove organometal (tin) from contaminated natural medium in column study.

The results showed that even using different surfactants systems, the phenomenon taken place inside each column was the similar. The highest tin solubilized was observed at 1.5 PVs and gradually decreased until 5 PVs. From the results, the maximum solubilization of total tin was found using the AMA/Dowfax8390 system, which corresponded well with results obtained from batch solubilization study. The solubilization efficiency could be ordered from high to low as follows: AMA/Dowfax8390, AMA solely and AMA/Tween80, respectively. However, it should be noted that if the data was plotted using observed mass instead of using the normalized ones, the misinterpretation of results may be occurred caused by a previously mentioned problem about the unequal of pore volume and degree of residual saturation of TEL surrogate in each column prior flushing (see Table 4.4). In term of solubilization accumulation, the system of AMA/Dowfax8390 still showed the highest accumulative solubilization, while no significant different was found from the systems of AMA/Tween80 and AMA as shown in Figure 4.13 .

According to the TEL surrogate oil used in this study is a LNAPL, the mobilization of oil did not cause a severe problem as compared to DNAPLs (Sabatini et al., 2000), which typically made things more complicated in term of remediaion since a vertical migration tends to occur. However, the oil mobilization was found in this study and attempts were made in order to determine the actual mass of oil mobilization. It was found that the composition of mobilized surrogate oil was different from the initiall prepared one. To solve this problem, the mass of tin mobilized was determined by a subtraction of an initial mass of tin with a mass of tin remained in the column (obtained from a back extraction of flushed soil) and a mass of tin solubilized (obtained from a direct measurement of tin in the flushed surfactant solution) as shown in the Appendix D.

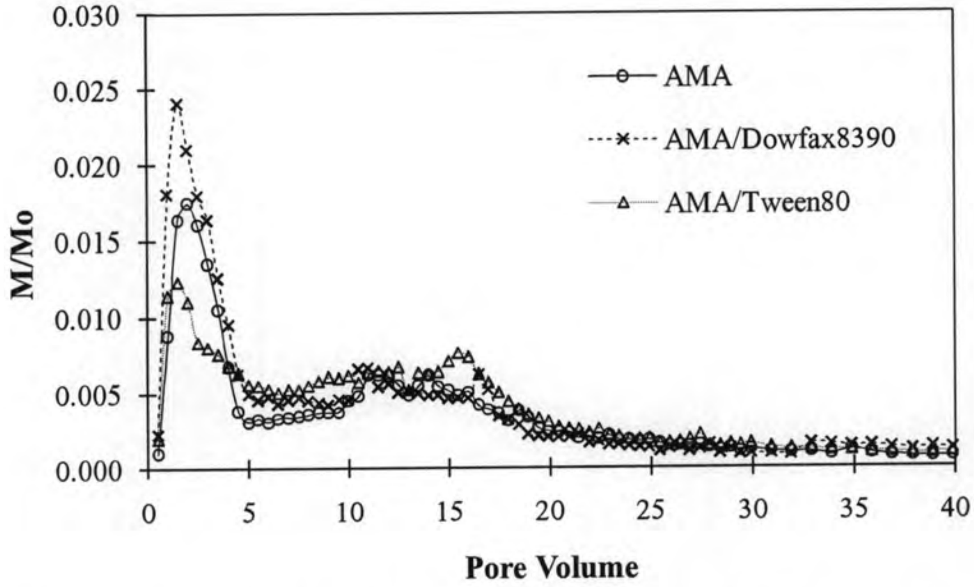

Figure 4.12 Plots between mass of solubilized tin normalized by initial mass of tin presented in the column (M/Mo) at 40 pore volumes using three surfactant systems at their supersolubilization condition

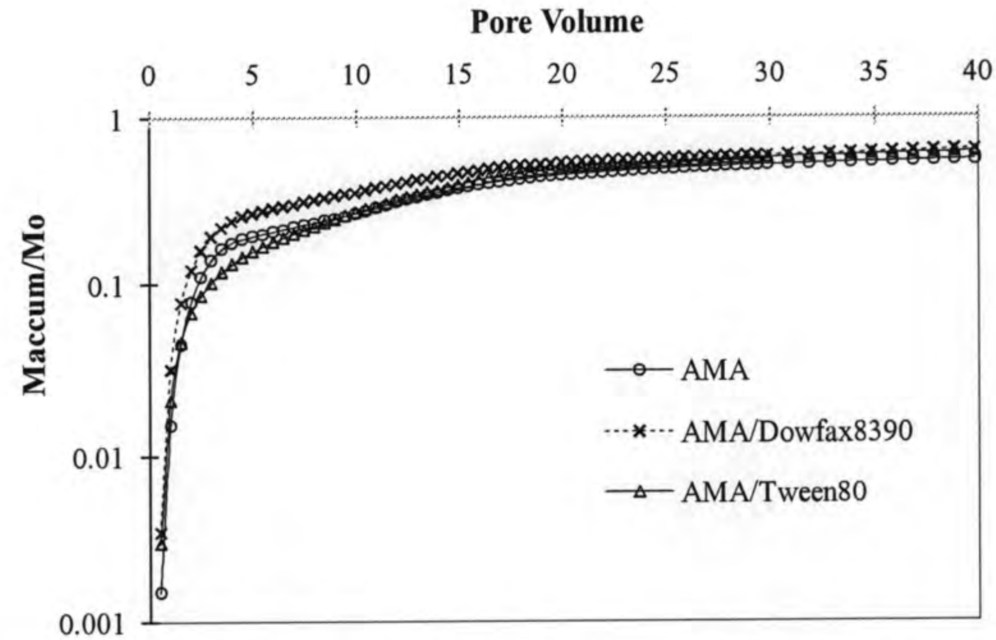

Figure 4.13 Plots between logarithms of accumulation mass of solubilized tin normalized by initial mass of tin presented in the column (M/Mo) at 40 pore volumes using three surfactant systems at their supersolubilization condition

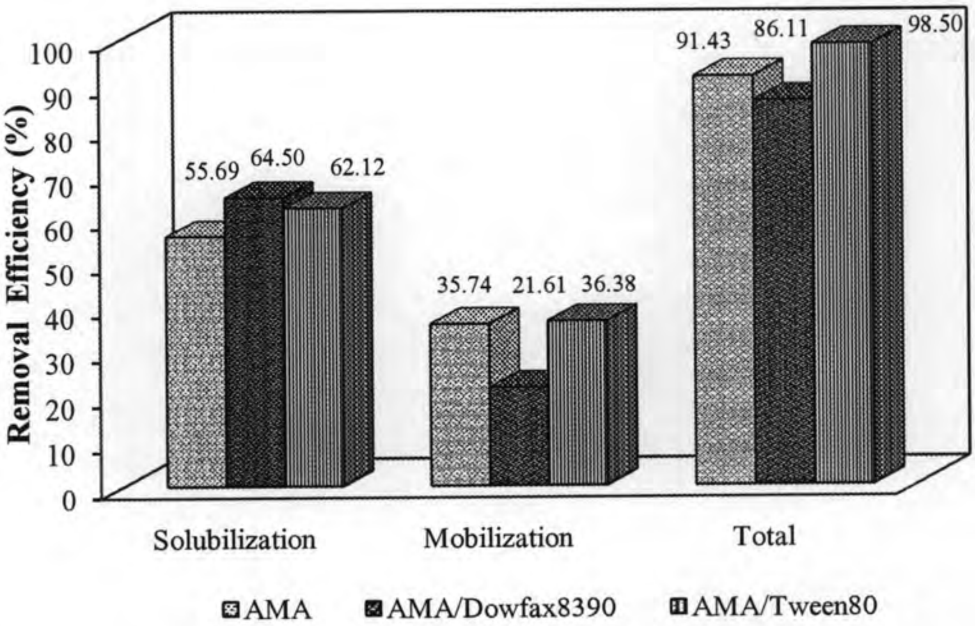

Figure 4.14 Removal efficiency of tin classified as solubilization, mobilization and total removal using three surfactant systems at their supersolubilization condition.

Conclusively, a comparison on removal efficiency classified as total tin removal, removal by solubilization, and removal by mobilization using three surfactant systems at their supersolubilization condition were summarized in Figure 4.14. It was found that the total TEL surrogate removal using these three surfactant systems considered based on mass of tin removed were high where 86 to 98 % of oil surrogate could be removed according to both solubilization and mobilization within 40 PVs. If the TEL surrogate oil was DNAPL, a different aspect needed to be incorporated in a suitable surfactant system selection to flush the soil since the mobilization of oil needs to be avoided. Thus, the surfactant system provided the highest percentage of DNAPL removal may not be the best formulation if it also provides a high DNAPL mobilization rather than high solubilization.