

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Phase Behavior with Salinity Scan

Preliminary study for investigation of surfactant systems that are able to form microemulsion with diesel and motor oil was carried out as shown in Appendix A. The system that was found to form microemulsion with the two oils was the system of mixed anionic surfactant; C14 and C15 branched alcohol propoxylate sulfate (4 propoxy groups) (Alfoterra 145-4PO), and sodium dioctyl sulfosuccinate (AOT). Due to the desirable phase transition of surfactant system, only one mixed surfactant system (the same concentration of surfactant system but different salt concentration) that found to be able to formed microemulsion with these two oils were selected for further study in phase behavior which are 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 1 wt% NaCl at the optimum salinity of diesel and 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 5 wt% NaCl at the optimum salinity of motor oil.

According to Yanatatsaneejit (2004), Alfoterra 145-4PO alone cannot promote the formation of Winsor type III microemulsion. This is because Alfoterra 145-4PO is an anionic surfactant having a high value of HLB (hydrophilic-lipophilic balance). She proposed that to enhance the formation of Winsor type III microemulsion another surfactant having a low HLB is needed to act as a linker.

The interfacial tensions (IFT) between equilibrated phases (excess oil and water phases) of each system were measured by a spinning drop tensiometer to examine the existence of Winsor type III microemulsion. Table 4.1 and Table 4.2 show the results of phase transition and IFT values. The first surfactant system for diesel, 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT was scanned with NaCl in the range of 0-20.0 wt%. The results showed that at this range of NaCl concentration, the transition of microemulsion from Type I to Type III and to Type II were formed. As the concentration of salt increases, The IFT between diesel and surfactant solution gradually decreased from 0.0 wt% NaCl until the formation of Winsor type III microemulsion appears at a slightly low concentration of salt (1 wt% NaCl). And then, the IFT of the system increases gradually for the condition

that salinity increase from 1.0 to 20.0 wt% NaCl as the Winsor type II microemulsion (as shown in Table 4.1). For another surfactant system for motor oil, the transition of microemulsion from Type I to Type III and to Type II was observed with salinity scan in the range of 0-20 wt% NaCl at the same surfactant system. As the concentration of salt increases, the IFT between motor oil and surfactant solution decrease sharply in a magnitude of value from without NaCl to 0.5 wt% NaCl. However, after salinity was increase from 0.5 to 5.0 wt% NaCl, the IFT values of the system decreases gradually. After that, the IFT of the system increases gradually from 5.0 to 20.0 wt% NaCl (as shown in Table 4.2). Figure 4.1 and 4.2 demonstrate the relationship between IFT and salinity concentration of a system of 0.2 wt% Alfoterra 145-4PO and 0.5 wt% AOT at different salinity concentration for diesel and motor oil, respectively.

**Table 4.1 Interfacial tension between diesel and the surfactant solution system of 0.2 wt% Alfoterra 145-4PO and 0.5 wt% AOT at different NaCl concentrations.**

<b>Diesel microemulsion (Winsor type I to type III and to type II)</b>					
<b>No.</b>	<b>wt% Alfoterra 145-4PO</b>	<b>wt% AOT</b>	<b>wt% NaCl</b>	<b>Winsor type</b>	<b>IFT (mN/m)</b>
1	0.2	0.5	0.0	I	0.233
2	0.2	0.5	0.5	I	0.009
3	0.2	0.5	1.0	III	0.007
4	0.2	0.5	1.5	II	0.045
5	0.2	0.5	2.0	II	0.099
6	0.2	0.5	3.0	II	0.122
7	0.2	0.5	4.0	II	0.232
8	0.2	0.5	5.0	II	0.262
9	0.2	0.5	6.0	II	0.314
10	0.2	0.5	7.0	II	0.552
11	0.2	0.5	8.0	II	0.648
12	0.2	0.5	9.0	II	0.684
13	0.2	0.5	10.0	II	0.825
14	0.2	0.5	20.0	II	1.659

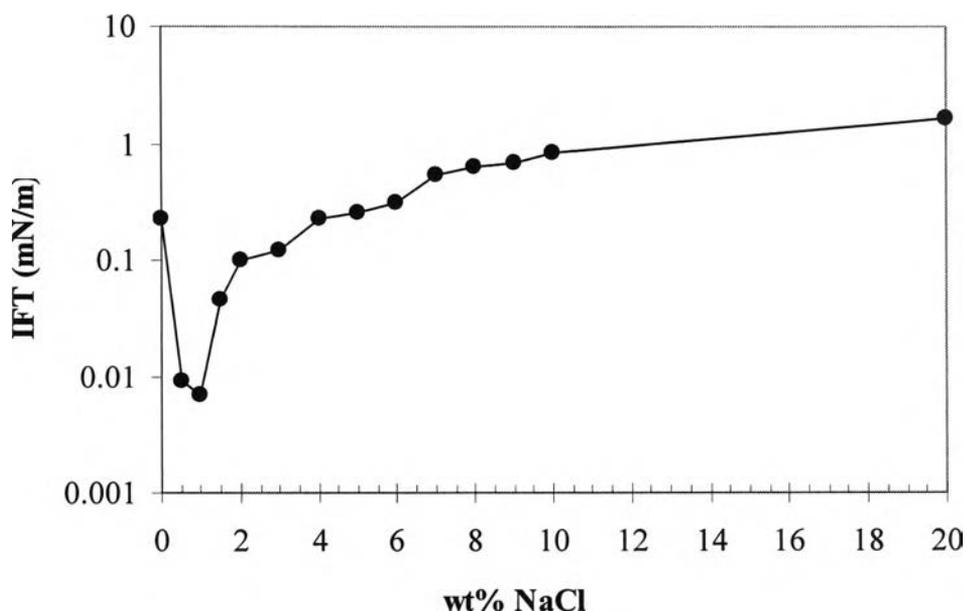
**Table 4.2 Interfacial tension between motor oil and the surfactant solution system of 0.2 wt% Alfoterra 145-4PO and 0.5 wt% AOT at different NaCl concentrations.**

Motor oil microemulsion (Winsor type I to type III and to type II)					
No.	wt% Alfoterra 145-4PO	wt% AOT	wt% NaCl	Winsor type	IFT (mN/m)
1	0.2	0.5	0.0	I	4.622
2	0.2	0.5	0.5	I	0.465
3	0.2	0.5	1.0	I	0.186
4	0.2	0.5	2.0	I	N/A*
5	0.2	0.5	3.0	I	0.176
6	0.2	0.5	4.0	III	0.148
7	0.2	0.5	5.0	III	0.088
8	0.2	0.5	6.0	III	0.224
9	0.2	0.5	7.0	III	0.248
10	0.2	0.5	8.0	III	0.350
11	0.2	0.5	9.0	III	0.365
12	0.2	0.5	10.0	III	0.208
13	0.2	0.5	15.0	II	0.632
14	0.2	0.5	20.0	II	0.878

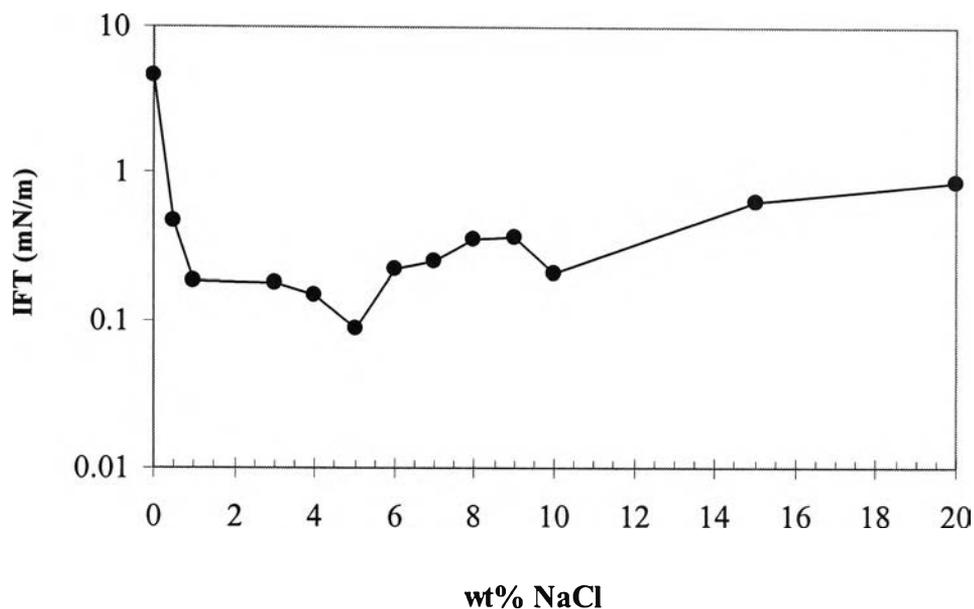
Note: N/A\* indicates value cannot measured

From Figures 4.1 and 4.2, phase transition occurs with increasing salinity. A Winsor type I microemulsion became a Winsor type III microemulsion and Winsor type II microemulsion since increasing salinity causes the system change to be more lipophilic or more hydrophobic. The phase transition of microemulsion and a decrease of IFT values are related to hydrophile-lipophile balance (HLB) of the system (Holmberg, 2003). HLB is a parameter that shows partitioning of surfactant between oil and water phases relative to surfactant hydrophobicity. With decreasing HLB of the system the surfactant moves from the water phase to the oil phase as the surfactant system becomes more hydrophobic. As a result, adding salt can promote the formation of middle phase

microemulsion because salt can reduce the repulsive force between the ionic charges of surfactants at their head group which can lead to decreasing the CMC while the aggregation number increases as well as increasing solubilization of oil into the inner core of micelles causing the decrease in the IFT. Therefore, the phase transition from Winsor type I to Winsor type III to type II microemulsion and decreasing of HLB for ionic surfactant system is induced by increasing salinity (Holmberg, 2003 and Rosen, 2004). Normally, at high salinity concentration, transformation from a Winsor type III to a Winsor type II microemulsion should occur since more surfactants are forced to move from the aqueous phase as well as the middle phase to the oil phase which enhances the formation of water in an oil microemulsion.



**Figure 4.1** Plot between interfacial tension values and NaCl concentrations in the system of 0.2 wt% Alfoterra and 0.5 wt% AOT with diesel.



**Figure 4.2 Plot between the interfacial tension values and NaCl concentrations in the system of 0.2 wt% Alfoterra and 0.5 wt% AOT with motor oil.**

Besides HLB of the system can effect to the microemulsion system, the structure of surfactants was also concerned as the effect of type of surfactants on microemulsion system. For Alfoterra 145-4PO, it is more hydrophilic because it prefers to solubilize in a water phase rather than in an oil phase while AOT is twin-tailed ester sulfonates, these twin tails are hydrophobic of surfactant. As a result, adding AOT reduces a HLB of this system leading to lowering salinity required to shift the system from Winsor type I to Winsor type III microemulsion.

According to the properties of diesel and motor oil as illustrated in Chapter II, the optimum salinity of these two oils are different conditions. The optimum salinity for diesel was found at 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 1 wt% NaCl while the optimum salinity for motor oil was found at 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 5 wt% NaCl. The optimum salinity of motor oil is higher than the optimum of diesel caused by EACN (Equivalent Alkane Carbon Number) of motor oil (23.5) is higher than EACN of diesel. A higher EACN signifies a higher hydrophobicity of the

mixed oils (Wu et al, 2000). This is the reason that why at 1wt% NaCl is the optimum salinity of diesel while at 5 wt% NaCl is the optimum salinity of motor oil.

## **4.2 Surfactant Gradient Approach in Column Study**

### **4.2.1 Column Preparation**

Preparation for soil column was adapted from Pennell (1994) and Childs et al. (2004) as mentioned in Chapter III. The pore volume of the column was determined by measuring the volume replace in the pore of packed column. The pore volume has to be examined because pore volume indicates the volume of solutions which is used for flushing through the column to get rid of the mixed oil from the column. The pore volumes for all of three columns were equal to 40 ml. Approximately 40 pore volume of de-aired water and 20 pore volumes of de-aired water containing 0.01 M  $\text{Ca}(\text{NO}_3)_2$  was pumped into the column at a flow rate of 0.60 ml/min. to simulate the real situation in the ground water.

### **4.2.2 Mixed Diesel and Motor Oil Saturation**

To saturate residual mixed oil, 1.5 pore volumes of mixed diesel and motor oil was pumped into the packed column in a downward direction at a flow rate of 0.60 ml/min. causing free phase mixed these two oils was displaced with water. The volume of entrapped mixed diesel and motor oil was calculated from a mass balance equation as illustrated in Chapter III. Table 4.3 indicated the oils saturation of mixed diesel and motor oil, diesel, and motor oil for all of three columns. The mass of entrapped mixed diesel and motor oil, diesel and motor oil for the first column were 6.986, 3.346, and 3.608 g, respectively. The mass of entrapped mixed diesel and motor oil, diesel and motor oil for the second column were 6.816, 3.264, and 3.520 g, respectively. For the last column, the mass of entrapped mixed diesel and motor oil, diesel and motor oil were 6.646, 3.182, 3.432 g, respectively.

**Table 4.3 Volume and mass of entrapped mixed diesel and motor oil, diesel, and motor oil in the packed column with initial flushing of 60 ml for all of three columns.**

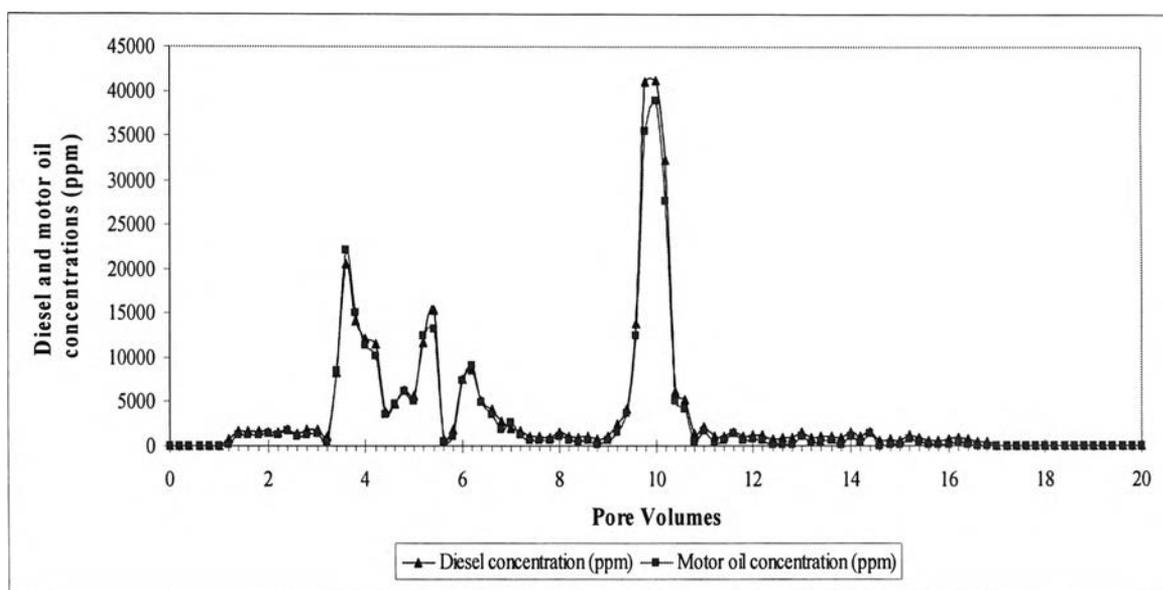
Column	Total of mixed oils in effluent (ml)	Total of mixed oils saturation (ml)	Total of individual oil saturation (ml)	Mass of oil saturation (g)		
				Mixed oils (g) (D=0.852 g/cm <sup>3</sup> )	Diesel (g) (D=0.816 g/cm <sup>3</sup> )	Motor oil (g) (D=0.880 g/cm <sup>3</sup> )
1	51.8	8.2	4.1	6.986	3.346	3.608
2	52.0	8.0	4.0	6.816	3.264	3.520
3	52.2	7.8	3.9	6.646	3.182	3.432

#### 4.2.3 Mixed Diesel and Motor Oil Removal from Soil Column

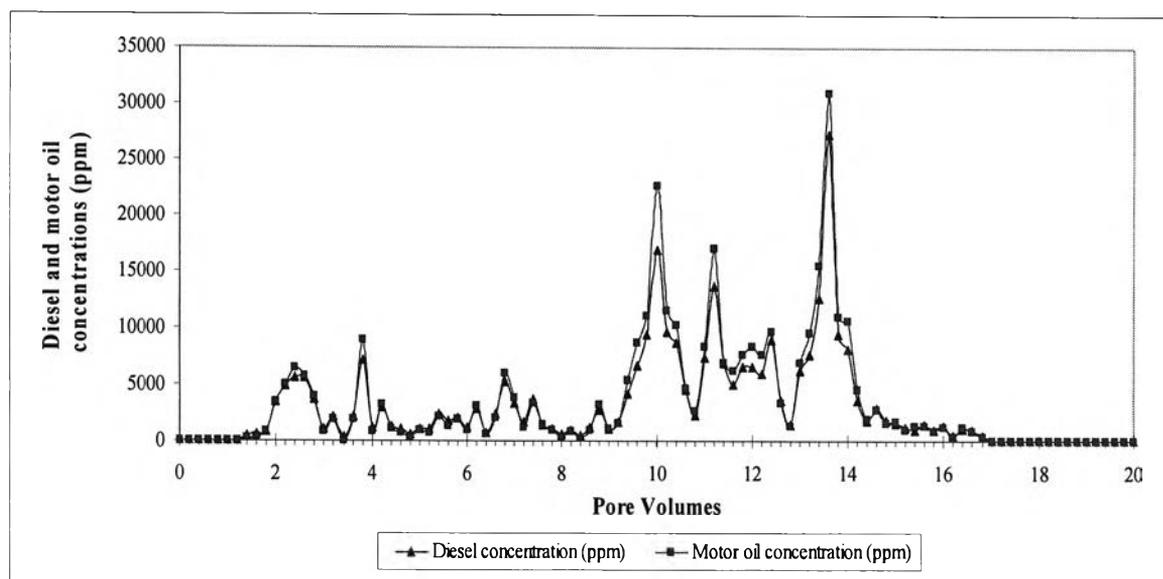
According to the phase behavior study, the optimum surfactant systems for diesel and motor oil due to its lowest IFT were the systems of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 1 wt% NaCl and 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 5 wt% NaCl, respectively. These two systems provided middle phase microemulsion with the minimal interfacial tensions (IFT) which giving a lowest IFT were 0.007 and 0.088 mN/m for diesel and motor oil, respectively. The experimental data for the column study is shown in Appendix B.

Figures 4.3, 4.4 and 4.5 illustrate the results of surfactant flushing through the experimental columns for three conditions of flushing; the system at the optimum condition of diesel, motor oil and the surfactant gradient flushing, respectively. For the surfactant flushing with the surfactant solution at 1 wt% NaCl and 5 wt% NaCl as shown in Figures 4.3, and 4.4, diesel and motor oil concentrations for the first two

columns were found to remove both oils (high peaks) in the range of 8.8-10.8 pore volumes and 12.8-14.4 pore volumes, respectively and gradually decreased until diesel and motor oil concentrations for both systems was not be able to detected at around 17.0 pore volumes.



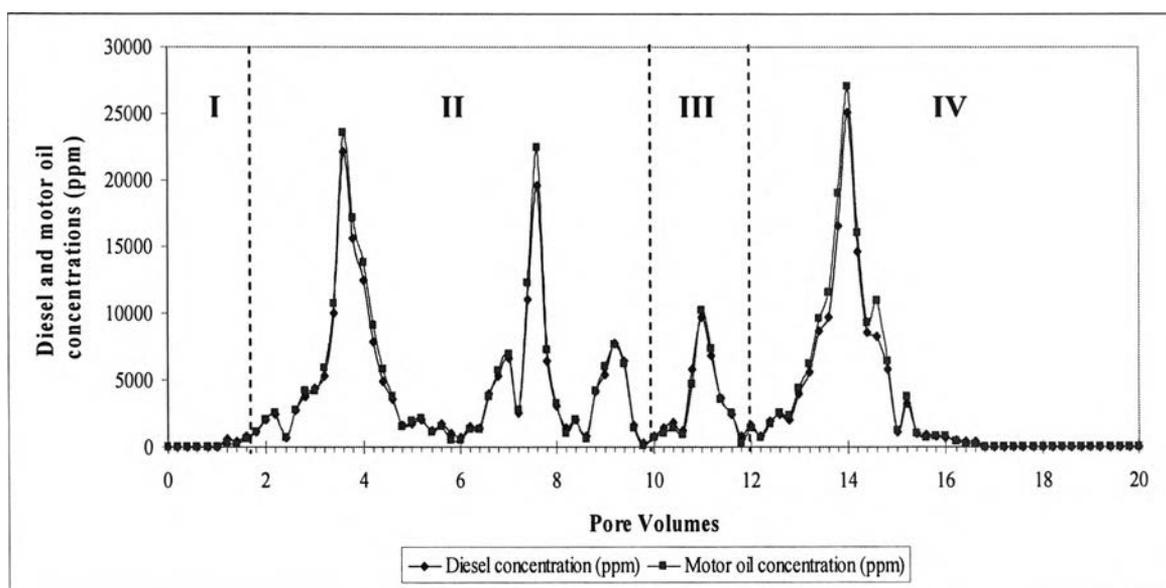
**Figure 4.3 Column experiment results for diesel and motor oil with the system of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 1 wt% NaCl flushing.**



**Figure 4.4 Column experiment results for diesel and motor oil with the system of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 5 wt% NaCl flushing.**

In the gradient approach, Childs et al. (2004) have hypothesized that by beginning the surfactant flush at a higher IFT (i.e. without added salt) and gradually lowering the IFT (increasing the salt concentration) in three or four stages it can maximize the solubilization enhancement while minimizing the vertical migration of DNAPLs. In addition to the criteria for gradient flushing that begins with high IFT surfactant solution as suggested by Childs et al (2004), the proportion of surfactant solutions in four stages was arbitrary. However, it was expected that high proportion of the surfactant solution with lower IFT would provide high solubilization which was desirable for our system. Thus, the overall of surfactant solutions were designed into four stages as mentioned earlier with the total of 20 pore volumes to remove mixed diesel and motor oil. The surfactant solutions at 1 wt% and 5 wt% NaCl which produce minimum IFT for diesel and motor oil removal were used to add at the second and fourth stage, respectively at the four times higher volume of surfactant solution than the volume of surfactant solution at 0 wt% and 3 wt% NaCl for obtaining the highest efficiency for removal of mixed oils from substrate.

For surfactant flushing system with gradient approach as shown in Figure 4.5, the first stage was started from the surfactant system without salinity providing a higher IFT (0.233 mN/m of diesel and 4.622 mN/m of motor oil) for 2 pore volumes. In the second stage, the surfactant system at 1 wt% NaCl, which giving a lower IFT at the optimum salinity of diesel (0.007 mN/m of diesel and 0.186 mN/m of motor oil), was flushed for another 8 pore volumes. Then in the third stage, the surfactant system at 3 wt% NaCl which giving a lower IFT (0.122 mN/m of diesel and 0.176 mN/m of motor oil) was flushed for 2 pore volumes and followed by the last stage of flushing by the surfactant solution with 5 wt% NaCl which giving a lower IFT at the optimum salinity of motor oil (0.262 mN/m of diesel and 0.088 mN/m of motor oil). It was observed that diesel and motor oil concentrations were slightly increased and gradually decreased continuously during 20 pore volumes until the concentrations of diesel and motor oil was not be able to detected at the around 16.8 pore volumes.

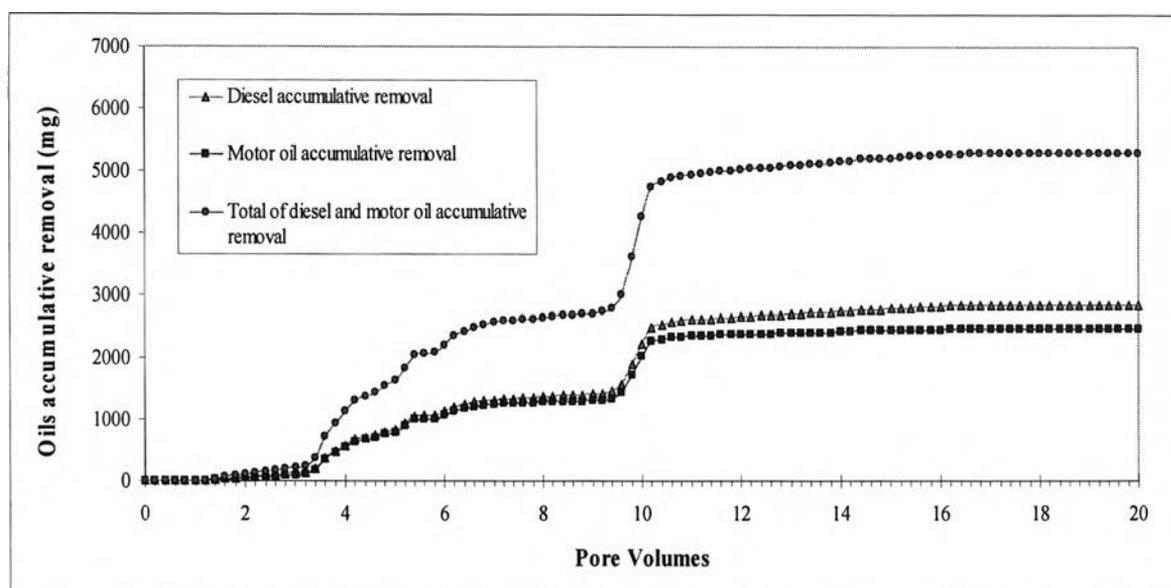


**Figure 4.5** Column experiment results for diesel and motor oil with the system of 0.2 wt% Alfoterra 145-4PO and 0.5 wt% AOT at different NaCl concentration: I-without NaCl, 2 PV; II-with 1% NaCl, 8 PV; III-with 3% NaCl, 2PV; IV-with 5% NaCl, 8 PV.

From Figures 4.3-4.5, it is quite interesting that both two oils were removed almost at the same amount and at the same time (same pore volume). This may be because the two oils are very miscible and homogeneous. In addition, if we consider the IFT between the two oils and the surfactant solution at different salinity (from 1 wt% NaCl to 5 wt% NaCl), it is in the range from 0.007 to 0.262 mN/m) which is insignificantly different and considerably low enough to remove oil from subsurface. Thus, it may be the reason why the two oils were removed at the same time. In Figures 4.3 and 4.4, Surfactant solutions for the optimum salinity of diesel and motor oil were approximately taken 3 and 9 pore volumes for the first elution, respectively. This may be because these two oils having very high viscosity especially motor oil, motor oil has viscosity higher than diesel as illustrated in Chapter III therefore; surfactant solution may take longer time to extract the mixed oil in the pore of the packed column. In Figure 4.5, surfactant gradient system by varying an electrolyte was shown the highest elution at second and fourth stages for the optimum salinity of diesel and motor oil, respectively. As a result, at 1 and 5 wt% NaCl which providing the minimum IFT of diesel and motor oil can remove both two oils from the substrate at the same time.

In Figures 4.6, 4.7, and 4.8 show the comparison between mass of diesel accumulative removal, mass of motor oil accumulative removal and total mass of diesel and motor oil accumulative removal in the first two columns for flushing with single surfactant system and the third column for surfactant gradient system, respectively. For flushing with single surfactant system at 1 wt% NaCl in the first column, it was observed that mixed surfactant system at the optimum salinity of diesel showed the sharp increase of removal from 9 to 11 pore volumes of flushing while in the second column, mixed surfactant system at the optimum salinity of motor oil showed gradually removal for both oils from pore volume 9 to 15 pore volumes of flushing. In the third column with surfactant gradient system, it was observed that diesel and motor oil are also gradually removed out of the column as well as gradually decrease IFT and diesel accumulative removal was slightly lower than motor oil accumulative removal.

From Figures 4.6-4.8, they show that diesel and motor oil can be effectively removed by surfactant system of 0.2 wt% Alfoterra 145-4PO and 0.5 wt% AOT at the optimum salinity of diesel and motor oil, respectively. While the surfactant gradient system shows higher performance for removal both types of oils at the same time. Moreover, removal of mixed diesel and motor oil, only diesel, and only motor oil by surfactant gradient system had a higher efficiency than using the surfactant system at the optimum salinity of diesel and motor oil.



**Figure 4.6 Comparison between diesel accumulative removal, motor oil accumulative removal, and total of diesel and motor oil accumulative removal for the system of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 1 wt% NaCl flushing.**

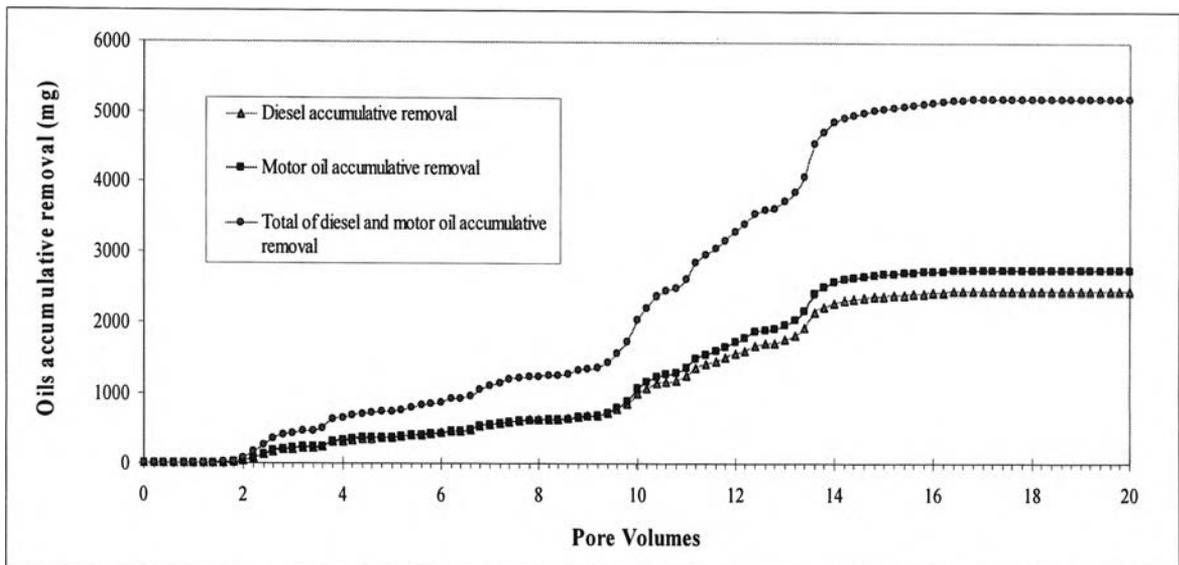


Figure 4.7 Comparison between diesel accumulative removal, motor oil accumulative removal, and total of diesel and motor oil accumulative removal for the system of 0.2 wt% Alforterra 145-4PO, 0.5 wt% AOT and 5 wt% NaCl flushing.

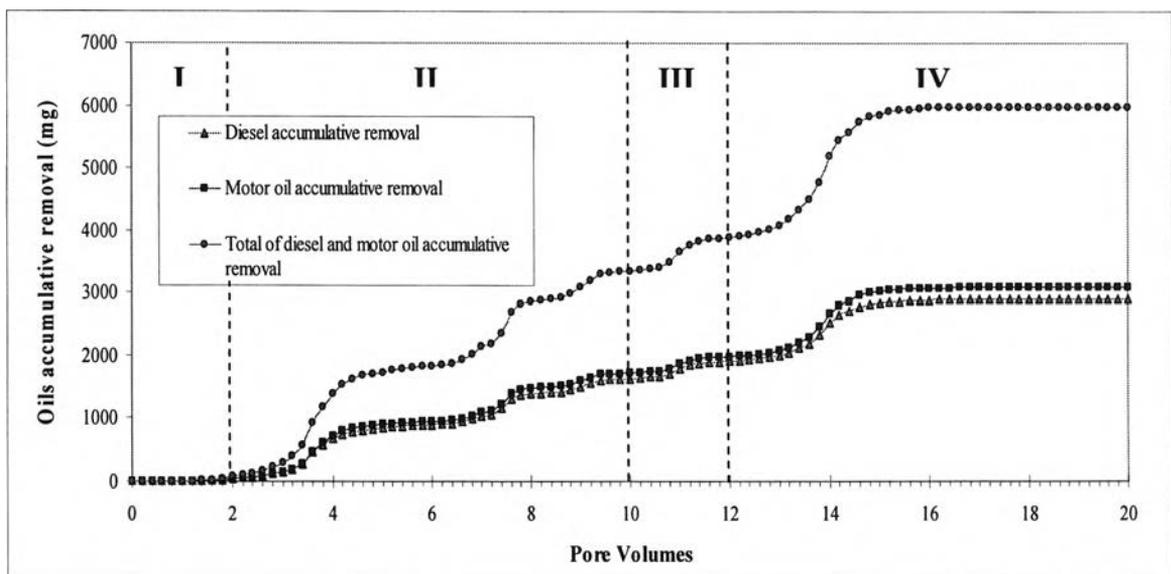
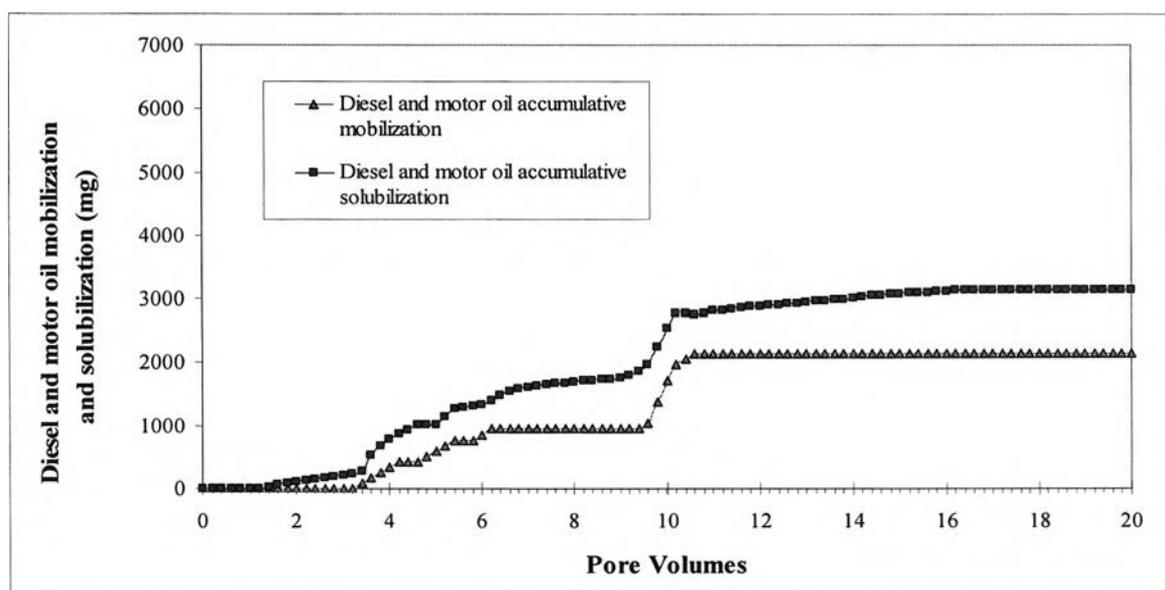
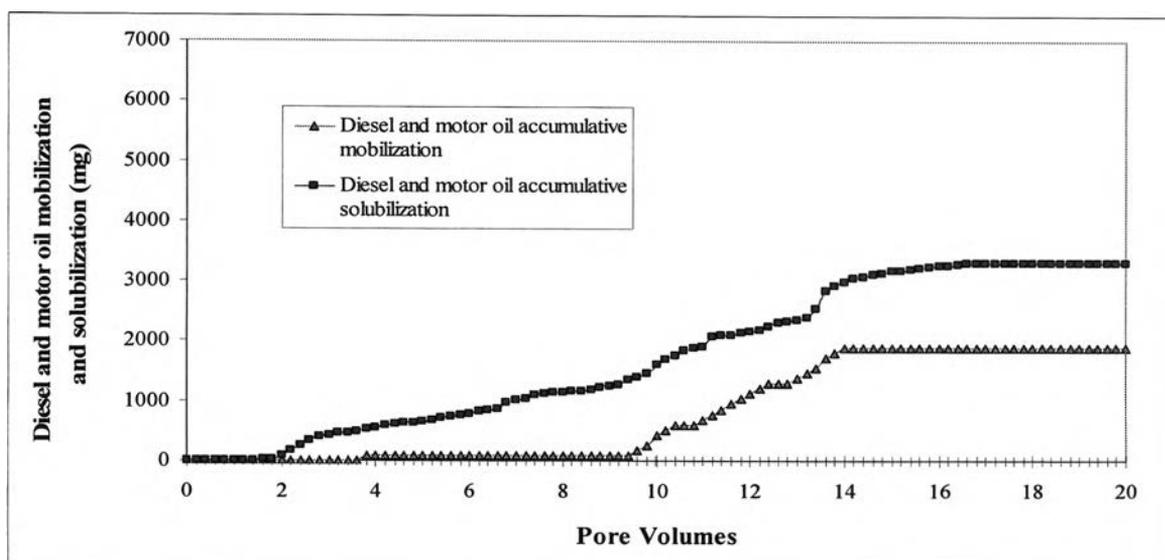


Figure 4.8 Comparison between diesel accumulative removal, motor oil accumulative removal, and total of diesel and motor oil accumulative removal for the system of 0.2 wt% Alforterra 145-4PO and 0.5 wt% AOT 5 wt% at different NaCl concentration: I-without NaCl, 2 PV; II-with 1% NaCl, 8 PV; III-with 3% NaCl, 2PV; IV-with 5% NaCl, 8 PV.

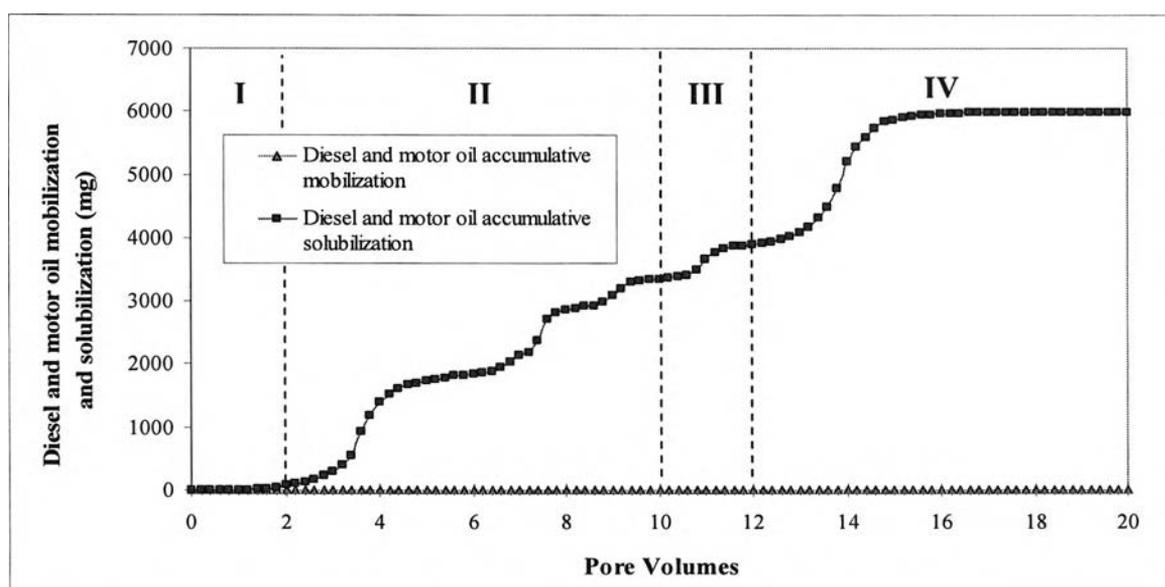
In Figures 4.9, 4.10, and 4.11 present the accumulated total mass of diesel and motor oil solubilization compare with the accumulated total mass of diesel and motor oil mobilization, respectively. As expected, using surfactant gradient system by varying an electrolyte can also enhance diesel and motor oil solubilization. This can be explained by the reason that gradually flushing surfactant solution at high IFT and follow by lower IFT allow the surfactant solution at lower IFT reduce the capillary force of the oils from subsurface and then the detached oils were solubilized in the lower IFT surfactant solution. Thus we found very small amount of free oil in the column of surfactant gradient flushing. It also should be noted here that for the first column flushing with the surfactant solution at 1 wt% NaCl (the optimum condition of diesel), the system provided quite low IFT between diesel and surfactant solution (0.007 mN/m). This low IFT may enhance oil detachment from subsurface; however, it may not be facilitate the motor oil to be solubilized in micelle. Consequently, it becomes free oil phase.



**Figure 4.9 Comparison between diesel and motor oil accumulative mobilization and diesel and motor oil accumulative solubilization for the system of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 1 wt% NaCl flushing.**



**Figure 4.10 Comparison between diesel and motor oil accumulative mobilization and diesel and motor oil accumulative solubilization for the system of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT and 5 wt% NaCl flushing.**



**Figure 4.11 Comparison between diesel and motor oil accumulative mobilization and diesel and motor oil accumulative solubilization for the system of 0.2 wt% Alfoterra 145-4PO and 0.5 wt% AOT at different NaCl concentration: I-without NaCl, 2 PV; II-with 1% NaCl, 8 PV; III-with 3% NaCl, 2PV; IV-with 5% NaCl, 8 PV.**

Table 4.4 summarizes the condition of surfactant flushing and the results of flushing with and without surfactant gradient system for all of three columns. Figures 4.12 and 4.13 illustrate the efficiency of oil removal by mixed surfactant system with the optimum salinity of diesel (1 wt% NaCl), the optimum salinity of motor oil (5 wt% NaCl), and surfactant gradient system (0, 1, 3, and 5 wt% NaCl). The first column with mixed surfactant system at the optimum salinity of diesel (1 wt% NaCl), diesel, motor oil, and mixed diesel and motor oil were removed by solubilization and mobilization mechanisms for 2.831, 2.448, and 5.278 g, respectively. The solubilization and mobilization for mixed diesel and motor oil were observed for 3.138 and 2.141 g. This results show that diesel, motor oil, and mixed diesel and motor oil were removed by both solubilization and mobilization mechanisms for 84.61%, 67.85%, and 75.55%, respectively while mixed diesel and motor oil was mainly solubilized and mobilized for 44.92% and 30.65%, respectively. The second column with mixed surfactant system at the optimum salinity of motor oil (5 wt% NaCl), diesel, motor oil, and mixed diesel and motor oil were removed by solubilization and mobilization mechanisms for 2.446, 2.741, and 5.187 g, respectively. The solubilization and mobilization for mixed diesel and motor oil was observed for 3.304 and 1.884 g, respectively. This results show that diesel, motor oil, and mixed diesel and motor oil were removed by both solubilization and mobilization mechanisms for 74.94%, 77.87%, and 76.10%, respectively while mixed diesel and motor oil was mostly solubilized and mobilized for 48.47% and 27.64%, respectively. The third column with surfactant gradient system (0, 1, 3, and 5 wt% NaCl), diesel, motor oil, and mixed diesel and motor oil were removed by both solubilization and mobilization for 2.897, 3.081, and 5.978 g, respectively. The solubilization of mixed diesel and motor oil was observed for 5.978 g while mixed diesel and motor oil mobilization was unable to be observed. It means that diesel, motor oil, and mixed diesel and motor oil were removed by both solubilization and mobilization mechanisms for 91.04%, 89.77%, and 89.95%, respectively whereas mixed diesel and motor oil was entire solubilized for 89.95%. As a consequence, using surfactant gradient system can be used to maximize solubility enhancement by trapping the mixed diesel and motor oil in the inner core of micelle in aqueous surfactant solution while minimizing the mixed two oils mobilization

as a free phase oil to prevent the potential negative outcomes such as mobilization of pollutants into a previously uncontaminated area.

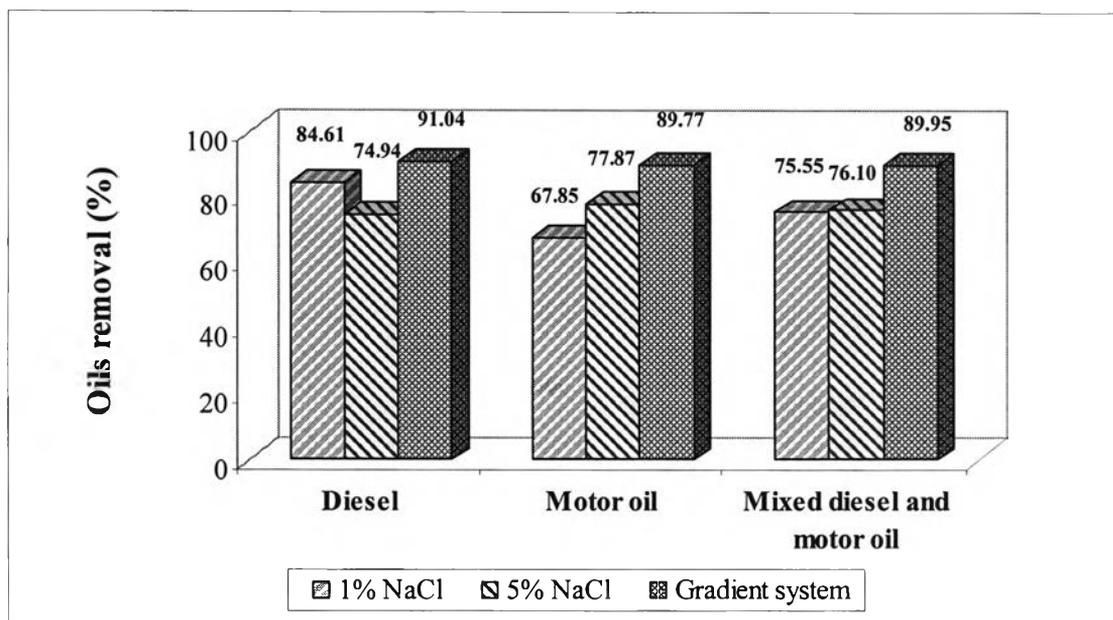
From this study, a surfactant gradient system flushing mixed diesel and motor oil from Ottawa sand show the effectiveness of surfactant gradient system compared to the surfactant flushing without the surfactant gradient system for removal of mixed diesel and motor oil from the column.

**Table 4.4 Conditions of surfactant flushing with and without surfactant gradient system.**

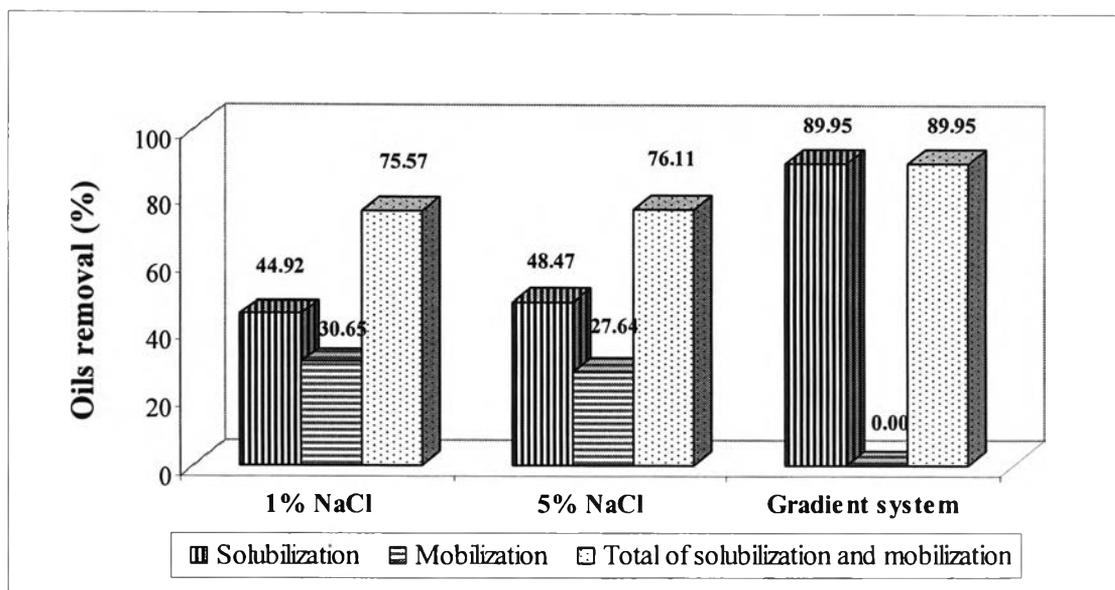
No.	Surfactant system	wt% NaCl	IFT (mN/m)	Saturated mixed diesel and motor oil (g)	Saturated diesel (g)	Saturated motor oil (g)	Mixed diesel and motor oil accumulative removal (g)	Diesel accumulative removal (g)	Motor oil accumulative removal (g)	Solubilized mixed diesel & motor oil (g)	Mobilized mixed diesel & motor oil (g)
1	0.2% Alfoterra 145-4PO, 0.5%AOT	1	0.077* 0.186**	6.986	3.346	3.608	5.278	2.831	2.448	3.138	2.141
2	0.2% Alfoterra 145-4PO, 0.5%AOT	5	0.262* 0.088**	6.816	3.264	3.520	5.187	2.446	2.741	3.304	1.884
3	0.2% Alfoterra 145-4PO, 0.5%AOT	0 1 3 5	0.233* 4.622** 0.007* 0.186** 0.122* 0.176** 0.262* 0.088**	6.646	3.182	3.432	5.978	2.897	3.081	5.978	0.000

Note: \* indicates the IFT of diesel

\*\* indicates the IFT of motor oil



**Figure 4.12 Efficiency of oil removal by mixed surfactant system with the optimum salinity of diesel (1 wt% NaCl), the optimum salinity of motor oil (5 wt% NaCl), and surfactant gradient system (0, 1, 3, and 5 wt% NaCl).**



**Figure 4.13** Efficiency of oil removal in case of solubilization, mobilization, and total of solubilization and mobilization by mixed surfactant system with the optimum salinity of diesel (1 wt% NaCl), the optimum salinity of motor oil (5 wt% NaCl), and surfactant gradient system (0, 1, 3, and 5 wt% NaCl).