CHAPTER IV
RESULTS AND DISCUSSION

4.1 Microemulsion formation

The experimental data of microemulsion formation are shown in Appendix A and the experimental results are described below.

4.1.1 Effect of single surfactant concentration on microemulsion formation

The effect of SDS concentration on microemulsion formation is illustrated in Figure 4.1. When SDS concentration increased from 1 to 9 wt. %, the height or volume of the water phase increased and the oil phase decreased slighty because SDS is more favor to solubilize in the water phase than the oil phase leading to dispersion of oil droplets in the water phase. As can be seen in Figure 4.1, the solution had only two phases of water and oil without the middle phase. It can be concluded that it is oil in water microemulsion or Winsor type I microemulsion.

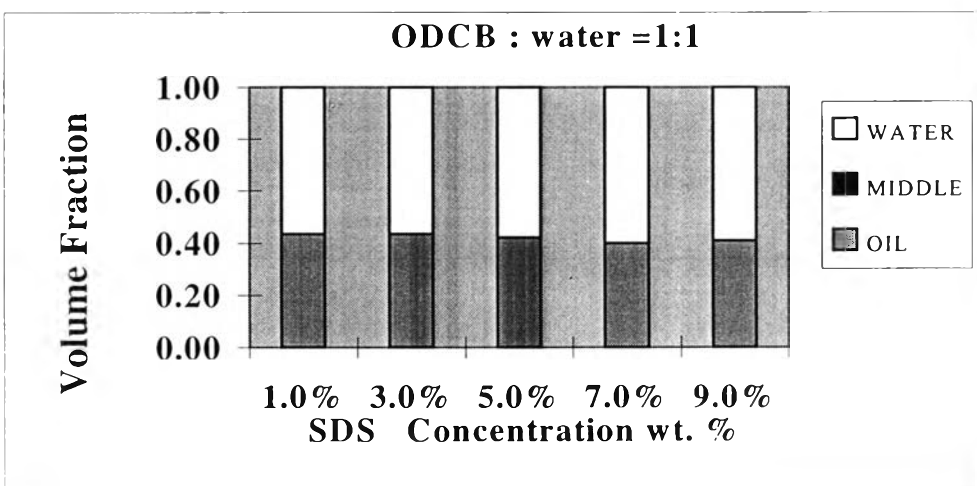


Figure 4.1 Volume fractions of water, middle and oil phases at different SDS concentrations with initial oil/water ratio = 1/1

The effect of $NP(EO)_{10}$ concentration on the phase behavior with the ODCB/water initial volume ratio of 1/1 is illustrated in Figure 4.2. When the $NP(EO)_{10}$ concentration increased from 1 to 9 wt. %, the volume of the water phase slightly decreased because $NP(EO)_{10}$ solubilizes in oil better than in water. In addition, the middle phase (Winsor type III microemulsion) appeared under the presence of $NP(EO)_{10}$. However, the volume of the middle phase had a little fraction when compared to the volumes of both the oil and water phases. Hence, the mixed surfactants containing SDS and $NP(EO)_{10}$ were investigated whether or not they could enhance the formation of the middle phase.

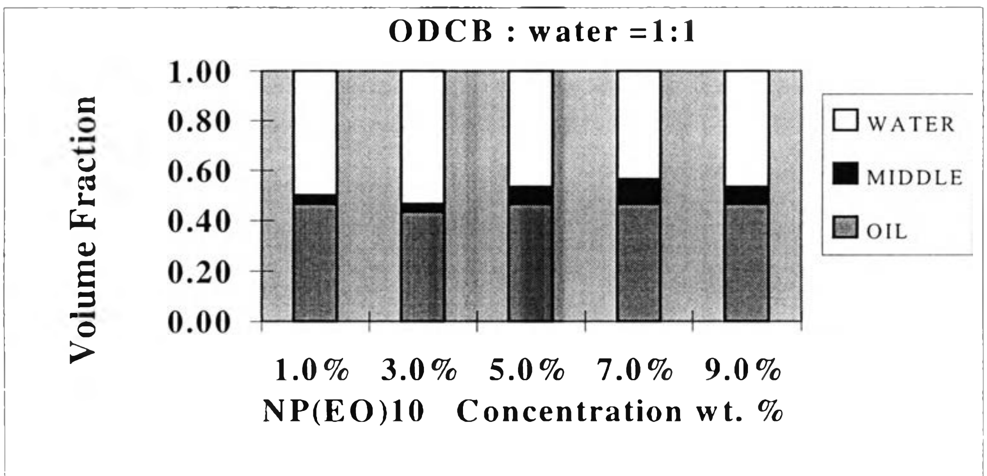


Figure 4.2 Volume fractions of water, middle and oil phases at different $NP(EO)_{10}$ concentrations with initial oil/water ratio = 1/1

4.1.2 Effect of mixed surfactants concentration on microemulsion formation

Figures 4.3 shows the phase behavior of the ODCB-water system under the presence of mixed surfactants having the total concentration of 1 to 9 wt. %. In comparison between the single surfactant and the mixed surfactants, it was clearly seen that a significant increase of the middle phase was achieved

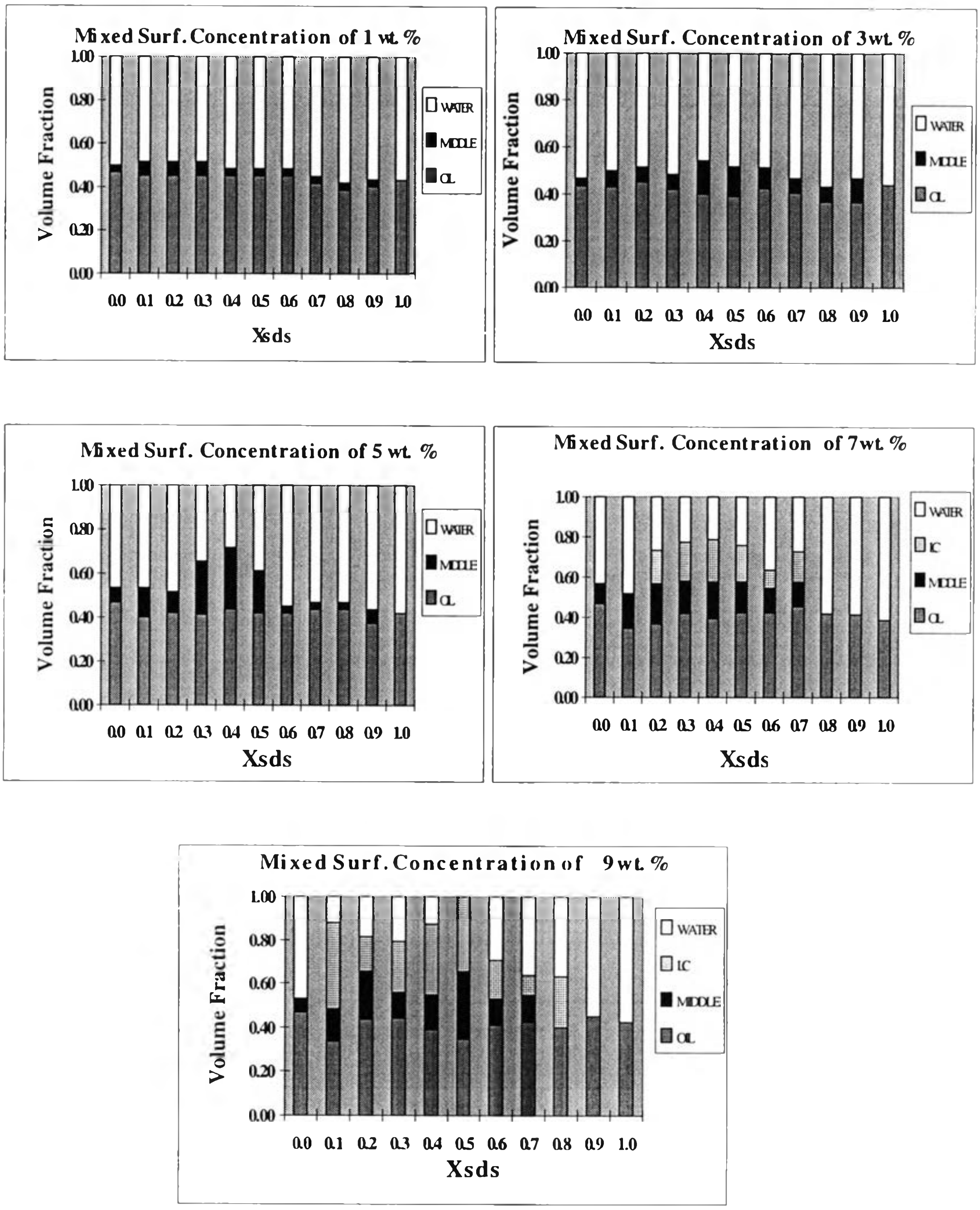


Figure 4.3 Volume fractions of water, middle and oil phases at different mixed surfactants concentrations with initial oil/water ratio = 1/1

by using the mixed surfactants. This is because SDS enhances the solubilization of water while $NP(EO)_{10}$ enhances the solubilization of oil. Therefore, they help each other to expand the volume of the middle phase. As Xsds increased from 0.1 to 0.9 for all of mixed surfactants concentration, the volume of the middle phase increased and then it reached the maximum value. The maximum volume of the middle phase appears when the system has the proper balance between hydrophilicity and hydrophobicity resulting in increasing the volume of the middle phase. The volume of the middle phase then decreased when Xsds continuously increased after its optimum concentration. It is very interesting to point out that for the total concentration of mixed surfactants equal to and greater than 7 wt. %, liquid crystal appeared. As can be seen from Figure 4.4, the volume of the middle phase is governed by both the total surfactants concentration and the SDS fraction. At a low mixed surfactants concentration, the volume of the middle phase had a little volume fraction but at a high mixed surfactants concentration greater than 7 wt. %, the middle phase had a larger volume fraction as well as the formation of liquid crystal that limits solubilization capacity. The maximum volume fraction of the middle phase was obtained at the total surfactants concentration of 5 wt. % and the Xsds volume of 0.5. The results can be explained clearly that the reduction of the middle phase appears as a result of the liquid crystal formation when the total surfactants concentration is greater than 7 wt. % as shown in Figure 4.3. Again, the optimum effect between hydrophilicity and hydrophobicity appeared at the Xsds of 0.5. Figure 4.5 is a plot the average volume fraction of the middle phase for all values of Xsds against the total surfactants concentration.

3 and 5 wt. % of the mixed surfactants were chosen to study in froth flotation experiment because they had high volume fractions of the middle phase without liquid crystals.

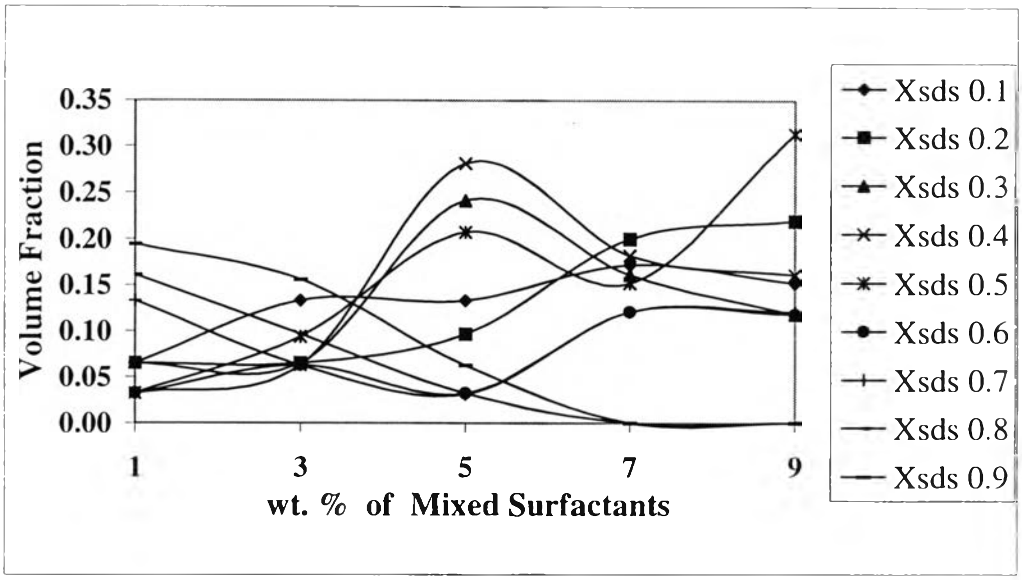


Figure 4.4 Volume fraction of middle phase at different Xsds and mixed surfactants concentrations with initial oil/water ratio = 1/1

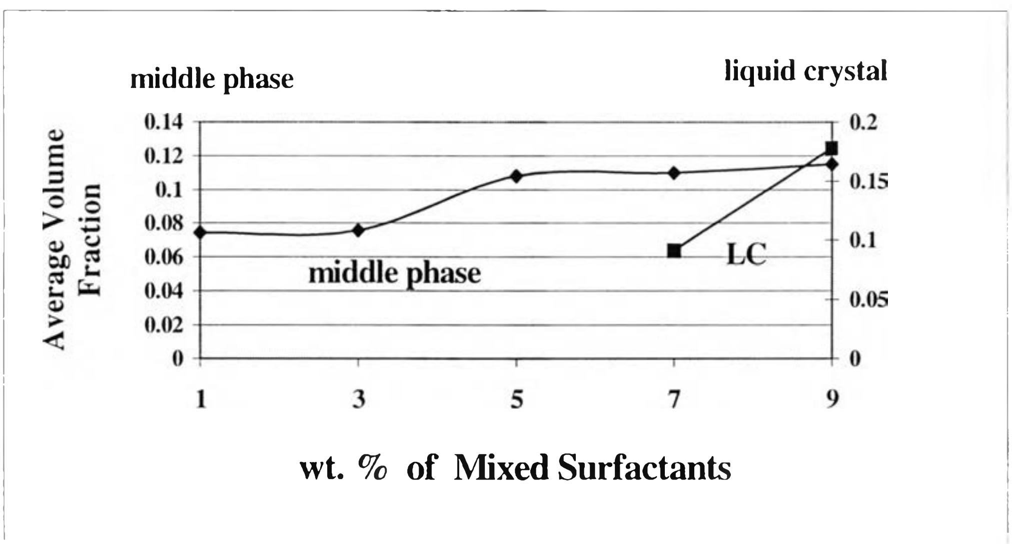


Figure 4.5 Average volume fraction of middle phase at mixed surfactants concentrations with initial oil/water ratio = 1/1

4.1.3 Effect of NaCl on microemulsion formation of mixed surfactants system

NaCl was added together with the mixed surfactants (SDS and $NP(EO)_{10}$) in the studied system in order to determine the effect of NaCl on microemulsion formation. The NaCl concentration was varied from 0.5 to 2.5 wt. %. The effect of NaCl on microemulsion formation with 1 wt. %. mixed surfactants is illustrated in Figure 4.6. The results showed that, for Xsds = 0.1, the optimum NaCl for the maximum volume of the middle phase was 0.5 wt. %. For Xsds = 0.2 up to 0.4, the volume of the middle phase reached the maximum volume at 1.0 wt. % NaCl. For Xsds greater than 0.5, as NaCl was added, the precipitation of NaCl and surfactant occurred as well as reduction of the volume of the middle phase or Winsor type III microemulsion. In addition, in the range of Xsds from 0.1 to 0.4, the solutions transferred from Winsor type III or three phases microemulsion to Winsor type II or water in oil microemulsion as the concentration of NaCl increased from 1 to 1.5 wt. %. At a very high Xsds of 0.9, an increase in NaCl concentration resulted in disappearance of the middle phase and liquid crystal formation when NaCl was added. The maximum volume of the middle phase was obtained at 1 wt. % NaCl with the optimum range of Xsds from 0.3-0.4.

Figure 4.7 shows the effect of NaCl on microemulsion formation with 3 wt. % mixed surfactants. The results showed that, for Xsds = 0.1 to 0.5, the system had the maximum volume of the middle phase at 0.5 wt. % NaCl. For Xsds = 0.6, the volume of the middle phase reached the maximum volume at 1 wt. % NaCl. For Xsds greater than 0.6, the volume of the middle reduced due to the precipitation of both NaCl and surfactant. Furthermore, for Xsds = 0.1 to 0.5, the solutions transferred from Winsor type III (the middle phase) to Winsor type II or water in oil microemulsion when the concentration of NaCl increased from 0.5 to 1.0 wt. %.

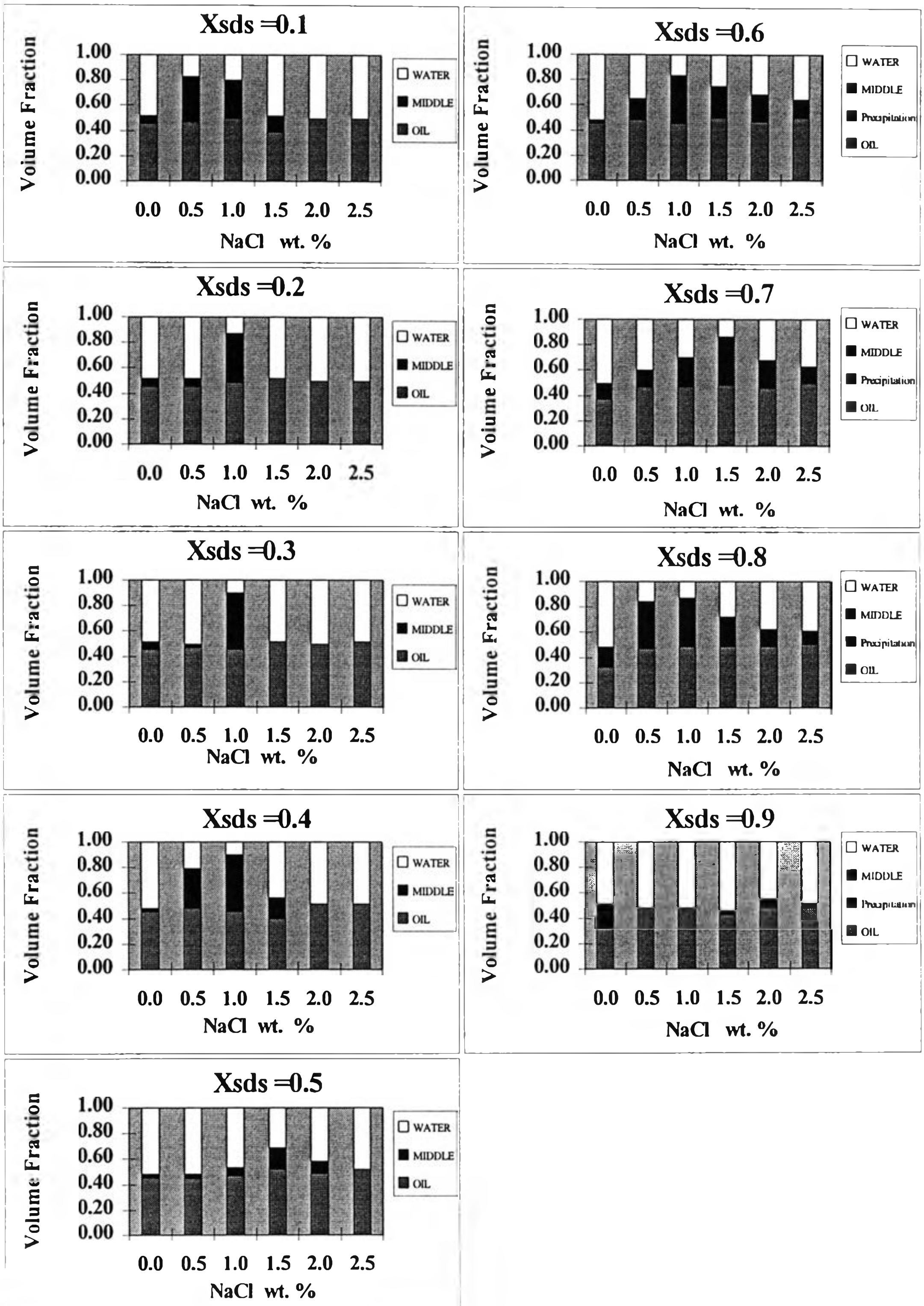


Figure 4.6 Volume fractions of water, middle and oil phases at 1 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 and at different SDS fractions

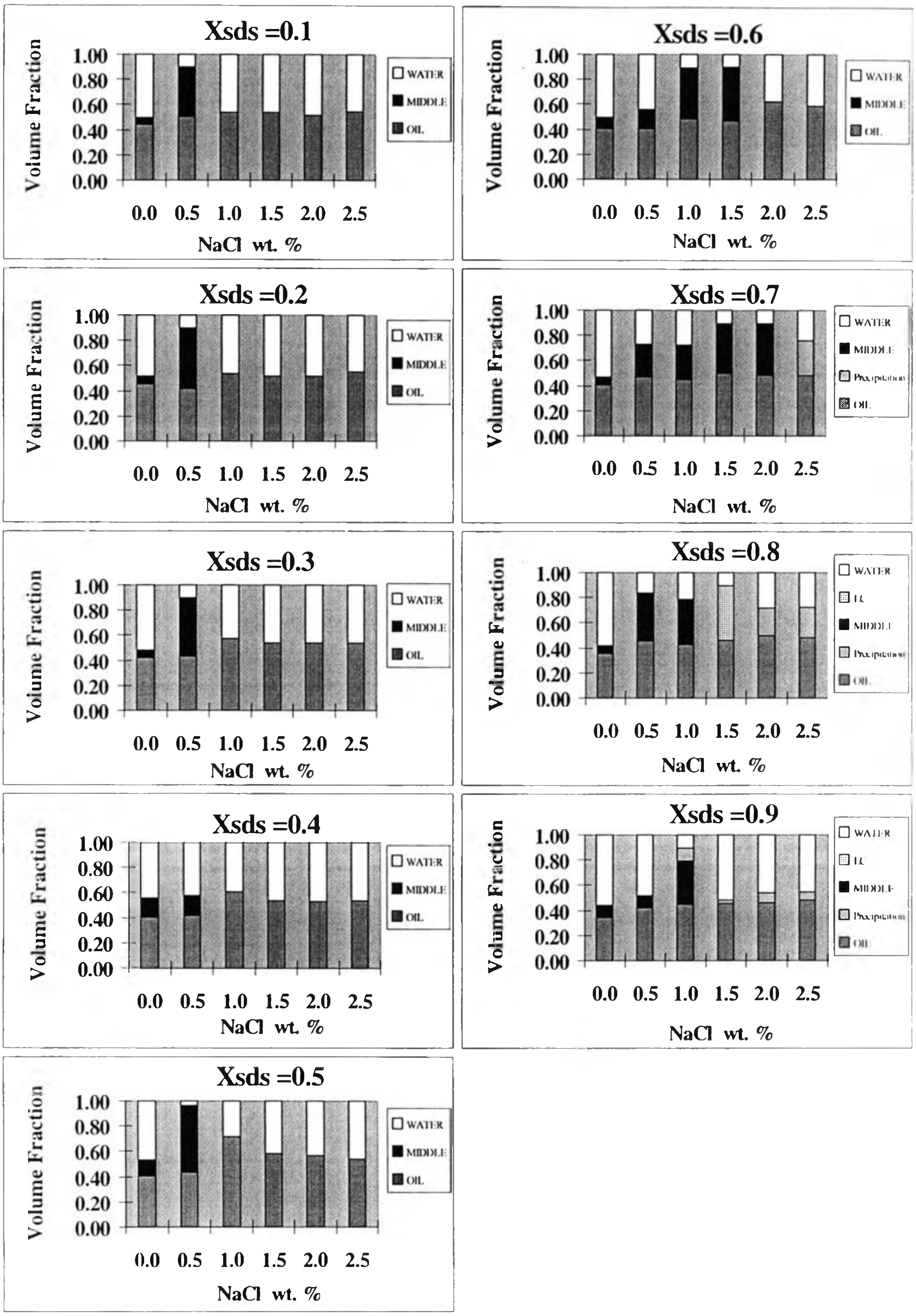


Figure 4.7 Volume fractions of water, middle and oil phases at 3 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 and at different SDS fractions

As compared between 1 and 3 wt. %. mixed surfactants, the requirement of NaCl for maximizing the volume of the middle phase reduced when the concentration of mixed surfactants increased.

The effect of NaCl on microemulsion formation with 5 wt. % mixed surfactants is shown in Figure 4.8. The results indicated that, for Xsds = 0.1 to 0.3, addition of NaCl caused disappearance of the middle phase and the inversion from Winsor type III to Winsor type II. When NaCl was continuously added, the solutions became less hydrophobicity resulting in decreasing the volume of the oil phase. For Xsds from 0.4 to 0.6, addition of NaCl could enhance the formation of the middle phase but at a very high NaCl concentration, it resulted in disappearance of the middle phase. At the range of the total surfactants concentration, NaCl was above 0.5 wt. %, the system transferred from Winsor type III to Winsor type II. The volume of the oil phase decreased and the solutions were more hydrophilicity as NaCl concentration increased. For Xsds =0.7, the volume of the middle phase including liquid crystal appeared and increased as NaCl concentration increased. For Xsds = 0.8 to 0.9, the precipitation and liquid crystal occurred as NaCl was continuously added.

In order to determine the phase behavior at a very high concentration of the mixed surfactants the studied system was carried out at 7 and 9 wt. % total surfactant concentrations. The results of 7 wt. % mixed surfactants are shown in Figure 4.9. The results indicated that an addition of NaCl did not enhance the formation of the middle phase and caused the disappearance of the middle phase when a small amount of NaCl was added. For Xsds = 0.1, the system transferred from Winsor type III microemulsion to Winsor type II microemulsion when NaCl was induced and the volume of the water phase increased slightly with increasing NaCl concentration. For Xsds = 0.2 to 0.6, the results showed that without NaCl, the system had the middle phase as well

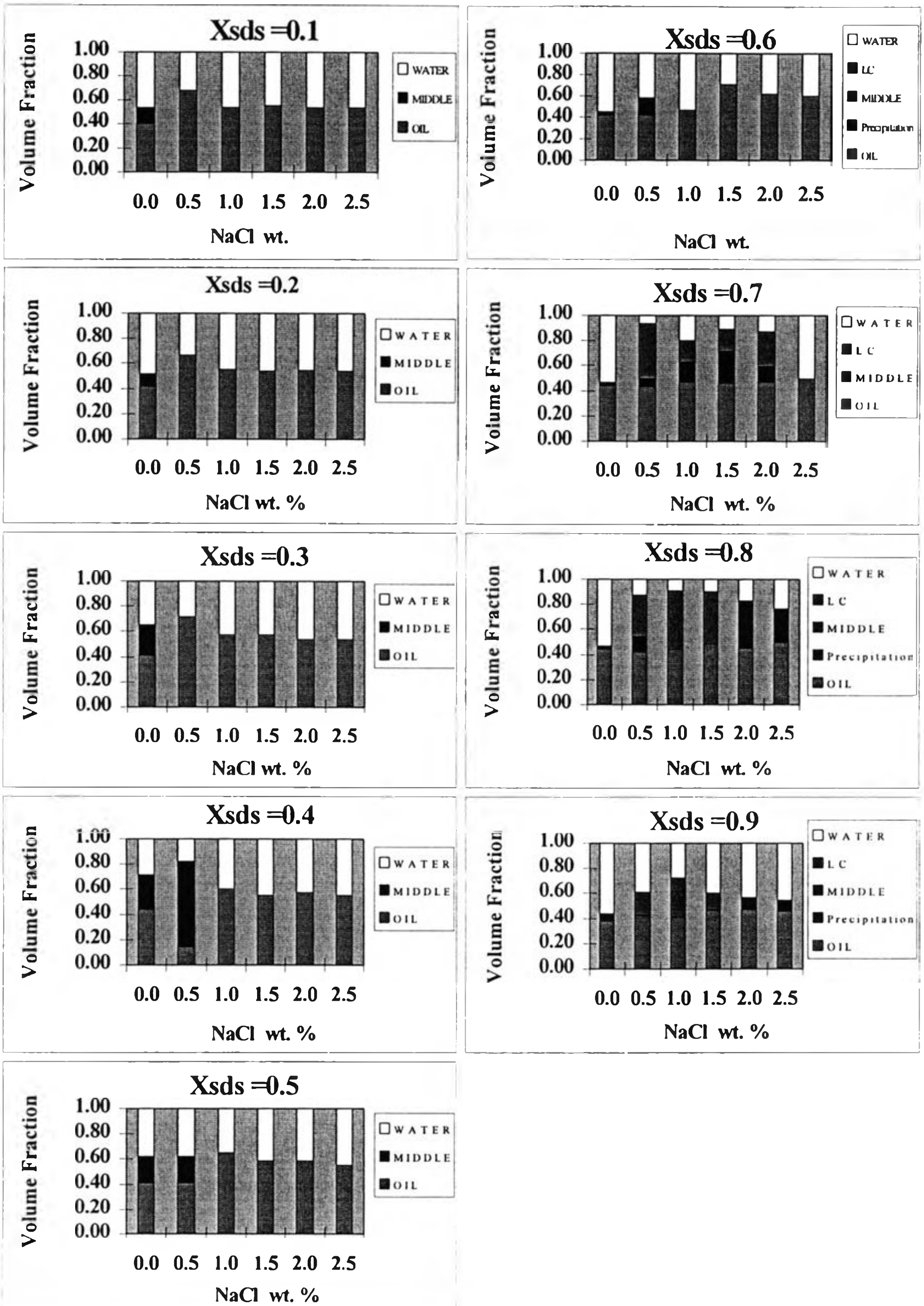


Figure 4.8 Volume fractions of water, middle and oil phases at 5 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 and at different SDS fractions

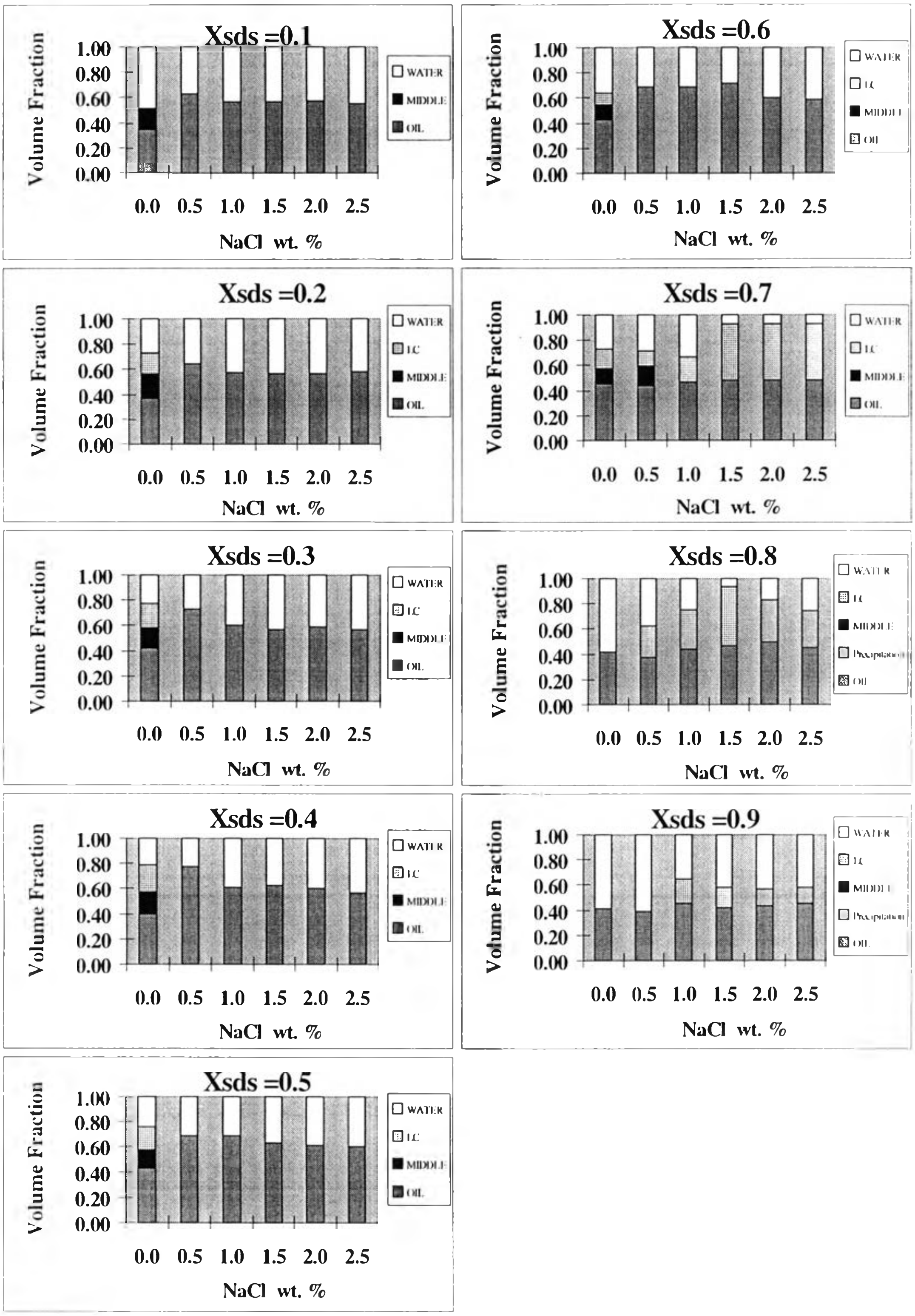


Figure 4.9 Volume fractions of water, middle and oil phases at 7 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1and at different SDS fractions

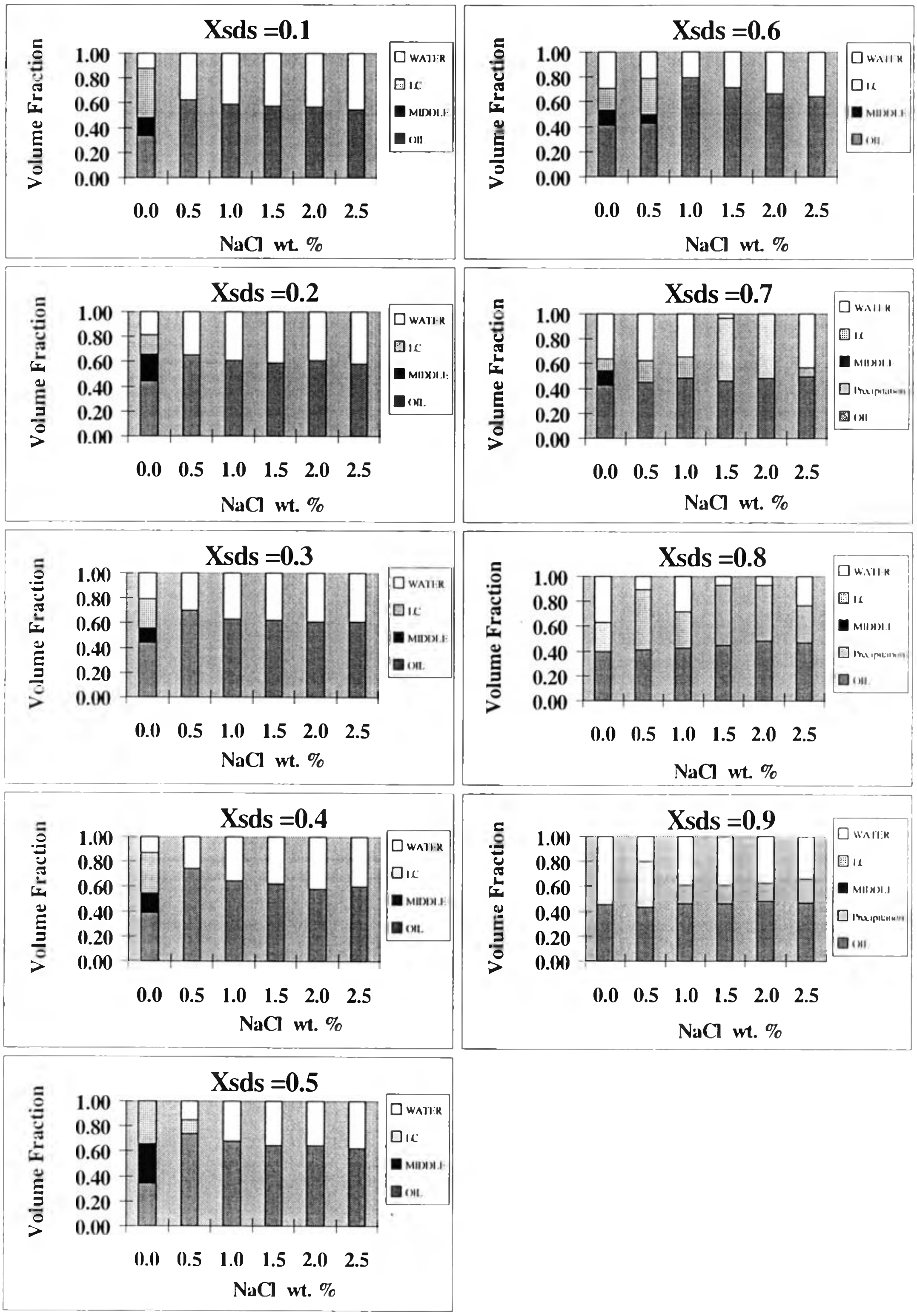


Figure 4.10 Volume fractions of water, middle and oil phases at 9 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 and at different SDS fractions

as liquid crystal. When the solutions were scanned with NaCl, both the middle phase and the liquid crystal disappeared. For Xsds = 0.7 to 0.9, the solutions had significant volumes of both liquid crystal including the precipitation of surfactant and NaCl.

Figure 4.10 illustrates the effect of NaCl on microemulsion formation with 9 wt.%mixed surfactants concentration. For Xsds = 0.1 to 0.6, the solutions had the middle phase with liquid crystal. Addition of NaCl caused both Winsor type III and liquid crystal disappeared. When NaCl concentration further increased, the volume of the water phase increased slightly because the system becomes less hydrophobic. For Xsds = 0.7 to 0.9, appearance of both liquid crystal and the precipitation of the surfactants were dominant. An increase in NaCl resulted in increasing both the volume fraction of liquid crystal and the precipitation phase.

From the experimental results, it can be concluded that for a low total surfactants concentration, addition of NaCl could maximize the volume of the middle phase. As Xsds increased, NaCl that required to enhance the volume of the middle phase increased because of higher amount of SDS which is an ionic surfactant. The addition of small amount of NaCl to the solution containing ionic surfactants appears to increase the extent of solubilization of oil so that it is solubilized in the inner core of the micelle and to decrease that of polar compounds that are solubilized in the outer portion of the palisade layer (Rosen, 1992). NaCl can reduce the repulsion between similarly charged ionic surfactant head groups which can lead to decreasing CMC and increasing the aggregation number. Furthermore, the addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsion between the charged surfactant heads and greatly facilitate mixed micelles formation. (Shiloach and Blankschtein, 1998). For these reasons, mixed surfactants with small amount of NaCl can enhance the solubilization of oil and the volume of the middle phase.

However, at a high mixed surfactants concentration, addition of NaCl could not enhance the formation of the middle phase and also produced the inversion from Winsor type III to Winsor type II. This is because of the formation of crystal and precipitation of the surfactants.

4.2 Froth flotation experiment

The experimental data of froth flotation study are shown in Appendix B and the experimental results are described below.

4.2.1 Effect of initial mixed surfactants concentration on ODCB removal

The effect of initial mixed surfactants concentration on the ODCB removal can be seen in Figure 4.11. For a given aeration time, percentage of the ODCB removal increased significantly as initial mixed surfactants concentration increased from 3 to 5 wt.%. Since a higher surfactant concentration dramatically increases the dispersion of air which enhances flotation efficiency and carries the larger amount of dispersed oil molecules.

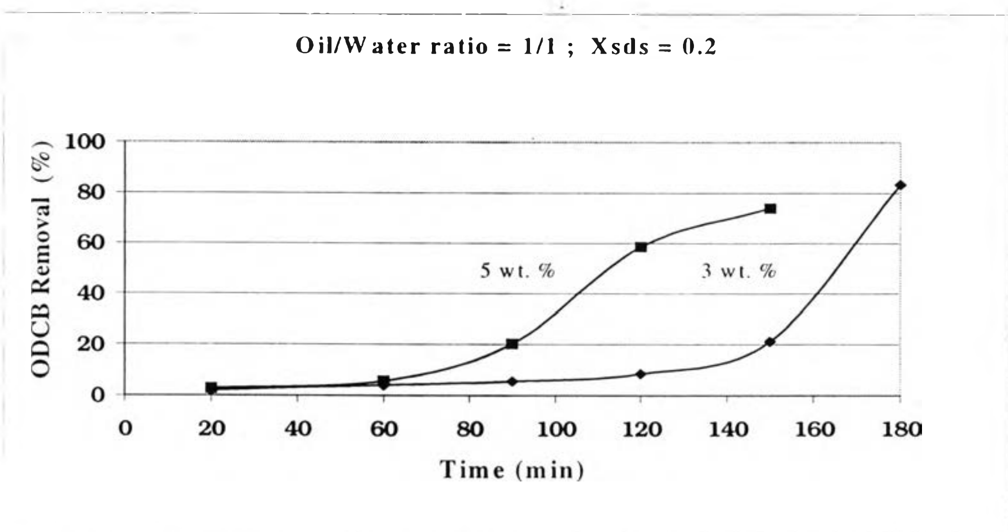
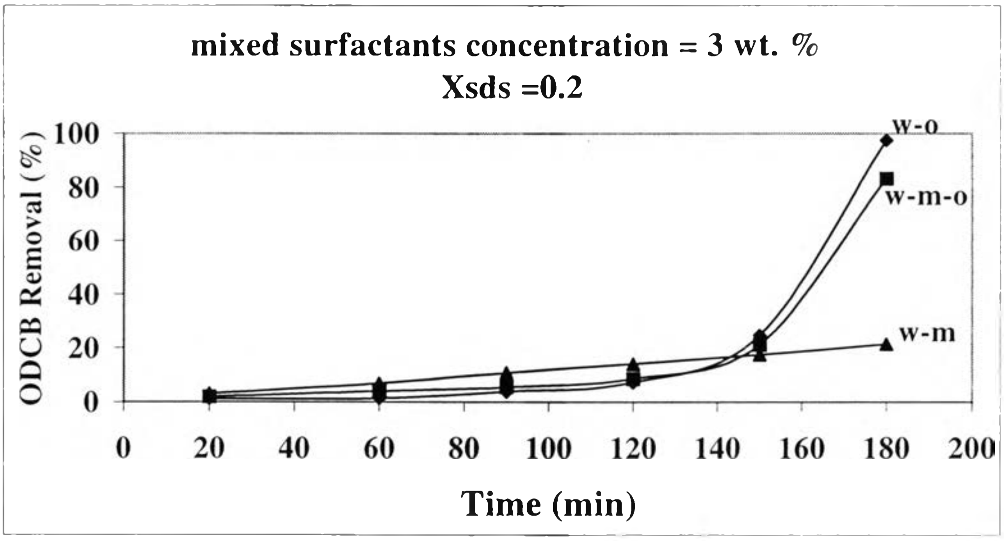


Figure 4.11 ODCB removal at two initial mixed surfactants concentrations and Xsds = 0.2 with initial oil/water ratio = 1/1

4.2.2 Effect of phase on ODCB removal

The prepared solutions of Winsor type III were chosen for the flotation experiment since in the previous study, the froth flotation system operated under the presence of Winsor type III gave the maximum removal of oil from water (Pongstabodee *et.al*, 1998). The prepared solutions composing of three phases were firstly separated into three systems of water and middle phases system (w-m), water and oil phases system (w-o) and water, middle and oil phases system (w-m-o). Figure 4.12 illustrates the effects of initial mixed surfactants concentration and phases on the ODCB removal. The results showed that percentage of ODCB removal in the w-o system was the highest while the w-m system had the lowest ODCB removal for both initial mixed surfactants concentrations. For the experimental results, an increase in the initial total surfactants concentration could enhance the ODCB removal efficiency for all three systems. This is probable due to an increase in foam fraction with increasing the total of surfactants concentration which results in increasing the ODCB removal.

The effects of phase and the weight ratio of SDS on the ODCB removal for both total surfactants concentrations are shown in Figures 4.13 and 4.14. The results showed that percentage of the ODCB removal of the w-m-o system was the highest value and the w-m system gave the lowest ODCB removal. This is because Xsds that equal to 0.4 and 0.6 have the proper balance between hydrophilic and hydrophobic of mixed surfactants molecules leading to high volume fraction of the middle phase and high mixed surfactants concentration in the middle phase. Therefore the ODCB removal efficiency in the w-m-o system was the highest value in these weight ratios. These conclusions could be confirmed by microemulsion formation experiment. As compared between the w-o and w-m systems, the w-o system had greater amount of oil than the w-m system therefore, percentage of the ODCB removal in the w-o system was greater than in the w-m system.



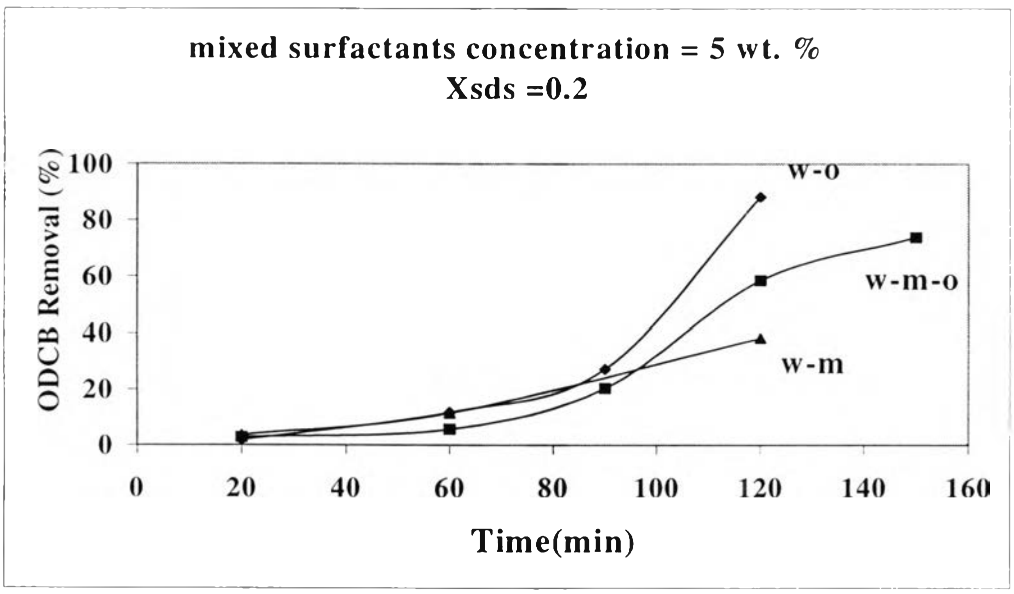


Figure 4.12 ODCB removal at 3 and 5 wt. % mixed surfactants concentrations and Xsds = 0.2 with initial oil/water ratio = 1/1

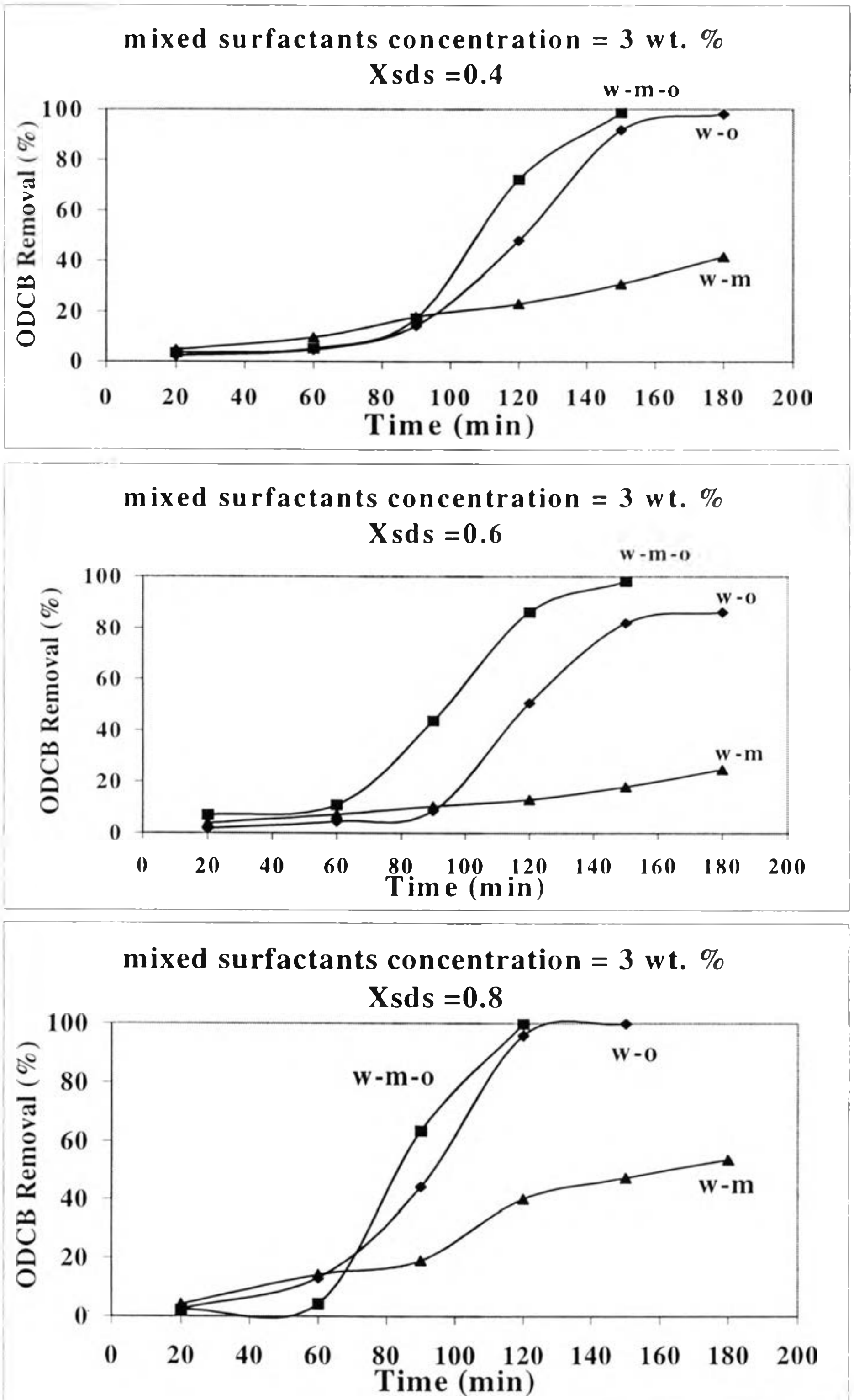


Figure 4.13 ODCB removal of three different systems at 3 wt. % mixed surfactants concentration and Xsds = 0.4, 0.6, and 0.8 with initial oil/water ratio = 1/1

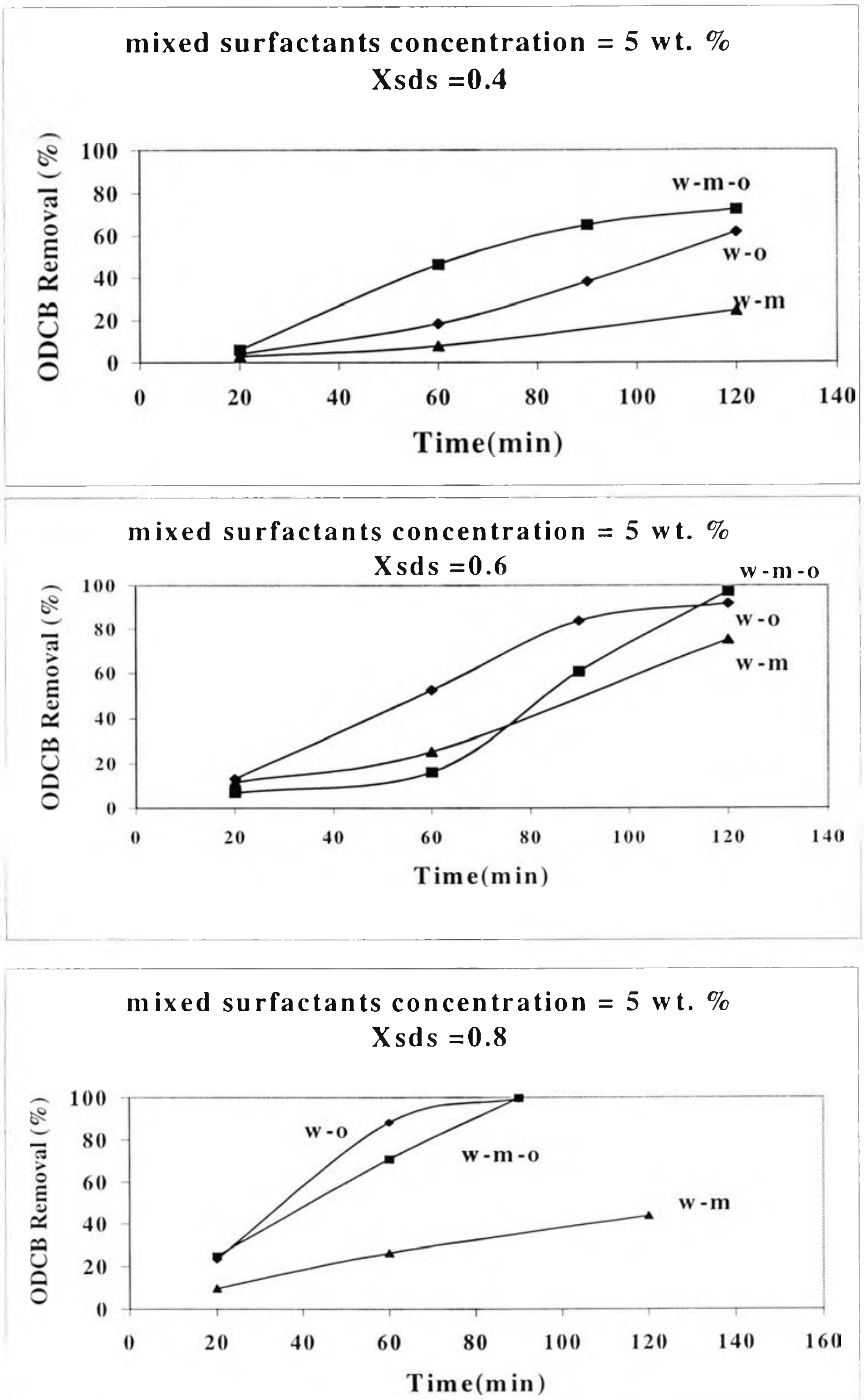


Figure 4.14 ODCB removal of three different systems at 5 wt. % mixed surfactants concentration and Xsds = 0.4, 0.6, and 0.8 with initial oil/water ratio = 1/1

4.2.3 Effect of NaCl concentration on ODCB removal

The effect of NaCl concentration in the w-m-o system on the ODCB removal can be seen in Figure 4.15. NaCl was added to the system containing 3 wt. % mixed surfactants concentration and Xsds of 0.6 in order to study the effect of NaCl on the ODCB removal. NaCl concentrations was varied from 0.5 to 2.0 wt. %. As can be seen from Figure 4.15, an increase in a small amount of NaCl about 0.5 wt. % could enhance the ODCB removal when compared with without NaCl. A small amount of NaCl can enhance the ODCB removal because NaCl can reduce the repulsion between the head group of ionic surfactant and extend solubilization of hydrocarbon, therefore it can reduce CMC (Critical Micelle Concentration) and increase the aggregation number of micelles. However, a higher NaCl concentration from 1 to 2.0 wt. %, percentage of the ODCB removal decreased significantly when comparing without NaCl. This is because liquid crystal and the precipitation in microemulsion solution that limits solubilization capacity.

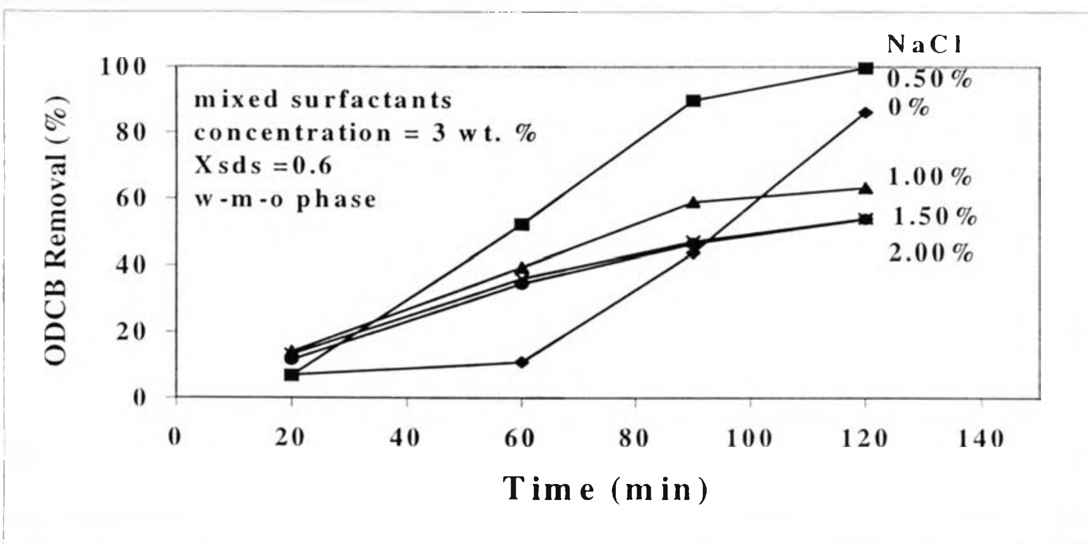


Figure 4.15 ODCB removal of w-m-o phase obtained from the microemulsion system with 3 wt. % mixed surfactants concentration at different NaCl concentrations

4.2.4 Effect of the weight ratio of SDS on ODCB removal

From the previous study, it was reported that when the microemulsion solution was in Winsor type III, the flotation efficiency was greater than the Winsor type II or type I systems (Ratanarojanatam, 1997). In this work, three phase of the microemulsion solution prepared at 3 wt.% mixed surfactants and different SDS fractions were mixed to form three different systems for the flotation experiment. Figure 4.16. shows the effect of Xsds on the ODCB removal for three different systems. The results showed that % ODCB removal increased as the weight ratio of SDS increased from 0.2 to 0.8 because SDS (anionic surfactant) produces more foam than $NP(EO)_{10}$ (nonionic surfactant). Table 4.1 gives the foam volumes at different Xsds for three systems.

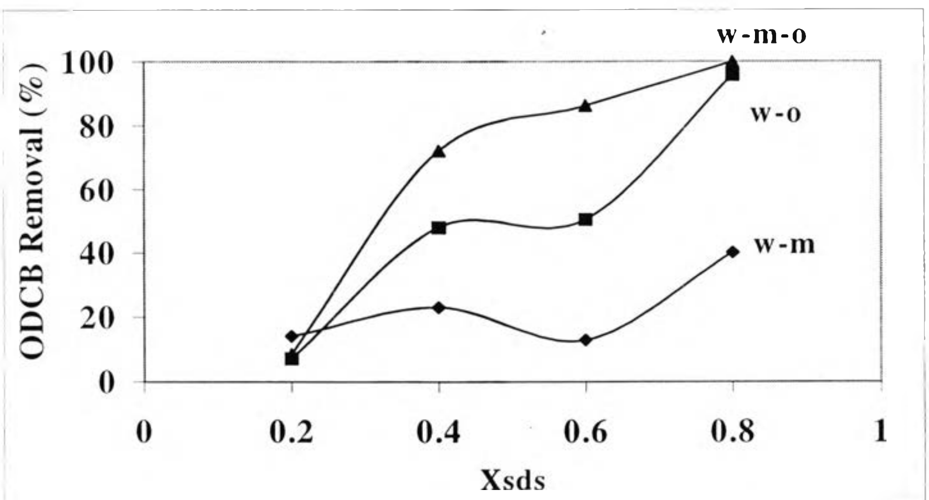


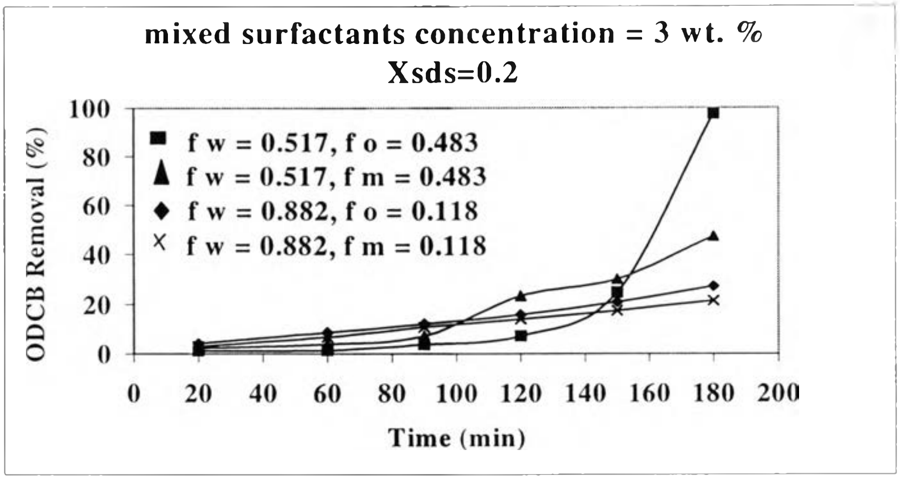
Figure 4.16 ODCB removal of w-m, w-o and w-m-o phases as a function of SDS fraction in the system containing 3 wt. % mixed surfactants concentration

Table 4.1 The foam volume of different systems having different Xsds

System	Volume of foam (ml)			
	Xsds = 0.2	Xsds = 0.4	Xsds = 0.6	Xsds = 0.8
w-m	81	103	103	85
w-o	47	300	399	469
w-m-o	81	479	294	309

4.2.5 Effect of phase volume on ODCB removal

The effect of the volume of each phase in the water and middle phases system and the water and oil phases system is illustrated in Figure 4.17. The results of the water and middle phases system showed that when the volume of the oil phase decreased and the volume of the water phase increased, percentage of the ODCB removal decreased due to less amount of oil. In froth flotation principle, air bubbles which are non polar like to attach molecules of dispersed oil which is also non polar. Therefore, the lesser the amount of oil is, the lesser percentage of the ODCB removal is obtained. For the water and middle phase system, when the volume of the middle phase increased and the volume of the water phase decreased, percentage of the ODCB removal increased because of the higher surfactant concentration in the middle phase. Hence, it had the greater amount of surfactant molecules, it could enhance the flotation efficiency.



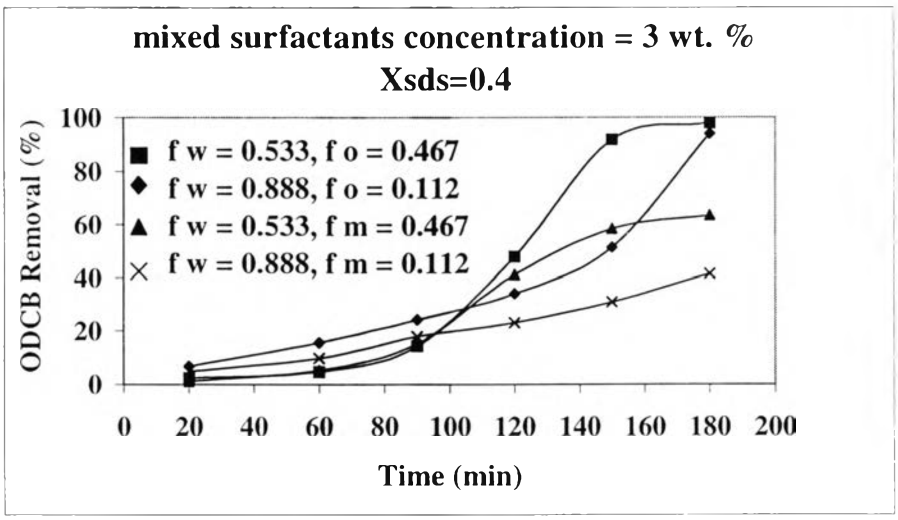
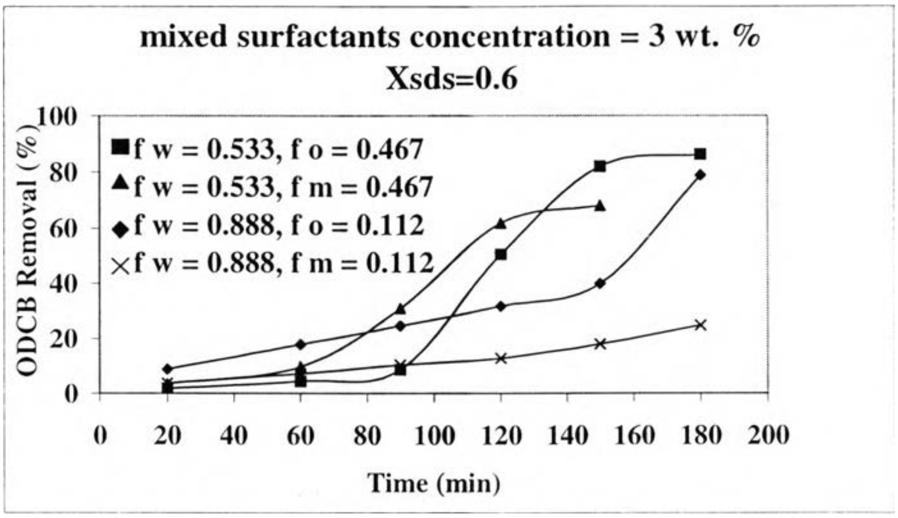
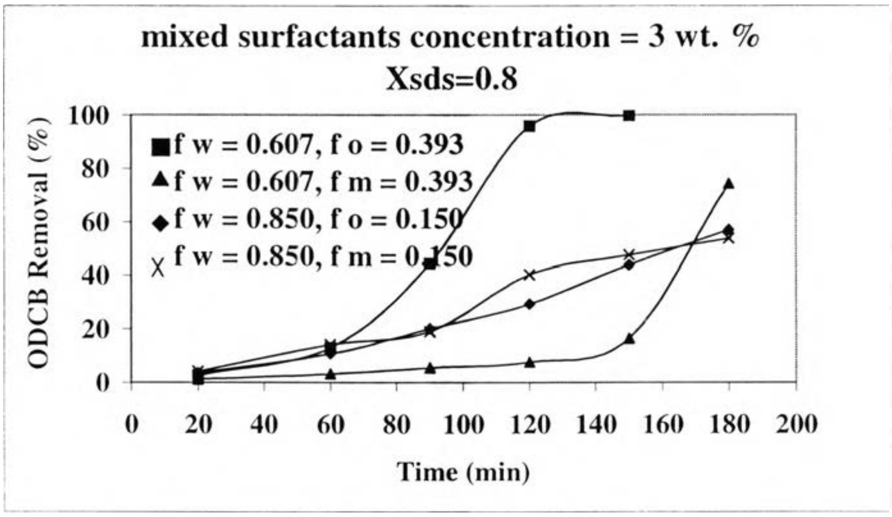
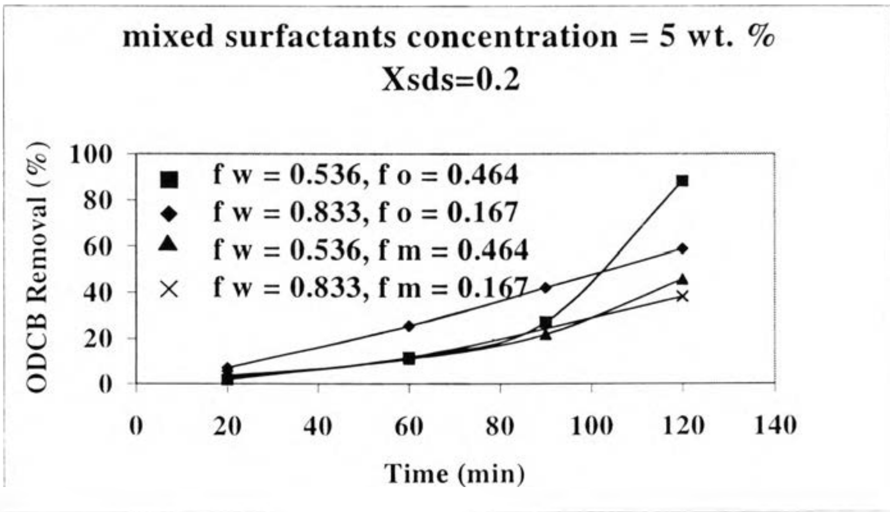


Figure 4.17 ODCB removal of different combination of two phases obtained from the microemulsion system under 3 and 5 wt. % mixed surfactants concentrations and at different SDS fractions (f w = volume fraction of water phase, f m = volume fraction of middle phase and f o = volume fraction of ODCB phase)







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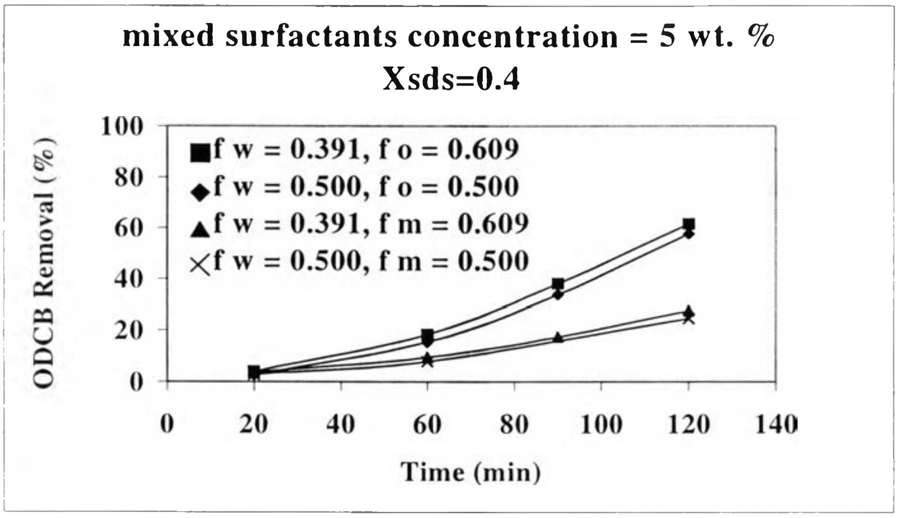

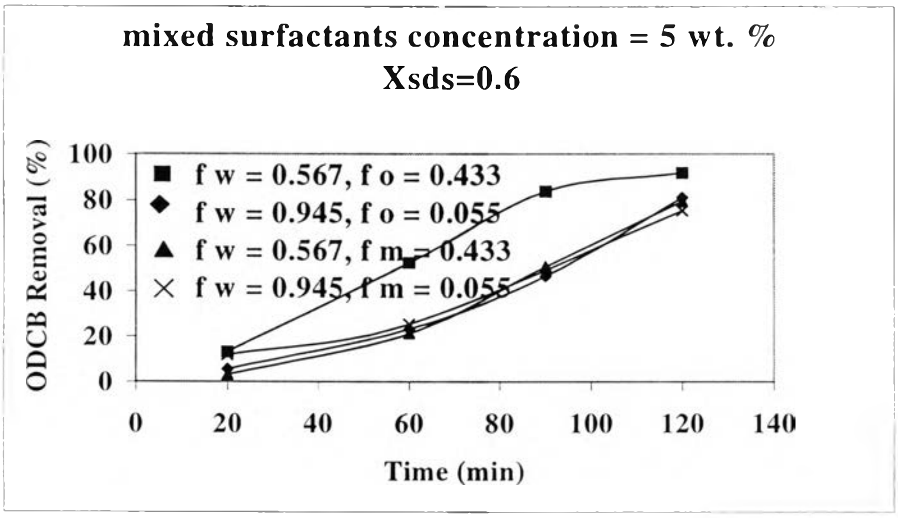

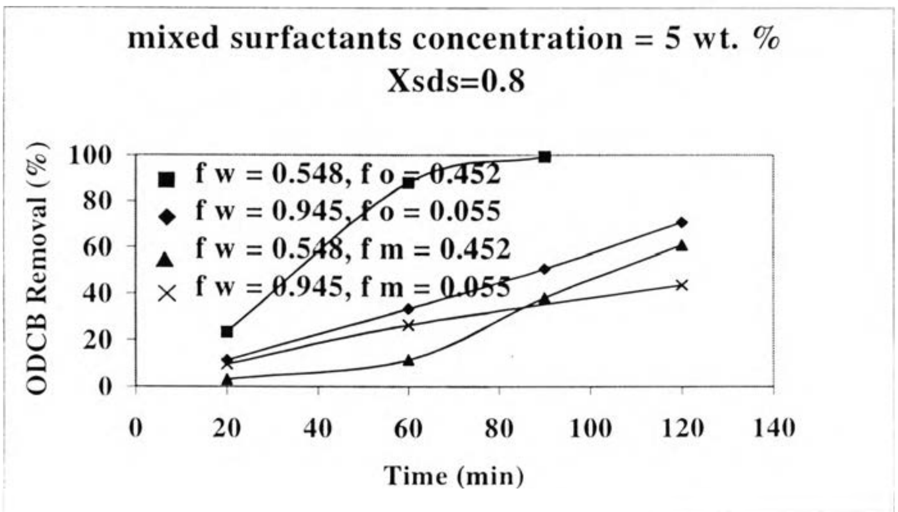

Figure 4.17 Continued -

As compared between w-o and w-m systems at the same volume fractions, of f w = 517, f o = 483 and f w = 517, f m = 483 , w-o system gave the higher ODCB removal than w-m system in both of 3 and 5 wt. % mixed surfactants concentrations and all of Xsds ratios. For w-o system having different volume fraction, when the volume fraction of water increased, the ODCB removal decreased. For the same w-m system having different volume fractions, the results also showed that as the volume fraction of water increased, the ODCB removal decreased. The whole results gave the same trends for w-o and w-m systems for all of conditions.