CHAPTER IV

RESULTS AND DISCUSSION

4.1 EQUILIBRIUM PHASE BEHAVIOR

Experimental data of the phase behavior study is given in Appendix B. The experimental results sre described below.

4.1.1 The Effect of Salinity

Figures 4.1 to 4.8 illustrate the effect of salinity on the phase behavior when oil to water initial volumetric ratio is 1/1 for different surfactant types and concentrations.   In the systems without salt, the two phases exhibit negligible volume change and very little oil solubilizes in the water phase and very little water in the oil phase. Increasing salinity causes the phase primarily containing the surfactant (microemulsion phase) to undergo the transition from upper phase (the oil in water microemulsion where water is the continuous phase) to a middle phase microemulsion. The middle phase microemulsion is in equilibrium with an excess water phase and an excess oil phase, neither of which contain substantial surfactant concentrations. This is the Winsor type III microemulsion system with the microemulsion phase containing substantial concentration of both oil and water. Using SDS as a collector, the phase volume of excess oil decreased
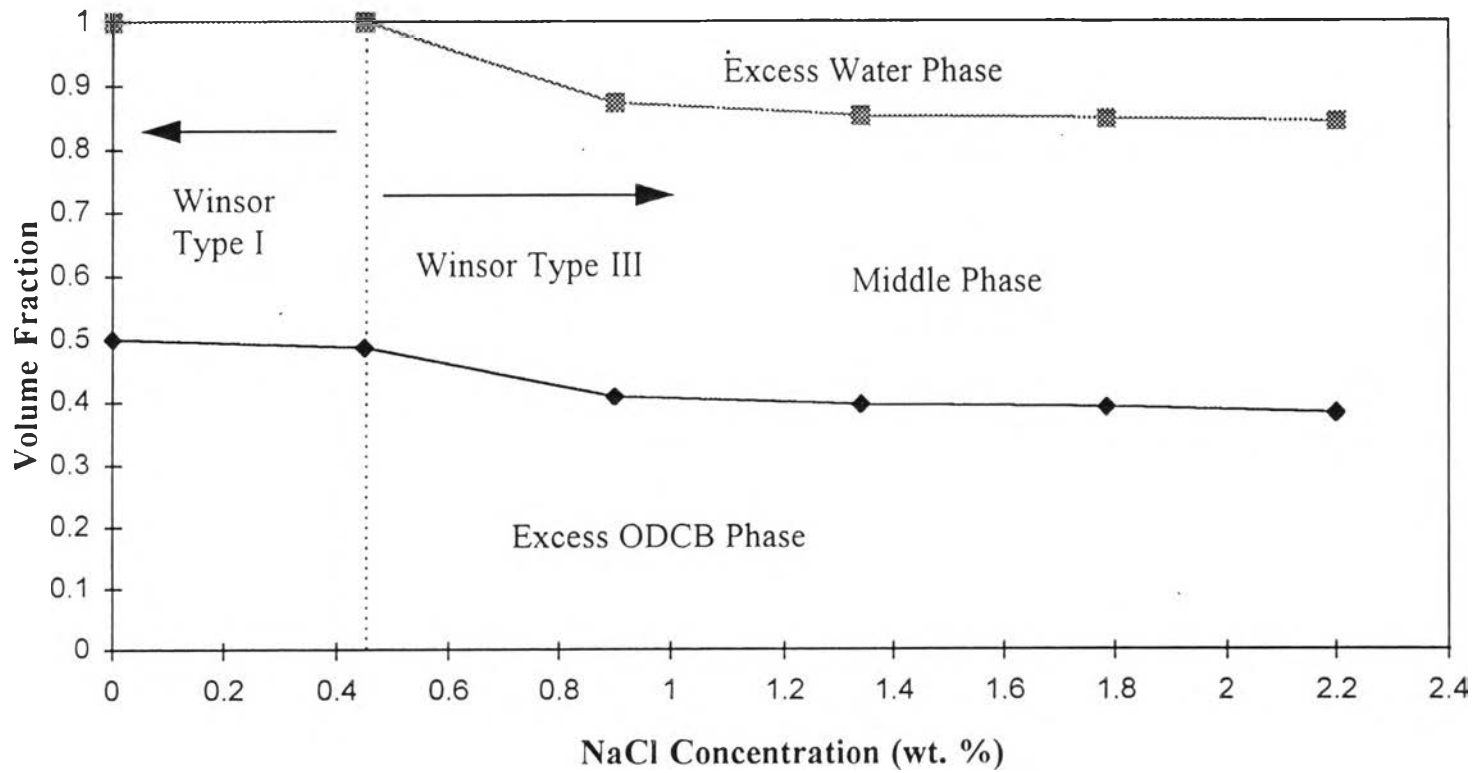
Figure 4.1   Phase volume of microemulsion system with SDS concentration = 1.0 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration
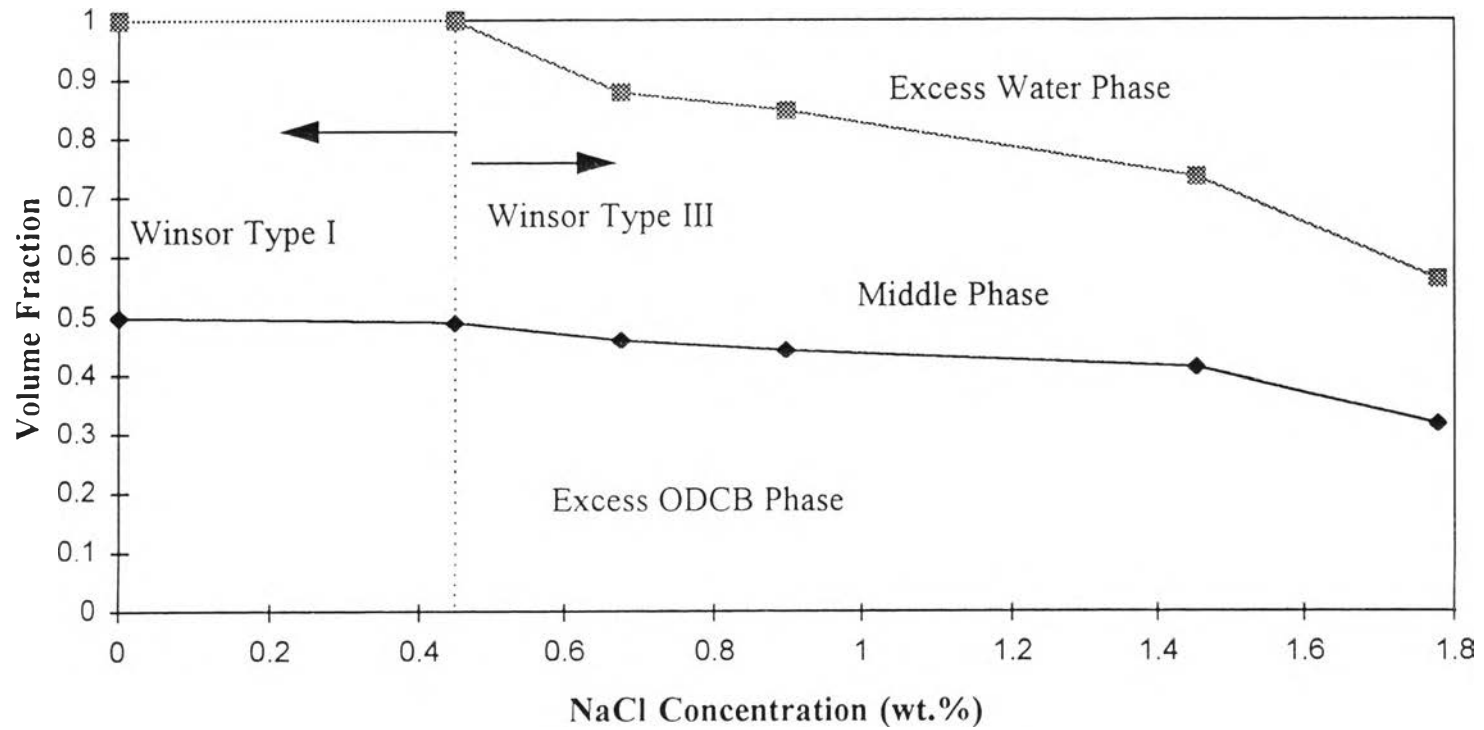
Figure 4.2   Phase volume of microemulsion system with SDS concentration =2.5 wt.%, initial
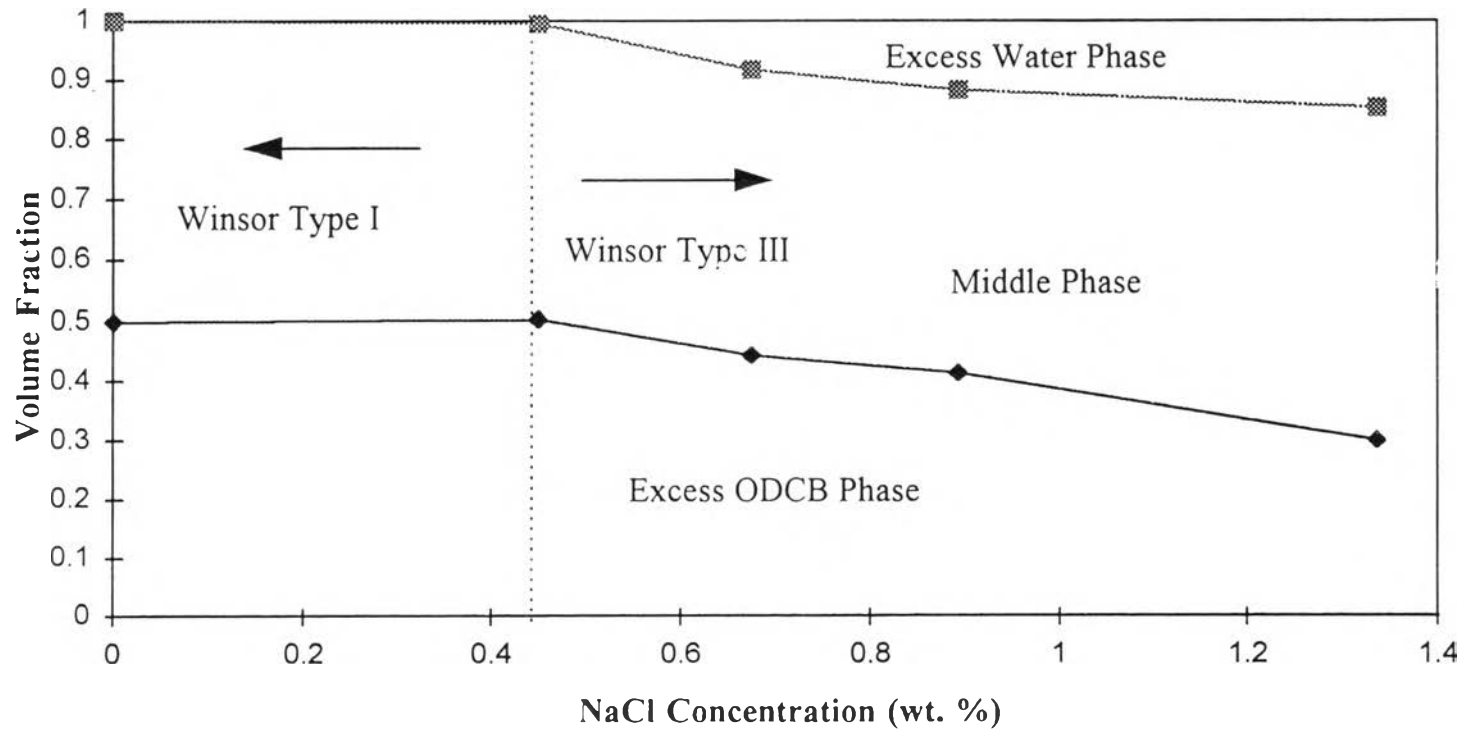oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration

Figure 4.3   Phase volume of microemulsion system with SDS concentration =3.5 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration

Figure 4.4   Phase volume of microemulsion system with CPC concentration = 0.5 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration
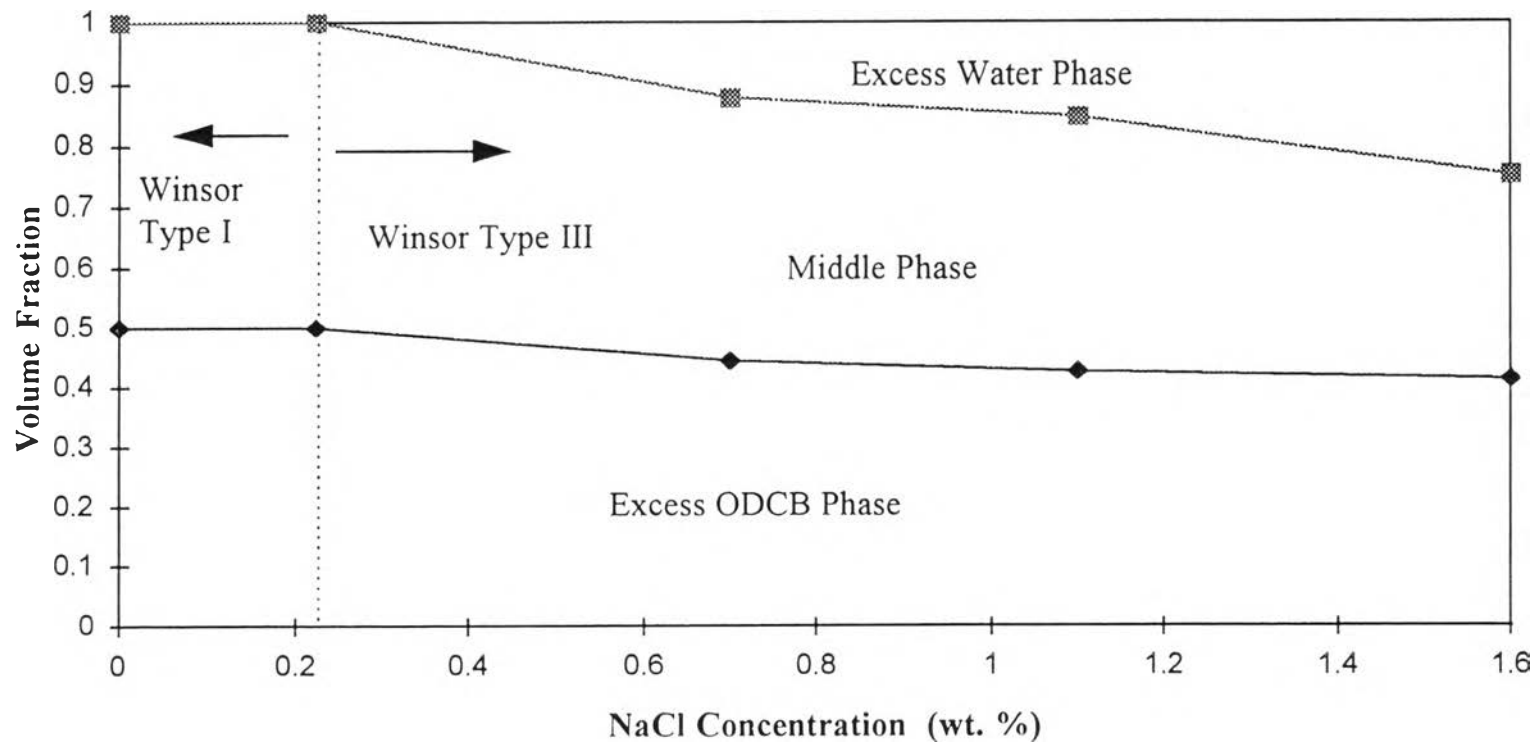
Figure 4.5   Phase volume of microemulsion system with CPC concentration = 3.5 wt.%, initial
oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration

Figure 4.6   Phase volume of microemulsion system with DADS concentration = 1.0wt.%, initial oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration
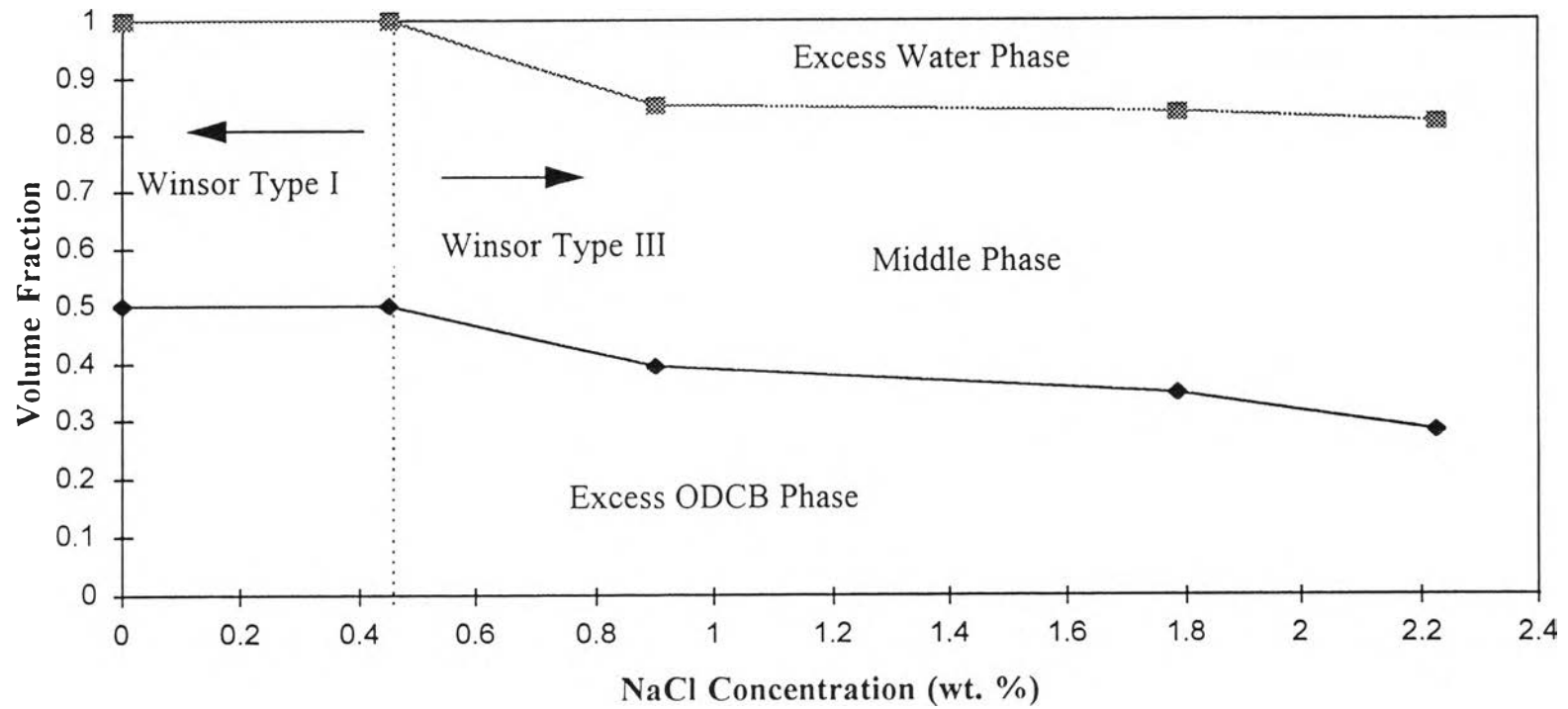
Figure 4.7 Phase volume of microemulsion system with DADS concentration = 3.5 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration
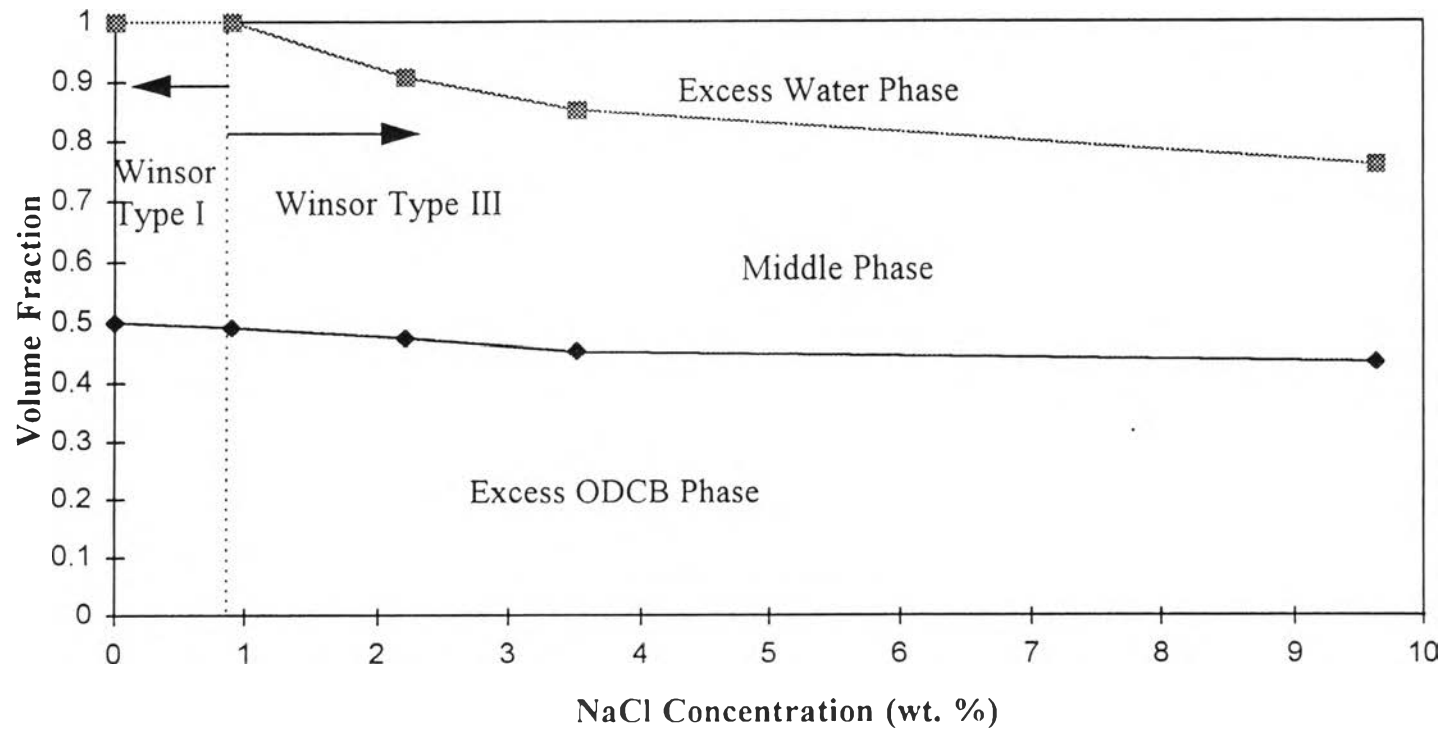
Figure 4.8 Phase volume of microemulsion system with DADS concentration = 10.0 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30° C at different NaCl concentration
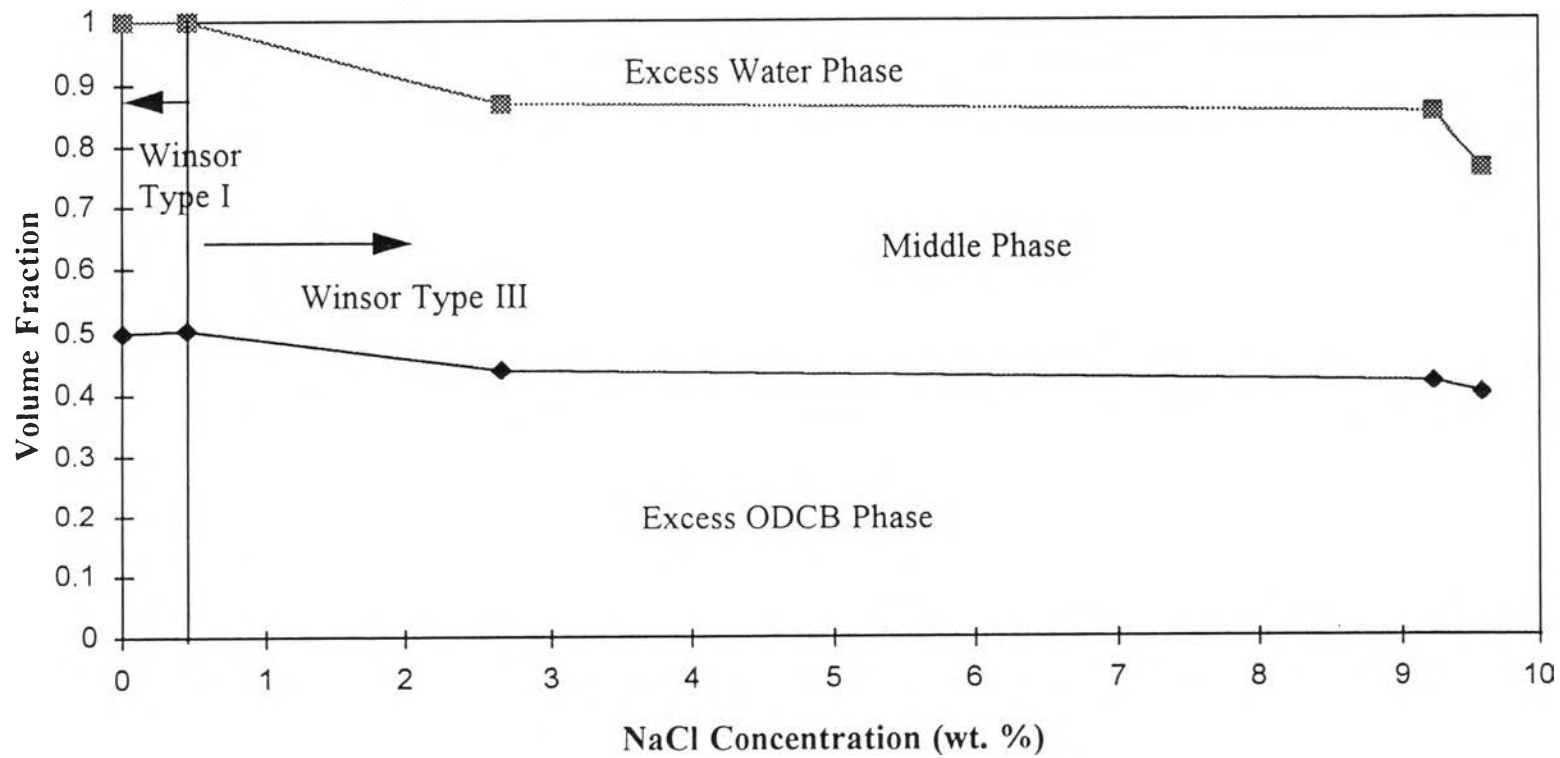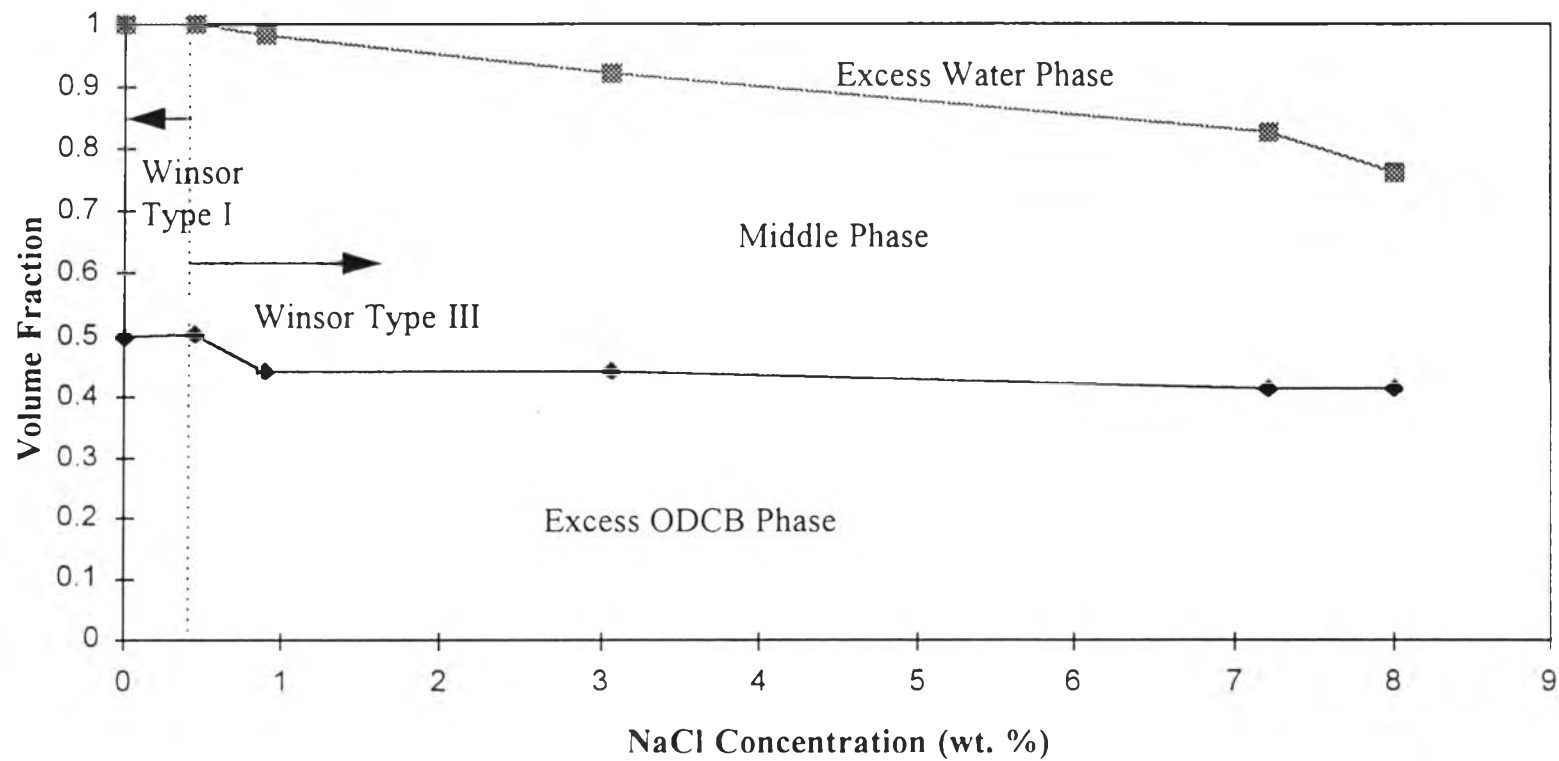
while the phase volume of excess water increased with increasing salinity. The same results were also obtained for CPC and DADS. The direction of phase transitions shows that adding an electrolyte to the system makes it more hydrophobic (Qutubuddin et al., 1984) or the surfactant solubility or compatability with the aqueous phase decreases. The drops in an oil-in-water microemulsion containing an ionic surfactant interact by the usual London-Van der Waals attractive forces and by electrical repulsion due to double layer overlap. As salinity increases, double layer thickness decreases and attractive forces between surfactant aggregates may become strong enough to overcome both electrical repulsion and random thermal motion (Hwan et al., 1979; Pugh and Manev., 1992), resulting in formation of a middle phase microemulsion. None of the systems studied here showed the Winsor Type II microemulsion behavior over the range of salinities studied here. At NaCl concentrations of 2.3 wt.% and higher, precipitation occured for both SDS and CPC used as a collector except DADS.

4.1.2 The Effect of Surfactant Concentration

As can be seen from Figures 4.1 to 4.8, for the salinity range causing the middle phase microemulsion, the salinity range decreases with increasing surfactant concentration. A lens at the aqueous-oil interface was observed when using low surfactant concentration without salt. When the complex mixtures of anionic surfactants were used, it showed a dependence of phase behavior and interfacial tension on surfactant concentration (Bourrel, 1980). The phase behavior depends on the surfactant concentration. As surfactant concentration increases, the hydrophobic portion and the water/oil interface is concentrated so that interaction energy between oil and surfactant

molecule increases. For sufficiently high surfactant concentrations, the interfacial layer attains a constant composition and phase transitions between type I, III, or IV and II do not occur (Bourrel and Schechter, 1988).

4.1.3 The Effect of Cosurfactant Concentration

Short chain alcohols (sometimes called co-surfactants) are often used to adjust the phase behavior of surfactant/water/oil systems (Bourrel and Schechter, 1988). The phase behavior of mixture of DADS and n-pentanol is shown in Figure 4.9. When the concentration of the DADS and pentanol increases, the volume fraction of the middle phase also increases significantly. Adding pentanol could cause a system to become more hydrophobic so more ODCB moved into the microemulsion phase. Since water-insoluble alcohol can enhance the effect of hydrophilic portion of surfactants, oil solubility increases with alcohol concentration (Jones and Dreher, 1976). In addition, the change of the phase behavior can be explained in terms of the partitioning of alcohol between the bulk phases and the interfacial film. In the DADS-pentanol system, an increase in surfactant-alcohol concentration leads to a higher alcohol concentration in the interfacial film. It is more hydrophobic and less salt is needed to drive the microemulsion into a middle phase. Therefore, the height of middle phase microemulsion increases with increasing DADS/pentanol concentration while maintaining constant DADS/pentanol ratio. The phase behavior clearly depends on the hydrophobic/hydrophilic nature of the both surfactant and alcohol (Bourrel and Chambu, 1983). However, pentanol (as a cosurfactant) is not absolutely necessary for the formation of microemulsion but will promote phase transformations.
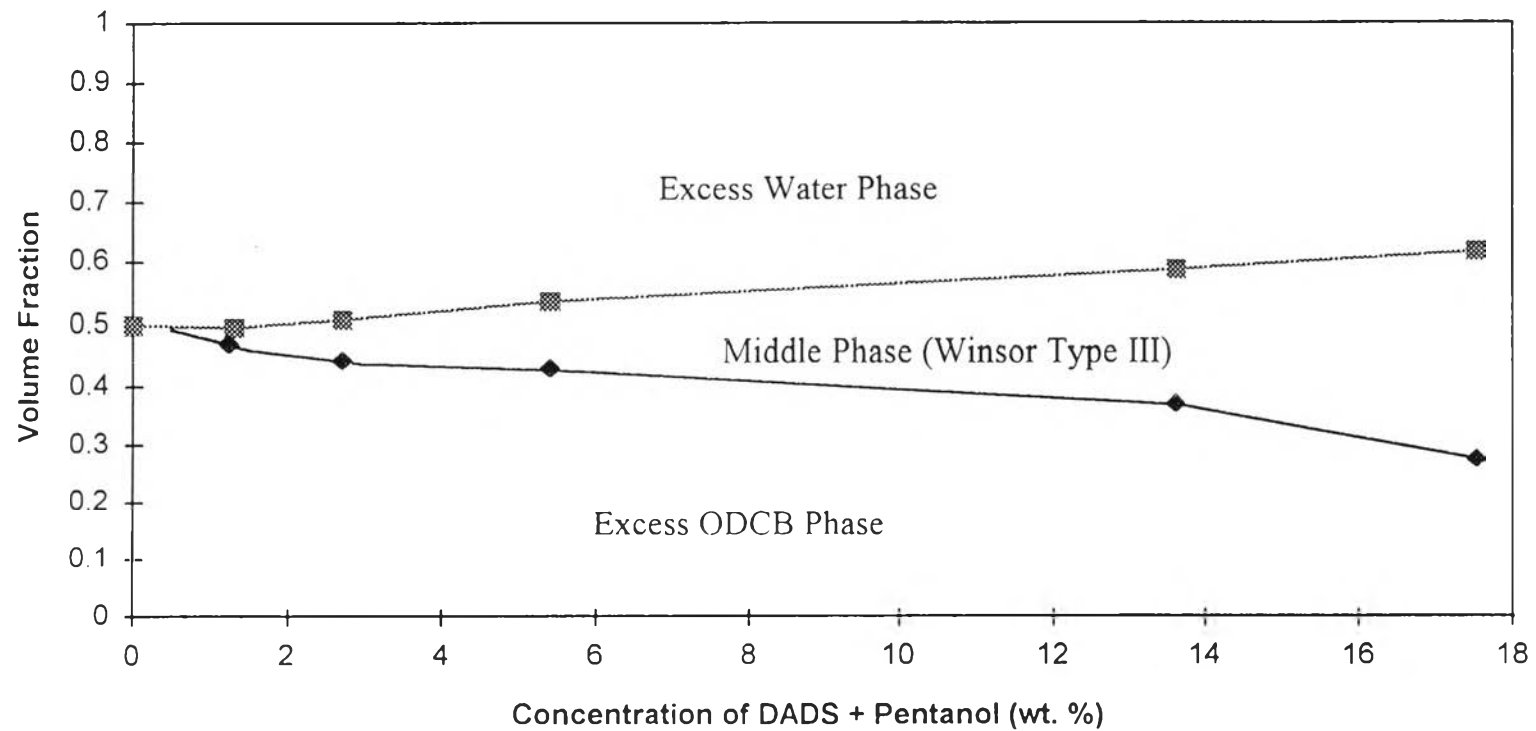
Figure 4.9   Phase volume of microemulsion system with DADS/pentanol weight ratio = 1/2, initial oil/water volume ratio = 1/1, and temperature = 30° C at different surfactant + pentanol concentration

4.1.4 The Effect of Overall Initial Oil-to-Water Volume Ratio

The range of salinity that is a cause of Winsor Type I and III microemulsion was used to studied the effect of the overall oil-to-water volume ratio on microemulsion phase behavior. The transitions have been noticed to depend on salinity. It was found that for the oil-to-water ratio of less than 9/100 for SDS, less than 7/100 for CPC, and 3/10 for DADS as collector, the liquid crystalline phase was clearly visualized when using PLS. Figure 4.10 illustrates the formation of liquid crystal under the studied conditions. This experimental result is in a good agreement with those obtained in the previous work (Overbeek et al., 1984; Shah et al., 1972; Falco, 1974); that changing the oil-to-water ratio to very large or very small value may lead to the formation of liquid crystalline or other phases.

4.2 EXPERIMENTAL RESULTS OF FROTH FLOTATION

Appendix C shows the experimental data of the study of froth flotation. The experimental results of the froth flotation study are described below.

4.2.1 The Effect of NaCl Concentration on the ODCB and Surfactant Removals

The effect of NaCl concentration on ODCB and on surfactant removals can be seen in Figures 4.11 to 4.13 and Figures 4.14 to 4.16, which respectively. Also shown in the Figures, there is the approximate salinity at the equilibrium phase behavior showed the Winsor type I to Type III

water

oil

Initial

excess water

liquid-

crystal

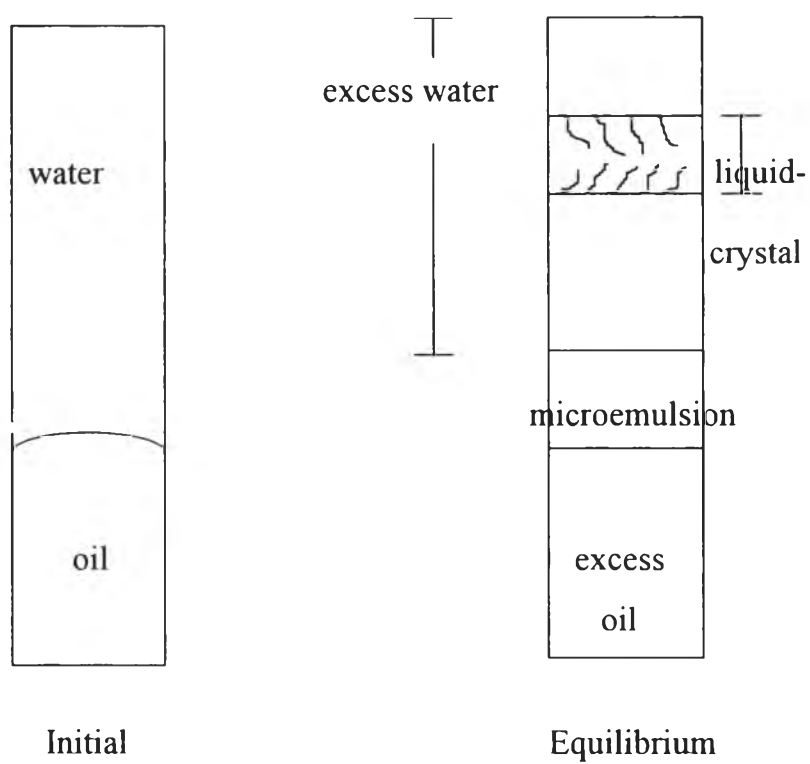microemulsion

excess
oil

Equilibrium

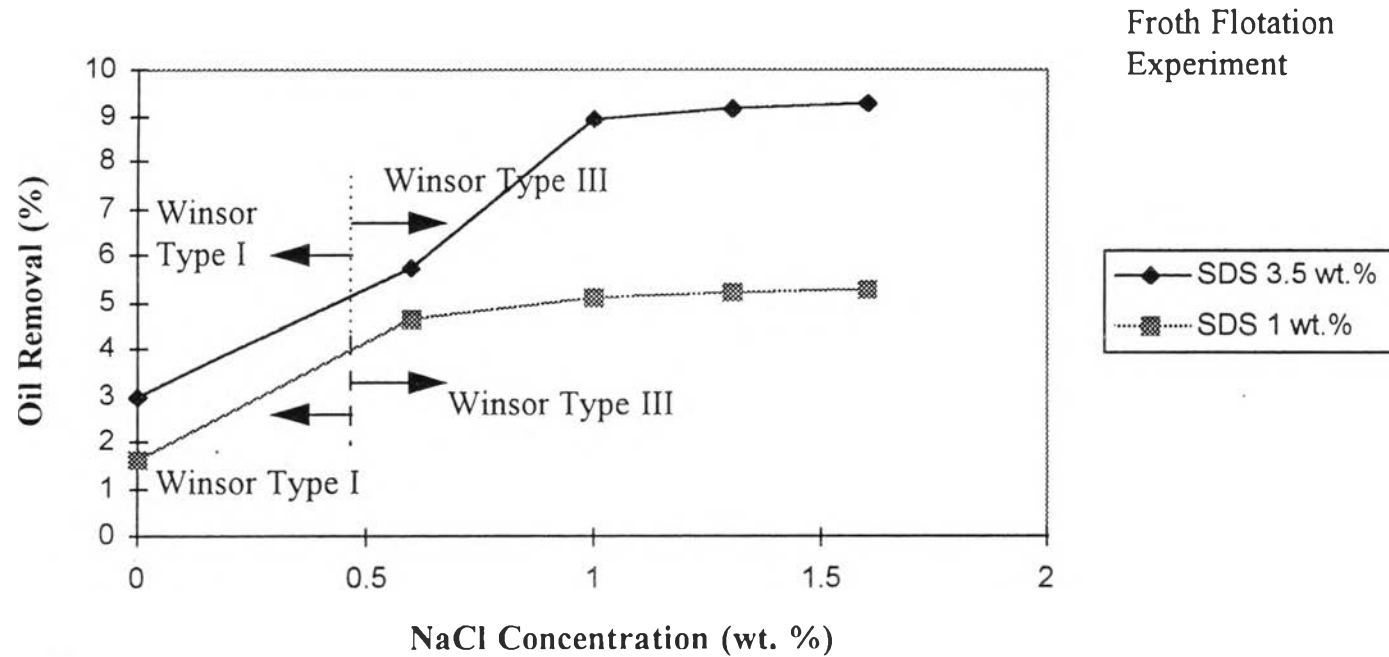Figure 4.10 illustrates the characteristic of liquid crystal phase.

Figure 4.11 Effects of SDS and NaCl concentrations on oil removal with SDS
concentrations = 1 and 3.5 wt.%, initial oil/water volume ratio = 1/1, and
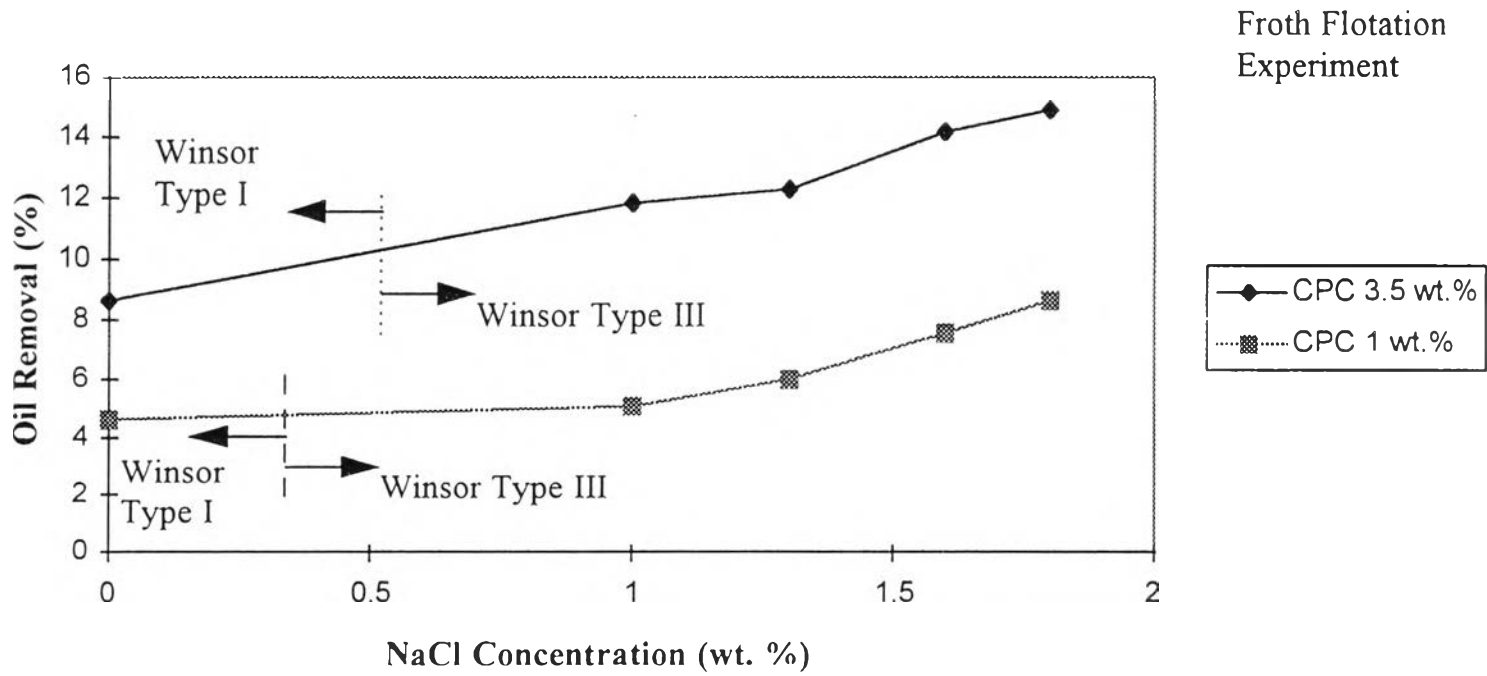temperature = 30 ° C at different NaCl concentration

Figure 4.12 Effects of CPC and NaCl concentrations on oil removal with CPC concentrations = 1 and 3.5 wt.%, initial oil/water volume ratio = 1/1, and temperature30 º C at different NaCl concentration
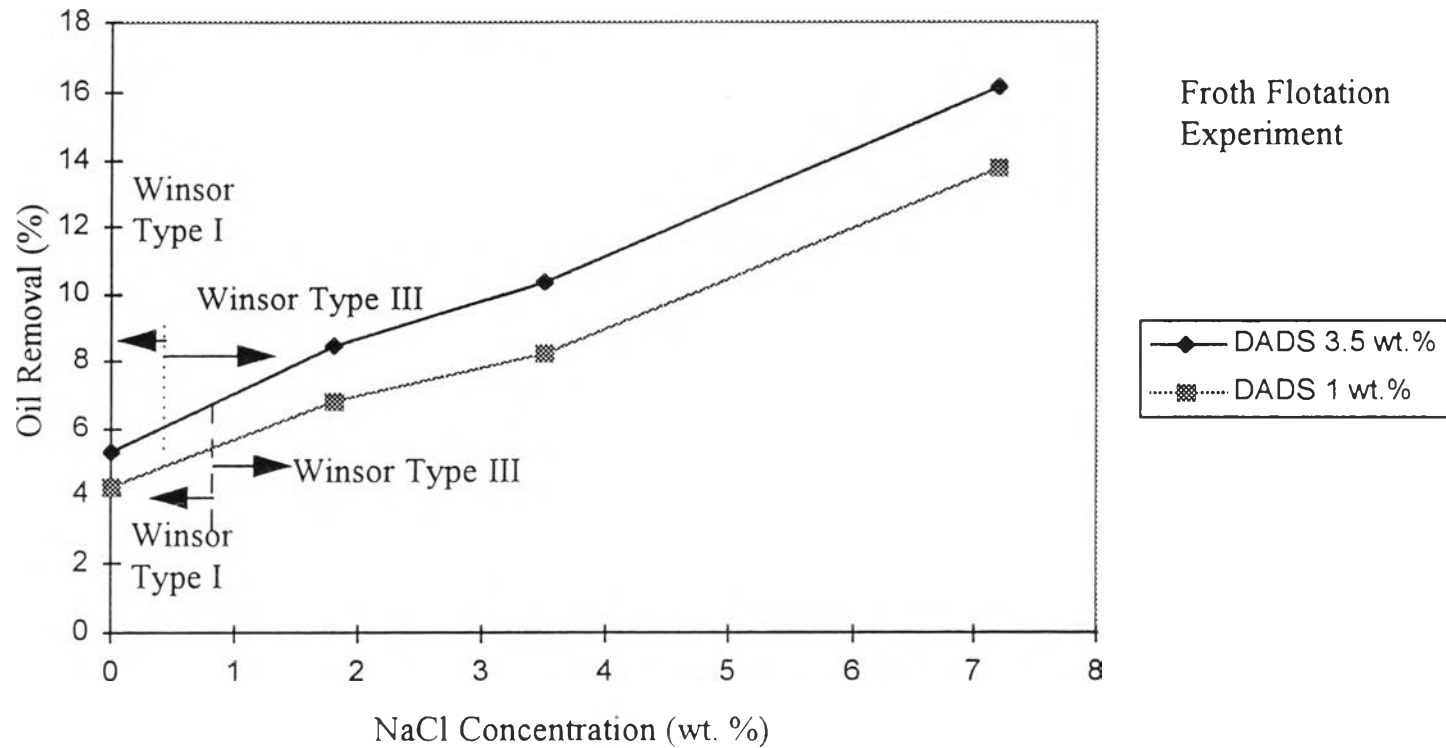
Figure 4.13 Effects of DADS and NaCl concentrations on oil removal with DADS
concentrations = 1 and 3.5 wt.%, initial oil/water volume ratio = 1/1, and
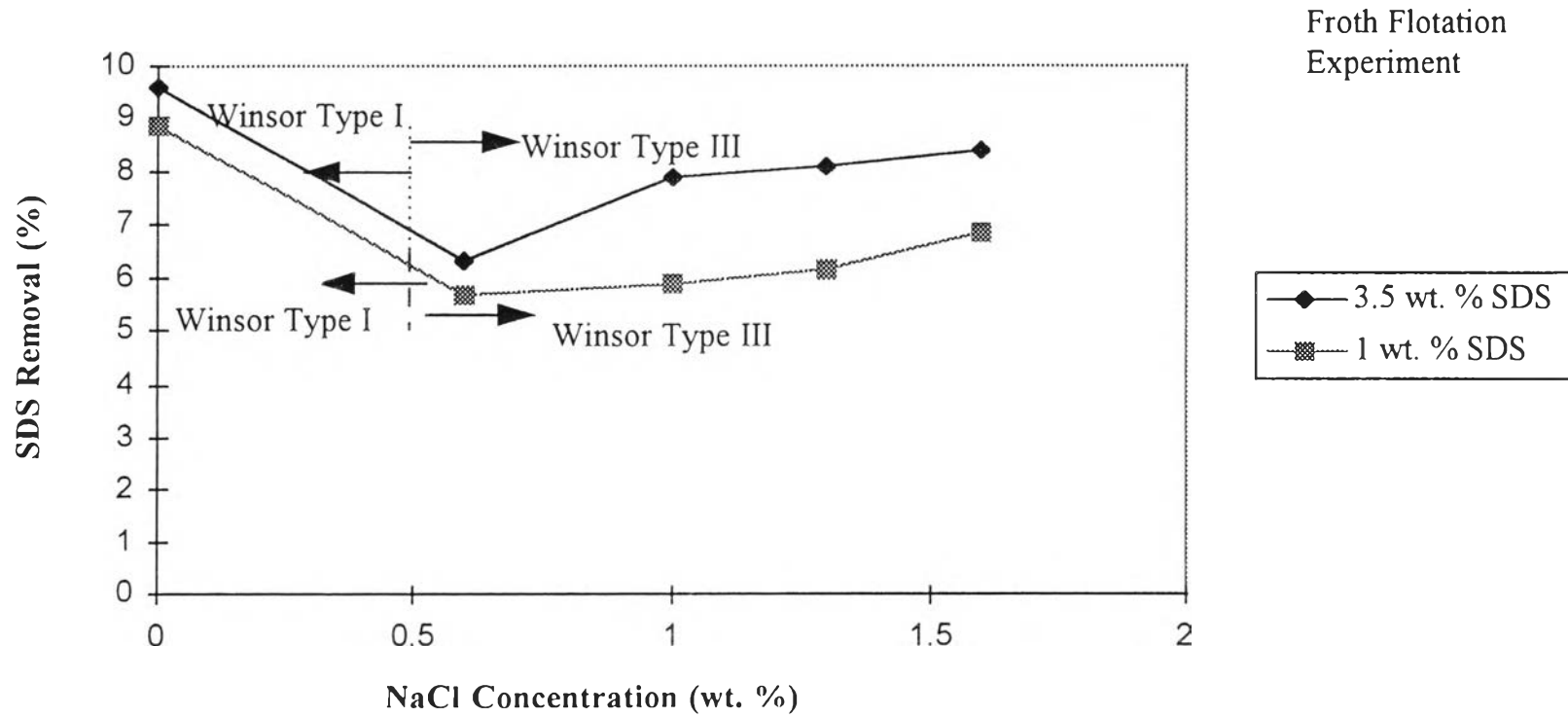temperature = 30 ° C at different NaCl concentration

Figure 4.14   Effects of SDS and NaCl concentrations on SDS removal with SDS concentrations = 1 and 3.5 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30 °C at different NaCl concentration

18 ┬
16 ┼ Winsor
     Type I   ◄──   ►Winsor Type III
14 ┼
12 ┼
     CPC Removal (%)
10 ┼   Winsor Type III
 8 ┼
 6 ┼   Winsor
        Type I
 4 ┼
 2 ┼
 0 ┴────┬────┬────┬────┬
   0   0.5   1   1.5   2
        NaCl Concentration (wt. %)
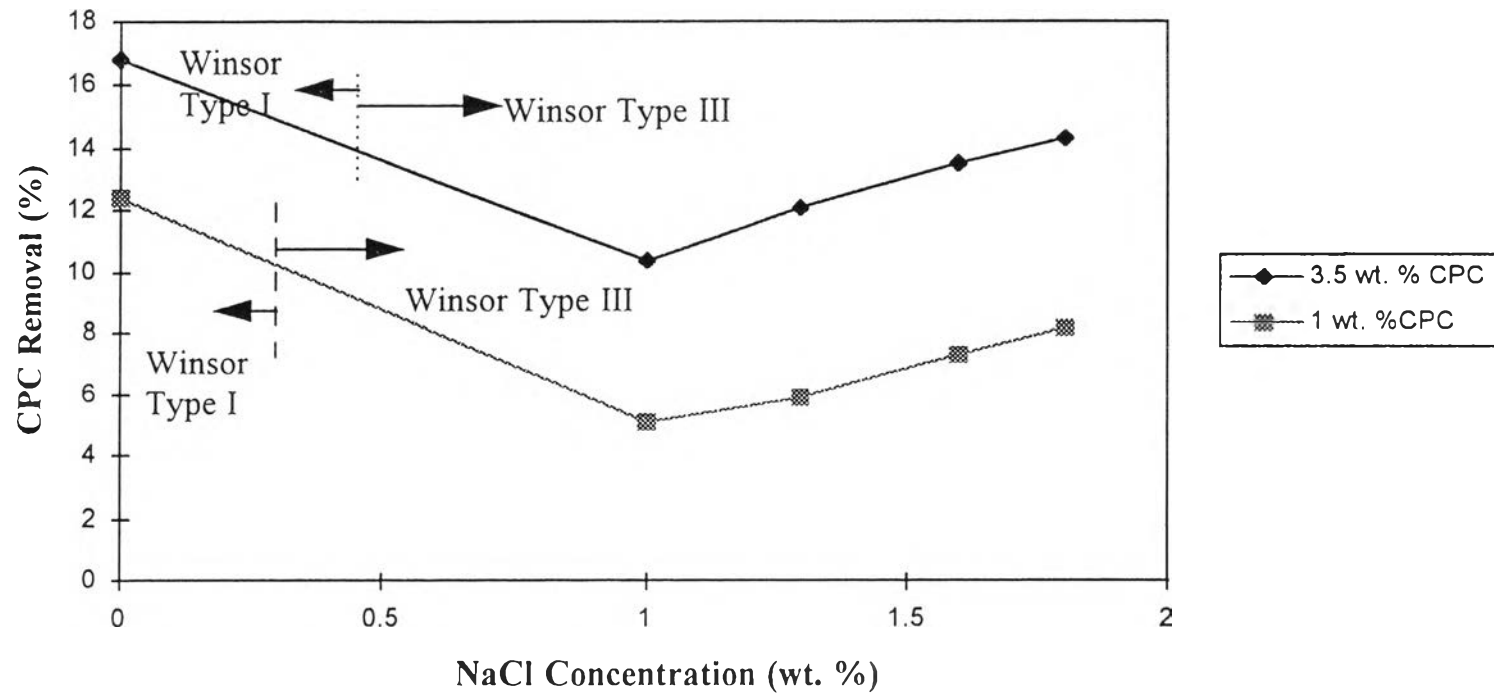
Legend:
◆ 3.5 wt. % CPC
▦ 1 wt. %CPC

Figure 4.15 Effects of CPC and NaCl concentrations on CPC removal with CPC concentrations =
            1 and 3.5 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30 ° C at
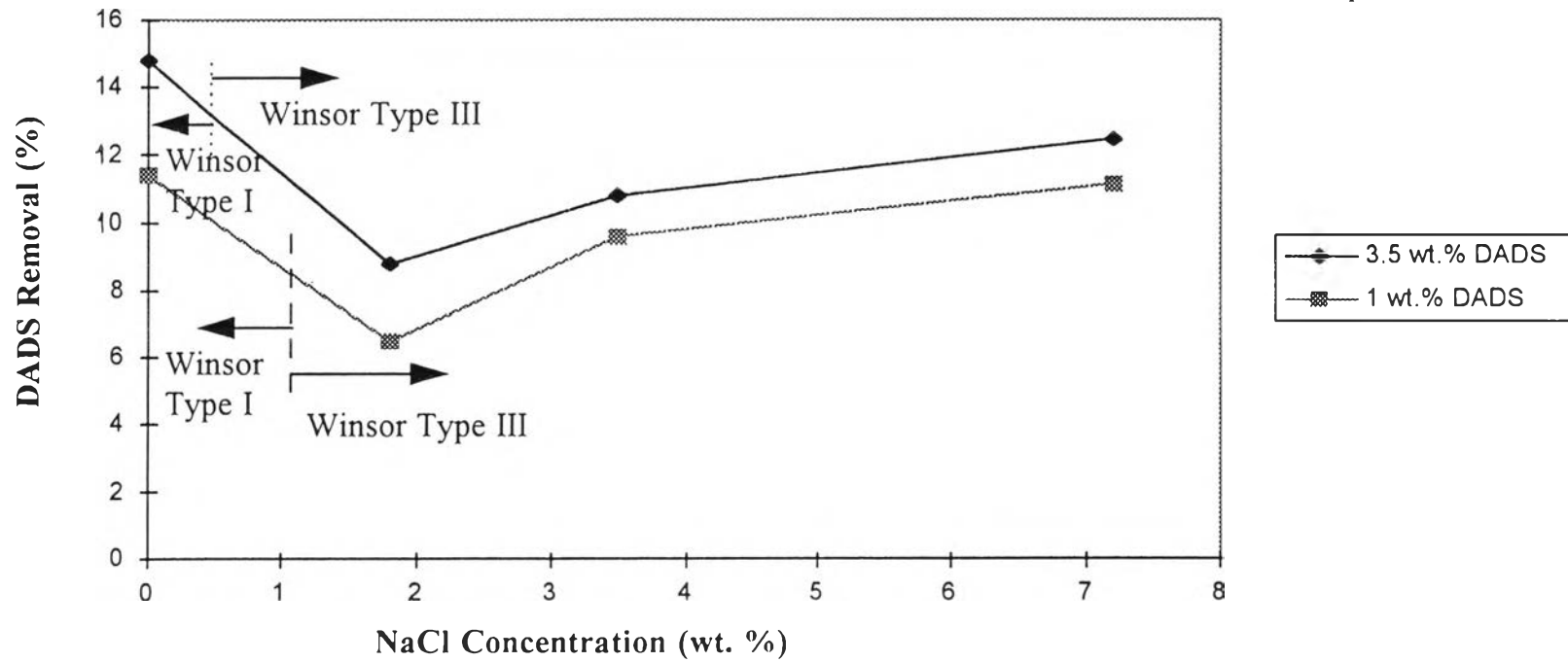   different NaCl concentration

Figure 4.16   Effects of DADS and NaCl concentrations on DADS removal with DADS concentrations = 1 and 3.5 wt.%, initial oil/water volume ratio = 1/1, and temperature = 30 °C at different NaCl concentration

transition.   The removal of oil increased with increasing salinity and increasing surfactant concentration. As the salinity increases in the Winsor Type III region, the interfacial tension between the microemulsion (middle) phase and the excess water and excess oil phases decreases until optimal salinity is attained (Healy et al., 1976). The salinity did not reach the optimal salinity in the flotation experiments reported here due to the aforementioned surfactant precipitation problems.   As the oil/water ratio decreases or surfactant concentration increases, a higher fraction of the ODCB is present in the microemulsion instead of the excess oil phase. The results reported here would imply that when the oil is in microemulsion form, the flotation efficiency is greater than when the oil is an excess phase (containing little surfactant, the efficiency increasing as the interfacial tension decreases). For DADS as a collector, the lifetime of the froth was too short to rise through the column into the receiver when the salinity was above about 7.5 wt. %. From the previous works, adding NaCl in the froth flotation process where no microemulsion was present and it resulted in lower oil removal (Peng and Di, 1994; Dhirendra, 1991). A similar behavior was also in the case of other particles(e.g. oil, boron) recovery (Hancer and Celik, 1993; Koutlemani, 1994).

As be seen from Figures 4.14 to 4.16, the effect of NaCl concentration and surfactant concentration on the surfactant removal efficiency were different when compared to the oil removal efficiency. For the low range of SDS concentration, the SDS removal decreased with increasing NaCl concentration but the SDS removal slightly increased with increasing NaCl concentration when NaCl concentration is greater than 0.6 wt.%. The similar results were obtained for the cases of both CPC and DADS.

4.2.2 The Effect of Surfactant Concentration on the ODCB and Surfactant Removal

As can be seen from Fgures 4.11 to 4.16, the ODCB removal and the surfactant removal increase as increasing in the surfactant concentration. It is interested to mention that a similar behavior is also in the case of other particles (e. g. oil, boron) recovery (Hancer and Celik, 1993: Koutlemani, 1994). In Addition, it implies that when the system is in the Winsor Type III microemulsion form, the percentage of surfactant removal is less than when the system is in the Winsor Type I microemulsion form. Therefore, the froth flotation system operated under the Winsor Type III loses amount of surfactant less than under the other conditions. This is a way to save the cost of clean-up the oil from the waste water.

4.2.3 The Effect of Initial Oil/Water Volume Ratio on the ODCB and Surfactant Removal

The effect of oil-to-water volume ratio on the ODCB removal is shown in Figures 4.17 through 4.19 and for surfactant removal from Figures 4.20 to 4.22, respectively. The percentage of oil removal and surfactant removal were dependent on the oil-to-water ratio. These tended to increase with decreasing the oil-to-water ratio. These results can be compared with the increase in the feed oil concentration. In addition, it implies that the liquid crystalline phase has an effect on the surfactant removal but no effect on oil removal. The liquid crystalline phase has already discussed in the phase diagrams. The result of removal oil in the liquid crystalline phase is similar to the result when the liquid crystalline phase dose not appear. This
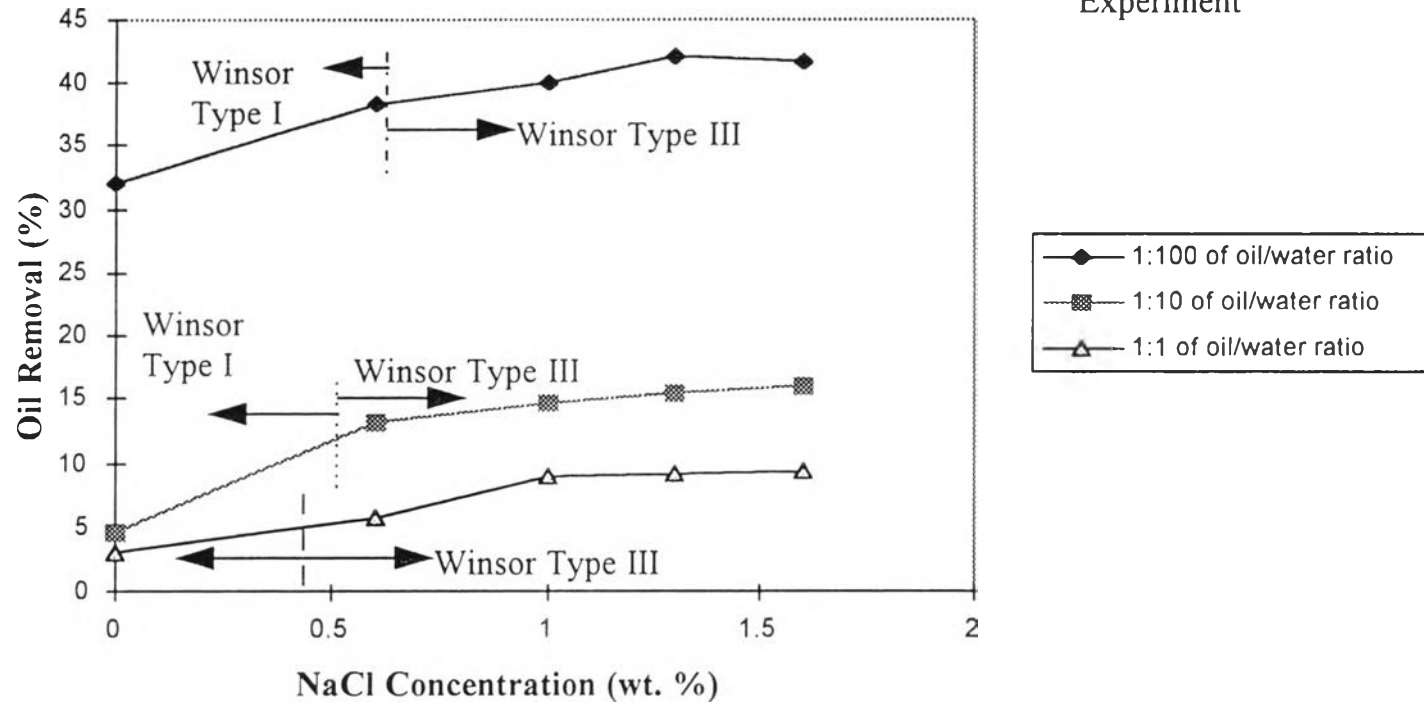
Figure 4.17 Effect of initial oil/water volume ratio on oil removal with SDS concentration =
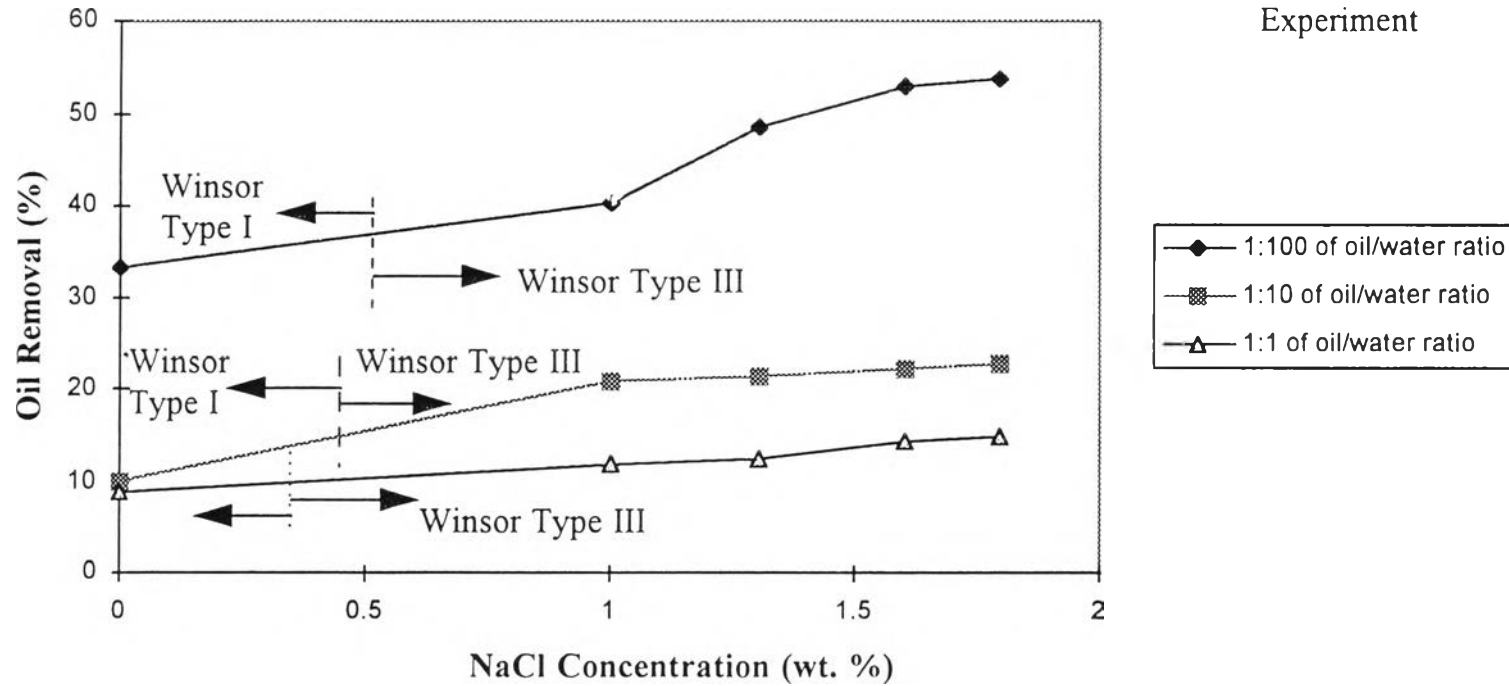3.5 wt.%, and temperature = 30 °C at different NaCl concentration

Figure 4.18 Effect of initial oil/water volume ratio on oil removal with CPC concentration = 3.5 wt.%, and temperature= 30 º C at different NaCl concentration
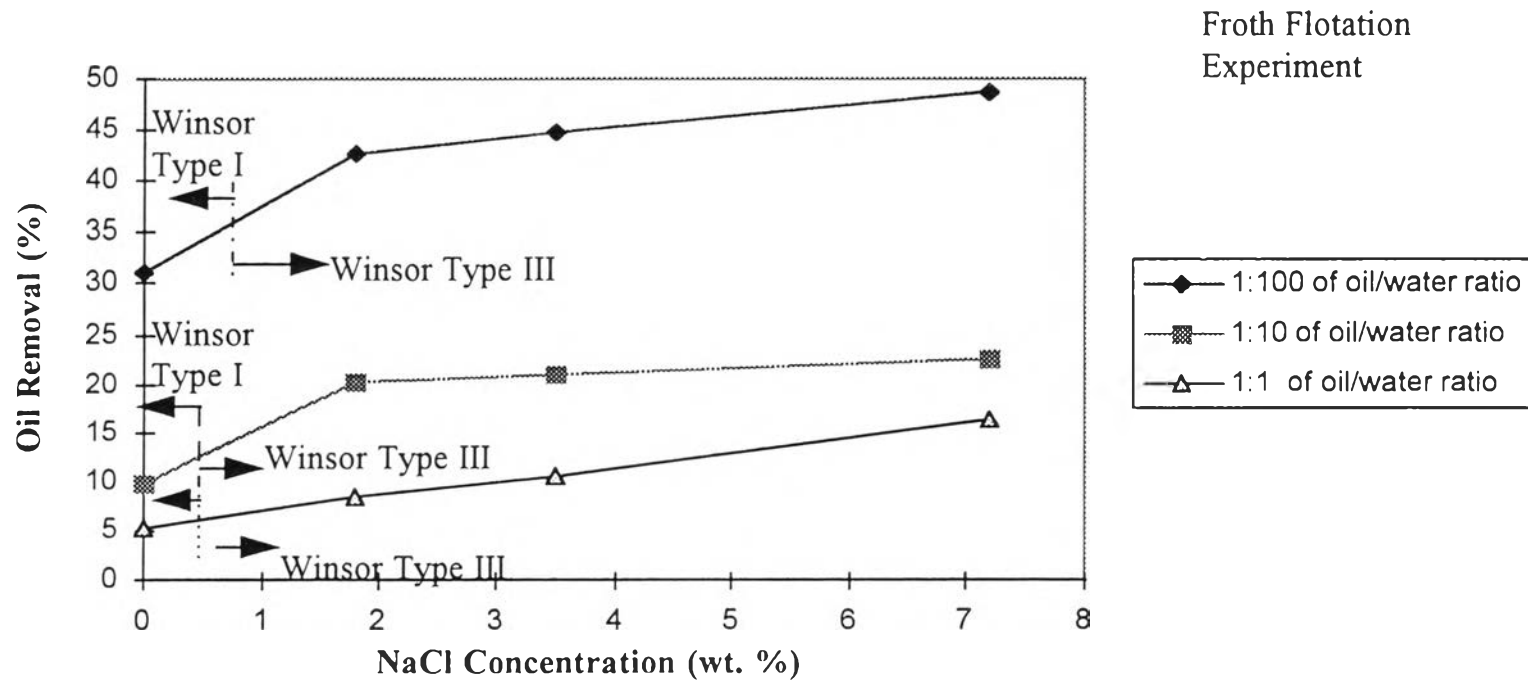
Figure 4.19 Effect of initial oil/water volume ratio on oil removal with DADS concentration = 3.5 wt.%, and temperature = 30 º C at different NaCl concentration
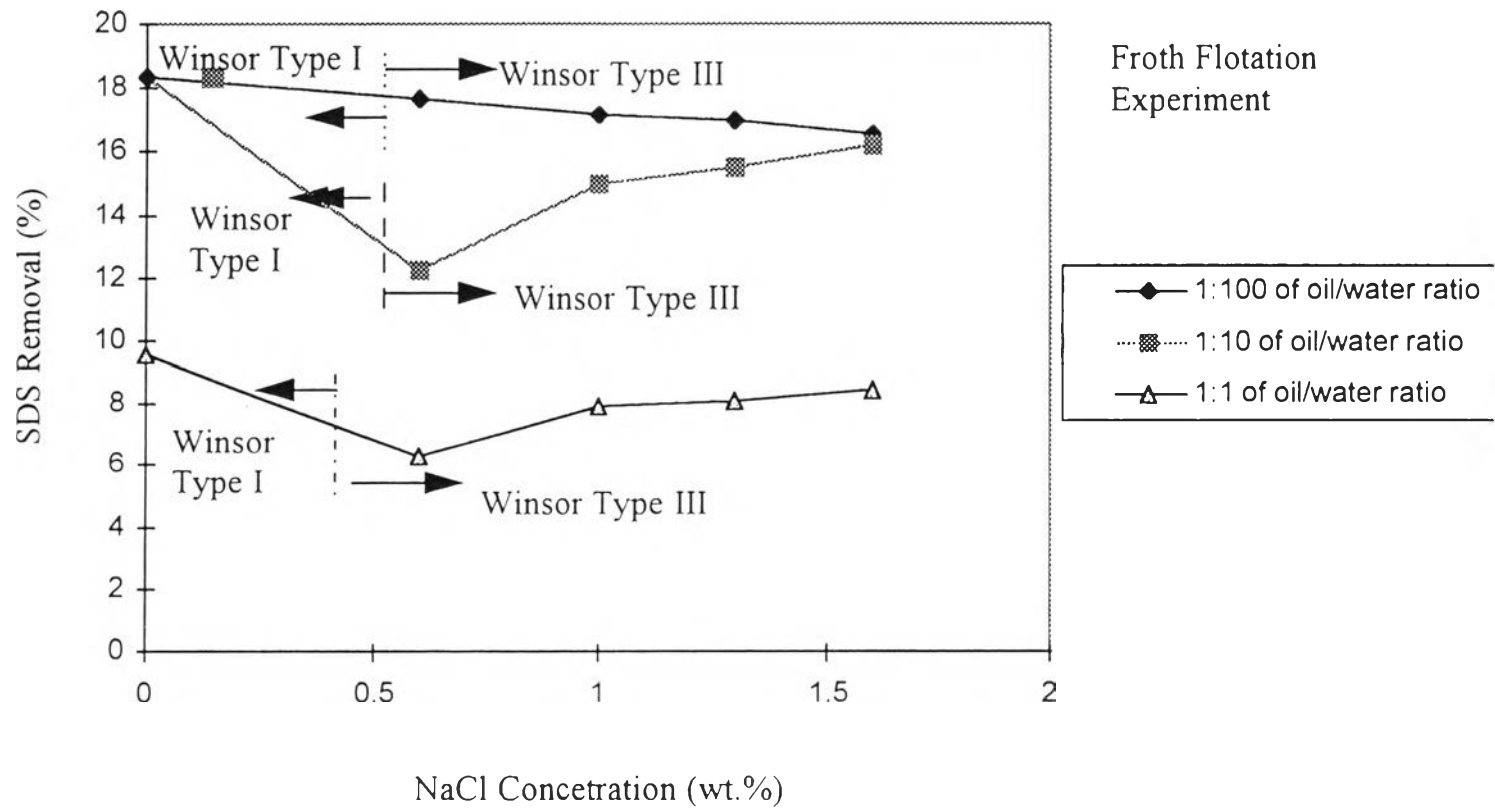
Figure 4.20 Effect of initial oil-to-water volume ratio on SDS removal with SDS concentration = 3.5 wt.%, and temperature = 30 ° C at different NaCl concentration
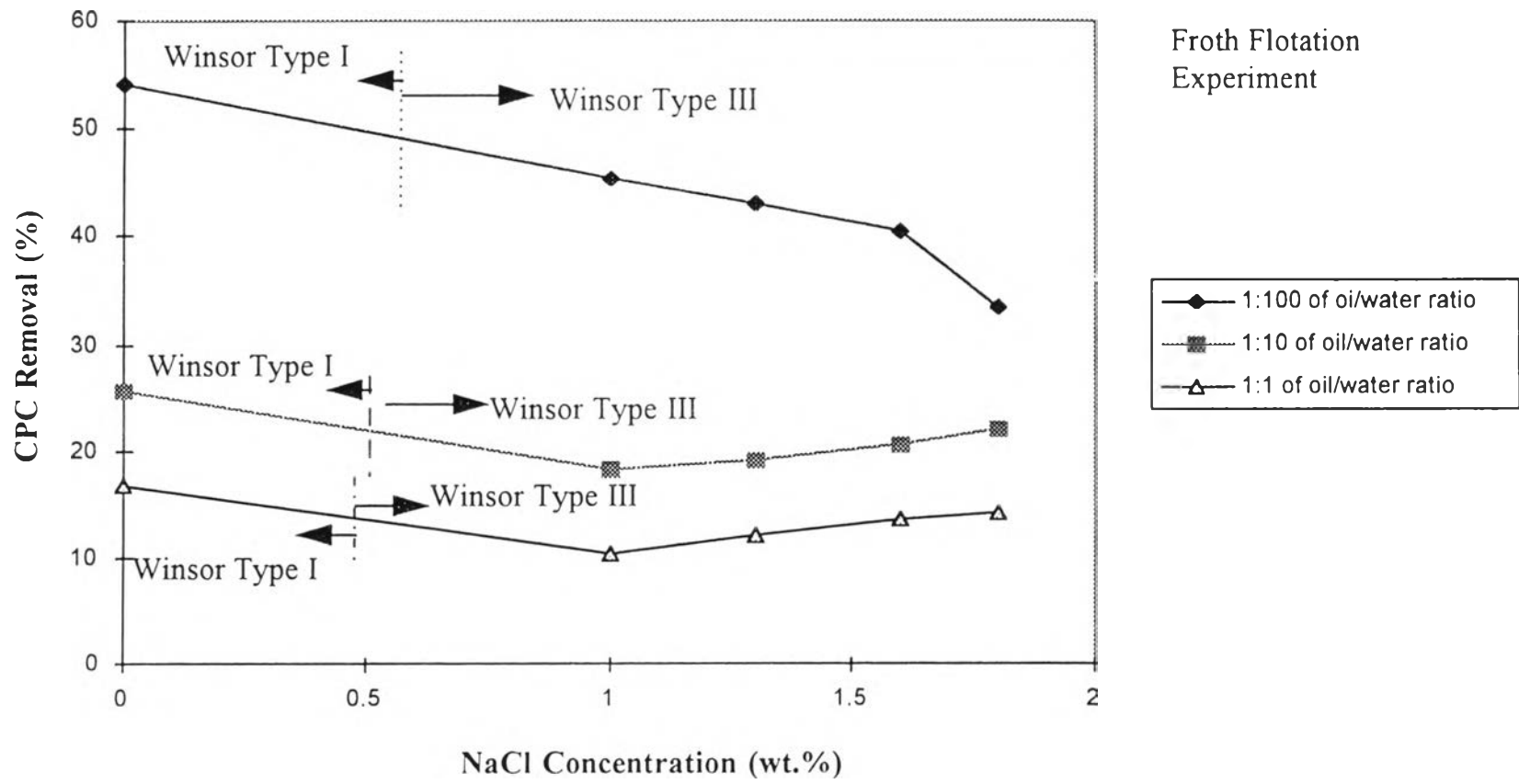
Figure 4.21   Effect of initial oil-to-water volume ratio on CPC removal with CPC concentration = 3.5 wt.%, and temperature = 30 °C at different NaCl concentration
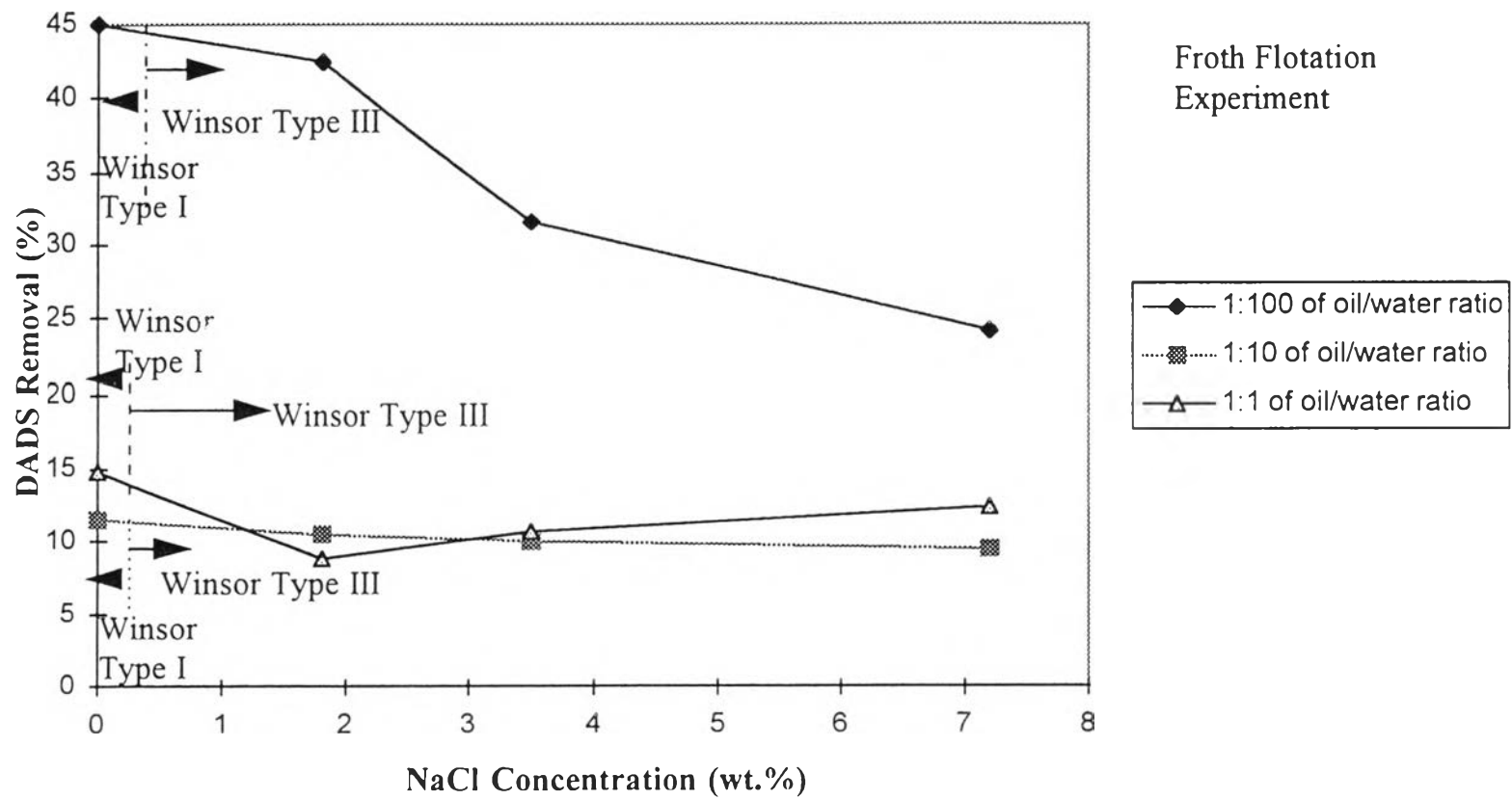
Figure 4.22 Effect of initial oil-to-water volume ratio on DADS removal with DADS concentration = 3.5 wt.%, and temperature = 30 ° C at different NaCl concentration

phase has an effect on the surfactant removal which decreases with NaCl concentration. This result opposes the effect of salinity on the surfactant removal when the liquid crystalline phase disappears. Since the mechanism of action of liquid crystalline phases in enchanted viscosity of film liquid, which increased surface viscosity of the interfacial film due to adsorption of liquid crystals at the air-liquid interface (Prud'homme and Khan, 1996).

4.3 COMPARATIVE EFFECTIVENESS OF EACH SURFACTANT FOR ODCB REMOVAL

Comparing the performance of each surfactant to remove oil in the same range of salinity, surfactant concentration and oil-to-water ratio, the percentage of ODCB removal by using CPC was higher than DADS and SDS. Using SDS to remove ODCB, results in the lowest percentage removal. Since CPC is a cationic and ODCB has high electronegativity, they attract each other. This occurs due to the effect of surface charges of oil droplets and bubbles in the oil-in-water flotation process. It is a strong effect on the oil removal efficiency. DADS has two aromatic rings in its structure that is more hydrophobic than SDS which has no aromatic ring in its structure. So DADS can be more applicable to ODCB removal than SDS.