

CHAPTER III
CLEAN-UP OF OILY WASTEWATER BY FROTH FLOTATION: EFFECT OF
MICROEMULSION FORMATION III: USE OF ANIONIC/NONIONIC
SURFACTANT MIXTURES AND EFFECT OF RELATIVE VOLUMES OF
DISSIMILAR PHASES

3.1 Abstract

Froth flotation, a surfactant-based separation process, can be used to remove emulsified oil from water. In previous work, the maximum removal of ortho-dichlorobenzene from water using froth flotation was achieved when a Winsor Type III microemulsion was formed. However, the exact relationship between the equilibrium microemulsion characteristics and the froth flotation operation is still not clear. In the Winsor Type III microemulsion, three phases are present: an excess water phase containing little surfactant or oil, an excess oil phase containing little water or surfactant, and a middle phase containing almost all of the surfactant and large volume fractions of both oil and water (even equal volumes of oil and water). The Winsor Type III microemulsion also corresponds to a minimum in interfacial tension between liquid phases at equilibrium. In order to elucidate which aspect of the microemulsion is responsible for flotation of oil, flotation experiments were performed with three different combinations of phases: water and middle phases (w-m), water and oil phases (w-o), and water, middle, and oil phases (w-m-o). Since it was deduced that most of oil being recovered when in the Winsor Type III microemulsion region is in the excess oil phase (not the middle phase), the reason why the Winsor Type III microemulsion results in excellent oil removal in flotation operation is probably the ultralow interfacial tensions present and formation of the middle phase is incidental.

3.2 Introduction

Flotation is widely used in several processes (1-10), including selective separation of minerals (4, 6), removing ink from paper fibers in paper recycling, and removal of emulsified oil from water (1, 11). In part I of this series of papers (1), it was

demonstrated that the highest recovery of the model oil pollutant, ortho-dichlorobenzene (ODCB) occurred when a Winsor Type III microemulsion was present, compared to a Winsor Type I microemulsion when a single anionic surfactant, sodium dodecyl sulfate (SDS), was used. That was the first study to relate efficiency of froth flotation to microemulsion phase behavior. A limitation of that study was the formation of surfactant precipitate and liquid crystals to prevent investigation of a wide range of conditions; for example optimum salinity in the Winsor Type III system could not be studied. Not only the microemulsion type, but also the stability of froth have the effect on the efficiency of flotation operation. Matis and Zouboulis (12) reported that the stability of the froth is described by bubble coalescence and breakage parameters. The bubble coalescence is mainly due to the higher pressure inside the smaller bubbles, while the breakage is mainly caused by lowering the thickness of the film due to the force of gravity. The mechanism of froth flotation for the removal of insoluble organic contaminants from water is shown in Figure 3.1 (1).

In part II of this series (13), a mixture of SDS and nonionic surfactant, nonylphenol polyethoxylate (NP(EO)₁₀), was used to allow investigation of a wide range of conditions. Also the composition of the foam was analyzed to address the issue of selectivity; i.e., high recovery of oil overhead in the froth is only of value if a small amount of water is being taken overhead. It was shown that the oil : water ratio in the foamate (broken foam from overheads) is substantially higher than that in the wastewater in a Winsor Type III microemulsion region where oil removal is maximized, so the separation has good selectivity. However, under some other conditions, more water than oil is carried over, making the separation inefficient and indicating the importance of relating operating conditions to phase space.

In this third part of the series, we address the following question: what is it about the Winsor Type III microemulsion that causes high flotation efficiency? Since the oil is present as both an excess oil phase and in the middle phase, from which phase is the oil coming overhead with the foam originating? Is the formation of the third or middle phase crucial or is it other characteristics (primarily ultralow interfacial tensions) of the Type III system which account for the high separation efficiency during flotation? In order to address these questions, we have separated the three phases formed in the Winsor Type III microemulsion system after equilibration: excess oil (o), excess water

(w), and middle phase (m). We then carried out the froth flotation experiments with different combinations of these phases (o-w, m-w, and w-m-o).

3.3 Experimental Section

3.3.1 Materials

Ortho-dichlorobenzene (product of Fisher Scientific Co.) with 99.9% purity was used as the model emulsified oil in this study. The surfactants were sodium dodecyl sulfate (SDS) from Henkel Co. with at least 90% purity and polydisperse nonylphenol ethoxylate (NP(EO)₁₀) From ICI Australia Operations Pty Ltd. with a purity greater than 99.9%. Sodium chloride (NaCl), analytical grade, from Aldrich Chemical Co. was used as added electrolyte. All the chemicals were used as received without purification. Deionized water was used in all experiments.

3.3.2 Methodology

In this study, the surfactant concentration and salinity were expressed as weight percent of the overall system composed of water, oil, surfactant, and salt. The experiments were conducted at 30°C.

Figure 3.2 shows a schematic diagram of the froth flotation apparatus used in this study. The froth flotation apparatus was composed of a cylindrical glass column with 5 cm internal diameter and 70 cm height and operated in batch mode. Filtered air was introduced into the bottom of the column at a constant flow rate of 250 mL/min through a sintered glass disk that has 16 – 40 µm pore diameter. At an initial oil : water ratio of 1:1 as just described, one liter of different combinations of three phases (w-o, w-m, and w-m-o) was transferred into the column. These three phases were separated from the solution reaching equilibrium in a water bath at 30°C for 1 month under conditions corresponding to a Winsor Type III microemulsion. The foam overflowed from the column was collected over different time intervals. After that, the foam was broken for analysis of the concentration of ODCB using a HPLC (Hewlett Packard, Series 1050) with a UV detector.

3.4 Results and Discussion

In this study, X_{SDS} is defined as the weight fraction of SDS (the weight of SDS divided by the total weight of mixed surfactants). The total surfactant concentration in weight percent refers to the total mass of the system consisting of the total oil, water, salt, and surfactant. Phase behavior studies of all systems used in this work were shown in Part II of this series (13).

3.4.1 Effect of Initial Mixed Surfactant Concentration on ODCB Removal

As shown in Figure 3.3, at low aeration time, the amount of oil removed increases when surfactant concentration increases. This is because increasing surfactant dosage can increase the number of air bubbles per unit volume and foam production (3). Absolutely pure liquid does not foam (14). Since one of the key mechanisms in the flotation is the attachment between air bubbles and oil droplets (11), the amount of oil removal increases when a number of air bubbles increases. However, increasing surfactant concentration causes highly hydrated foam to be produced (2) due to an increase in the amount of water in the foam lamellae. As a result, the separation of oil and water in the overhead froth declines. Oil removal and selectivity for oil compared to water is a trade-off with respect to surfactant concentration.

3.4.2 Effect of NaCl Concentration on ODCB Removal

The system containing 3 wt% mixed surfactant concentration and X_{SDS} of 0.6 was used to study the effect of NaCl concentration on ODCB removal. As shown in Figure 3.4, the amount of ODCB removal of the system containing 0.5 wt% is much higher than that of the system without NaCl. This might be because NaCl can reduce the repulsive force between anionic head groups of SDS leading to a higher density of surfactant molecule adsorbed at the surface of the foam lamellae. The resultant foam could be more stable and have a higher oil carrying capacity. For ionic surfactant systems, at higher electrolyte concentrations, foam stability can decrease due to the reduction in repulsion between adsorbed surfactant monolayers on each side of the foam lamellae, providing a possible explanation for the observed maximum in oil removal with added NaCl concentration observed in Figure 3.4.

3.4.3 Effect of the Presence of Different Phases on ODCB Removal

To investigate whether the formation of the third phase or middle phase in a Winsor Type III microemulsion influences the maximum oil removal, froth flotation of different combinations of three phases (w-o, w-m, and w-m-o) separated from Winsor Type III microemulsion solutions at equilibrium was performed. From Figures 3.5 – 3.12 for both total surfactant concentrations of 3 and 5% by weight, oil removal from w-o system is always higher than that from w-m system, and it is nearly as high as or higher as that from w-m-o system. It can be concluded that most of oil removed comes from the excess oil phase rather than from the middle phase in Winsor Type III microemulsion regime. This may be due to the oil surface in the middle phase being less hydrophobic than that in the excess oil phase. This is because oil droplets in the middle phase microemulsion are inside a bicontinuous structure (15). This result implies that the third phase or middle phase the Winsor Type III microemulsion regime is not responsible for the high separation efficiency during flotation. Other characteristics in the Winsor Type III microemulsion such as ultalow interfacial tensions and foam stability are believed to also be important for high flotation efficiency. It is a coincidence that the middle phase is present when maximum oil removal is observed.

3.4.4 Effect of Weight Fraction of SDS on ODCB Removal

From Figure 3.13 for the w-o system, foam volume increases with increasing weight fraction of SDS, but the weight fraction of SDS does not affect the foam volume of the w-m system. The w-m-o system exhibits a maximum in foam volume with increasing weight fraction of SDS. The result also shows that anionic surfactant produces more foam than nonionic surfactant does. Ionic surfactants are commonly better foamers than nonionic surfactants (16), so this is not unexpected. Consistent with this, high foam volume is achieved at high weight fraction of SDS. For all w-m-o, w-o, and w-m systems as shown in Figure 3.14, increasing weight fraction of SDS increases the oil removal probably partly due to the effect of foam volume. The effect of the weight fraction of SDS on ODCB removal is important in both w-m-o and w-o systems as a result of high foam volume produced compared with that of the w-m system. However, the weight fraction of SDS utilized should be appropriate to keep a

solution within Winsor Type III microemulsion regime in order to have high oil removal.

3.4.5 Effect of Weight Fraction of SDS and Initial Mixed Surfactant Concentration on Removal Time

In this study, only w-m-o and w-o systems can achieve 50% oil removal over the time intervals studied. Figures 3.15 and 3.16 show the effect of weight fraction of SDS on removal time for 50% oil removal in w-m-o and w-o system, respectively. To achieve 50% oil removal, the higher the weight fraction of SDS is, the shorter the operating time required. This is because more foam is produced at a higher weight fraction of SDS as shown in Figure 3.13. For both w-m-o and w-o systems, 5 wt% initial mixed surfactant concentration requires a shorter time for 50% oil removal than 3 wt% initial mixed surfactant concentration does due to the higher amount of foam generated in the 5 wt% system.

From this result, it is obvious that oil removal efficiency depends upon both some characteristics in Winsor Type III microemulsion regime and the amount of foam volume produced.

3.5 Acknowledgements

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3.6 References

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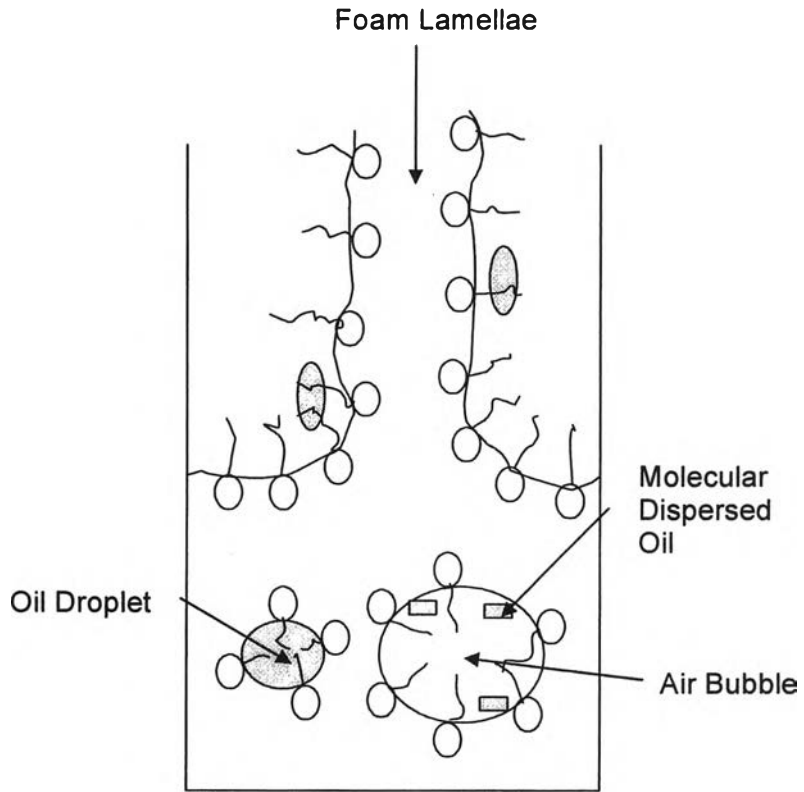


Figure 3.1 Schematic of the foam flotation process

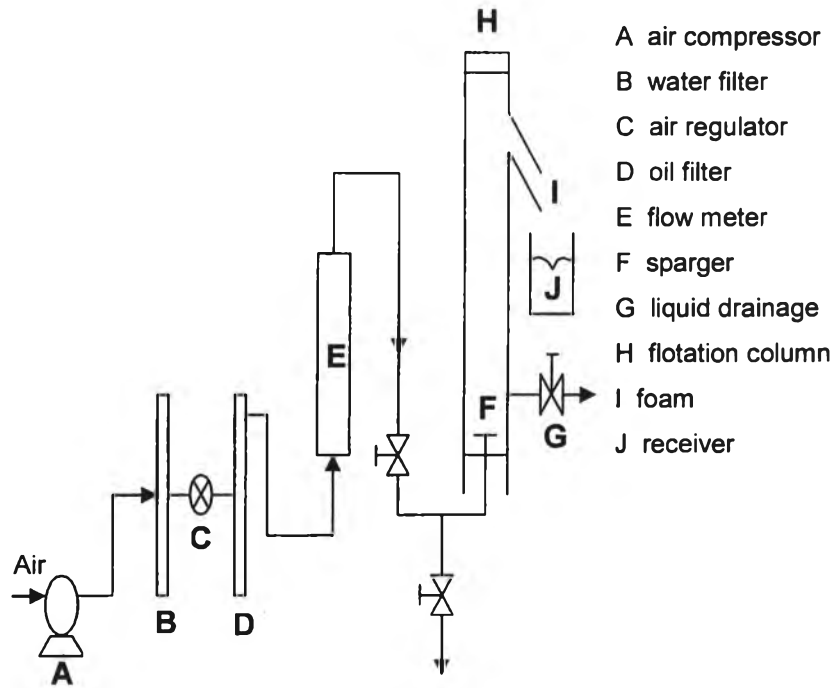


Figure 3.2 Schematic diagram of the froth flotation apparatus

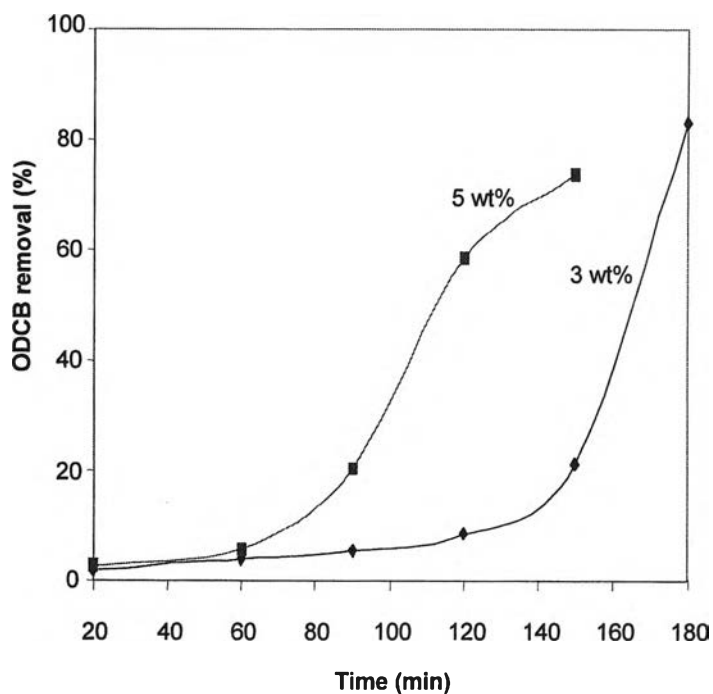


Figure 3.3 Comparison of ODCB removal between 3% and 5% by weight total surfactant concentrations at X_{SDS} of 0.2, without NaCl, and initial oil : water ratio of 1:1

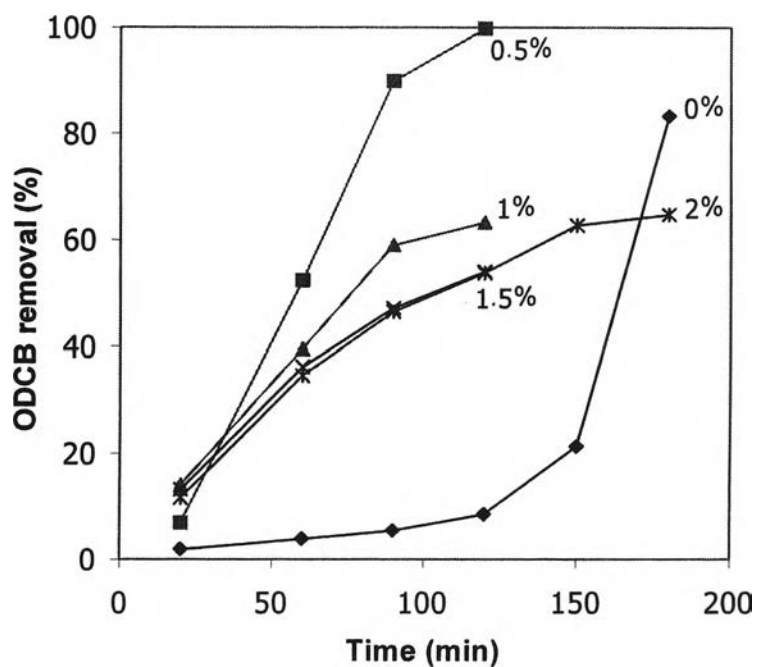


Figure 3.4 Comparison of ODCB removal at 3% by weight total surfactant concentration, X_{SDS} of 0.6, initial oil : water ratio of 1:1, and different NaCl concentrations

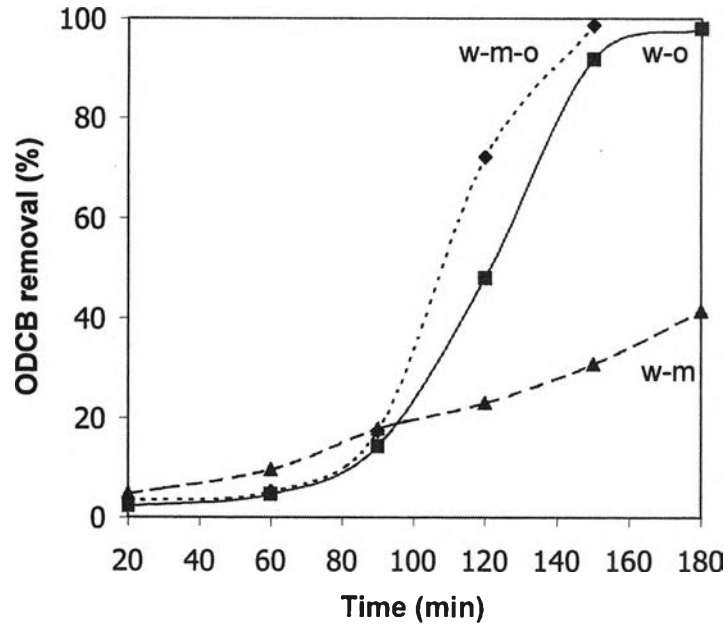


Figure 3.5 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.2, without NaCl, and initial oil : water ratio of 1:1

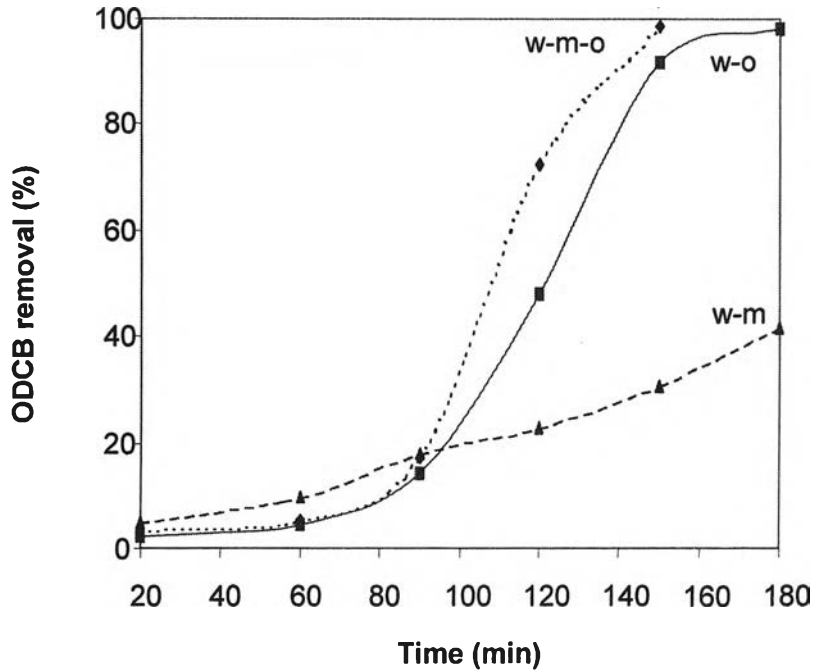


Figure 3.6 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.4, without NaCl, and initial oil : water ratio of 1:1

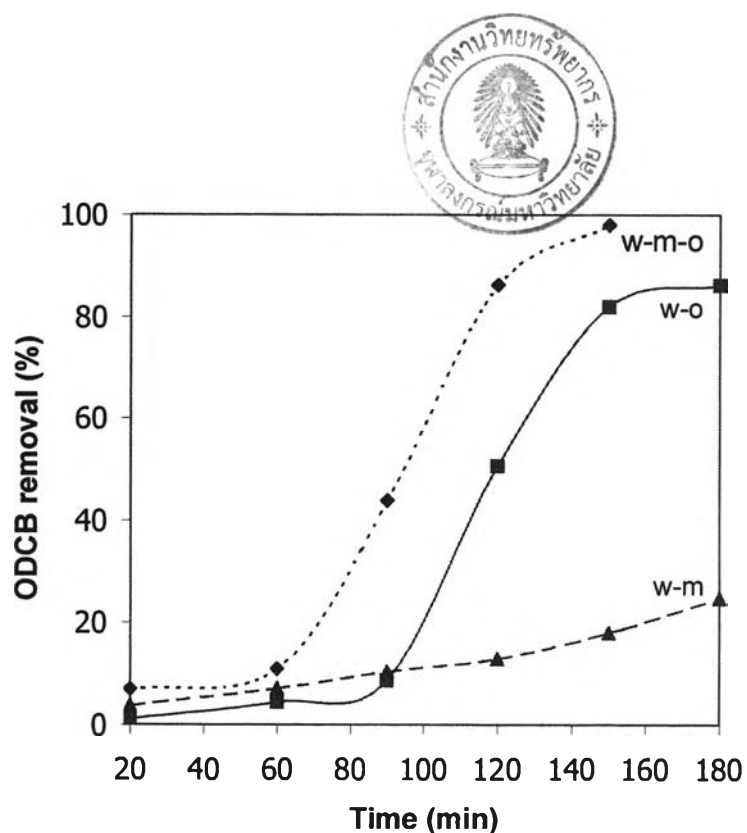


Figure 3.7 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.6, without NaCl, and initial oil : water ratio of 1:1

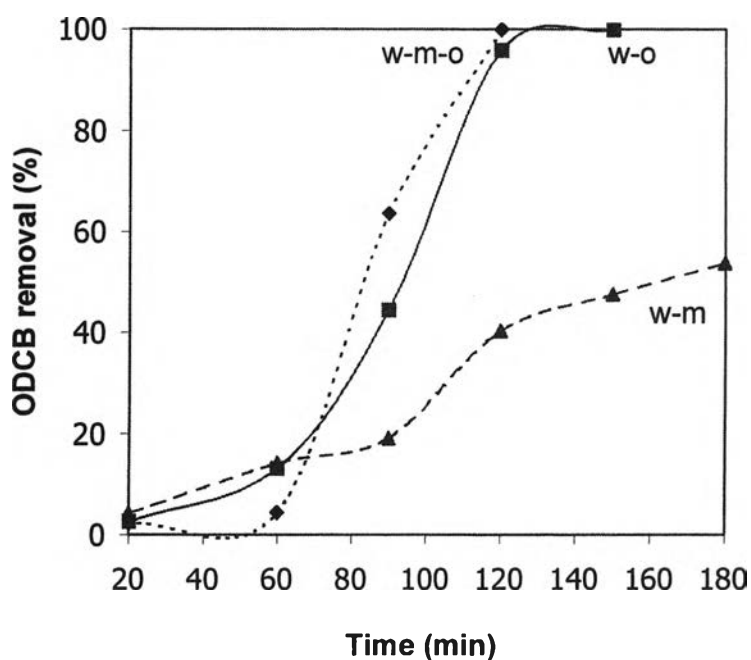


Figure 3.8 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, X_{SDS} of 0.8, without NaCl, and initial oil: water ratio of 1:1

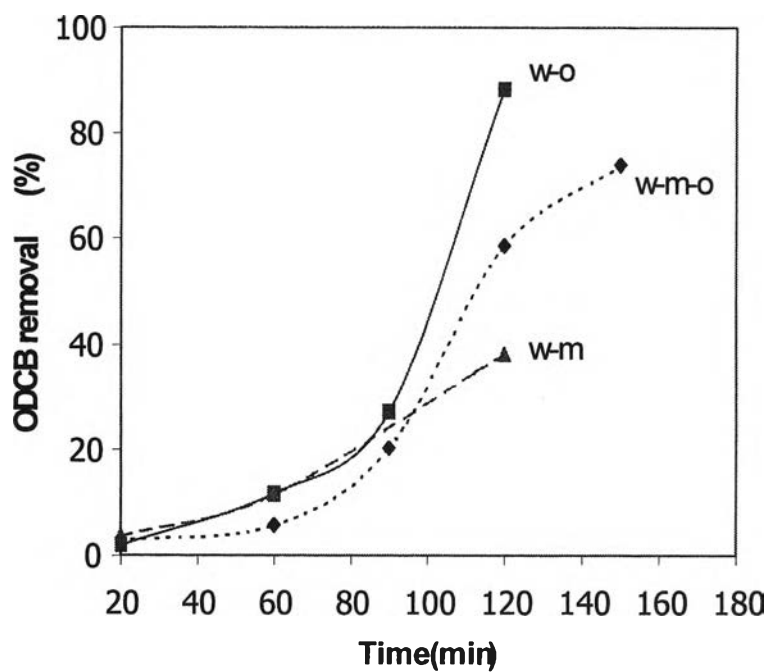


Figure 3.9 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.2, without NaCl, and initial oil: water ratio of 1:1

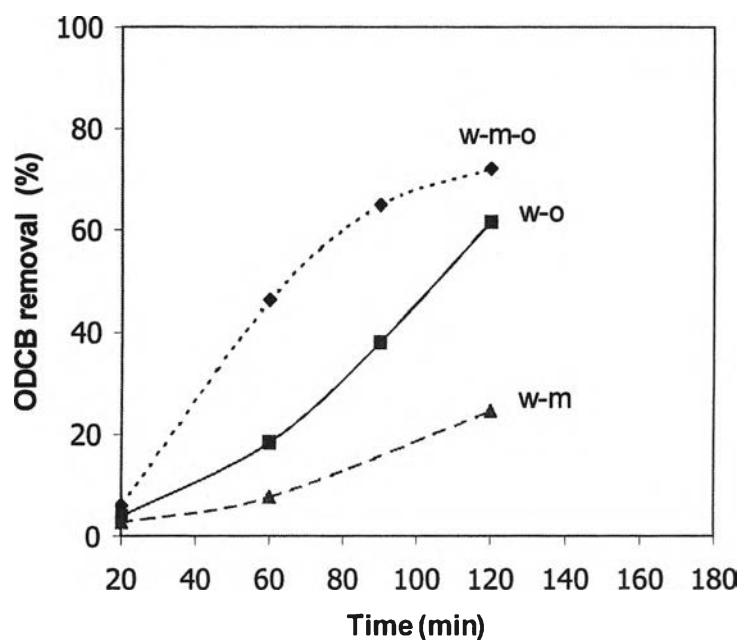


Figure 3.10 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.4, without NaCl, and initial oil: water ratio of 1:1

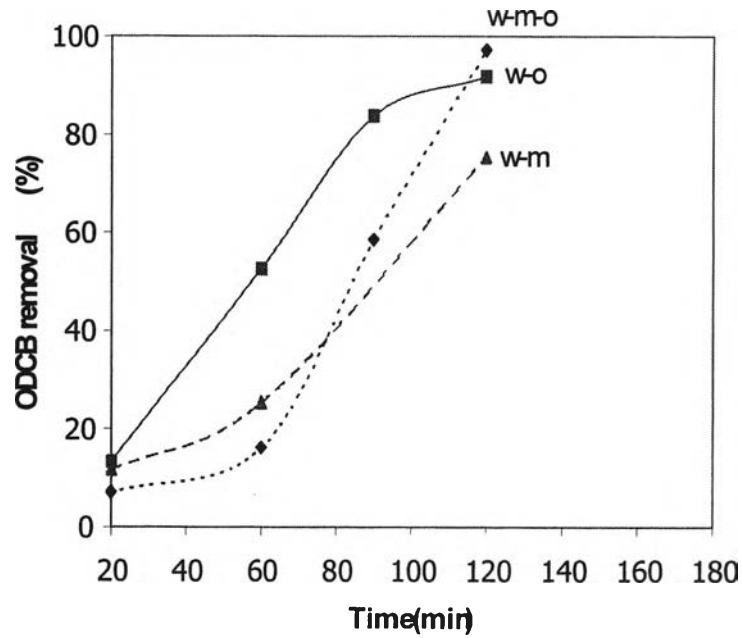


Figure 3.11 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.6, without NaCl, and initial oil: water ratio of 1:1

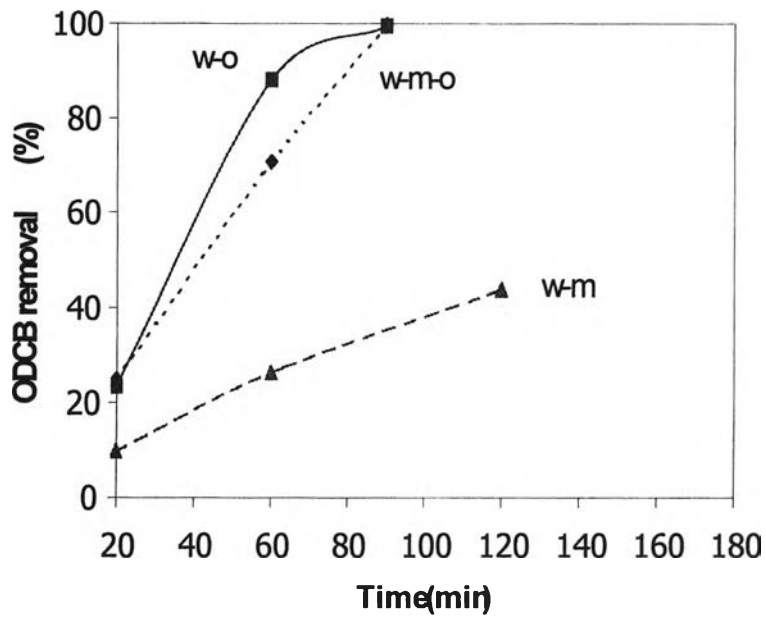


Figure 3.12 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 5% by weight total surfactant concentration, X_{SDS} of 0.8, without NaCl, and initial oil: water ratio of 1:1

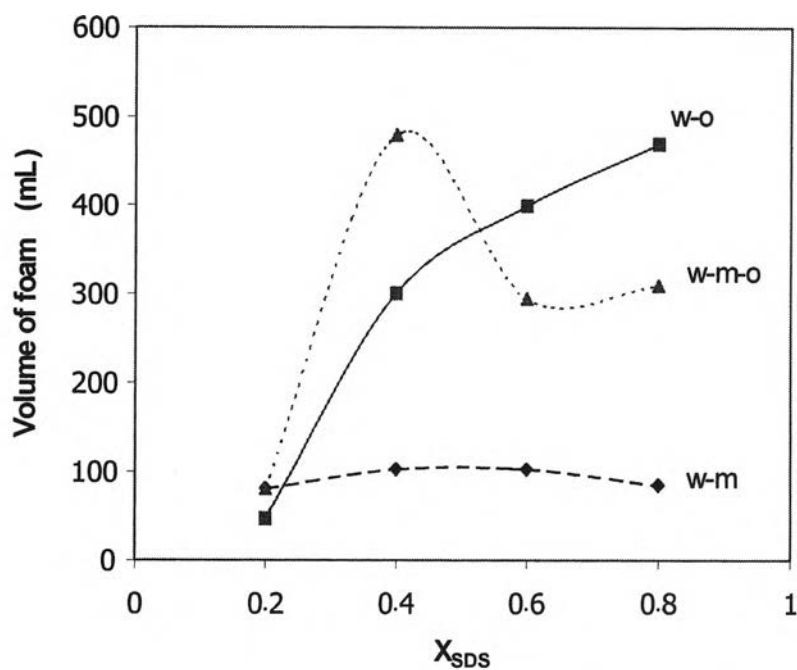


Figure 3.13 The foam volume of different systems having different X_{SDS}

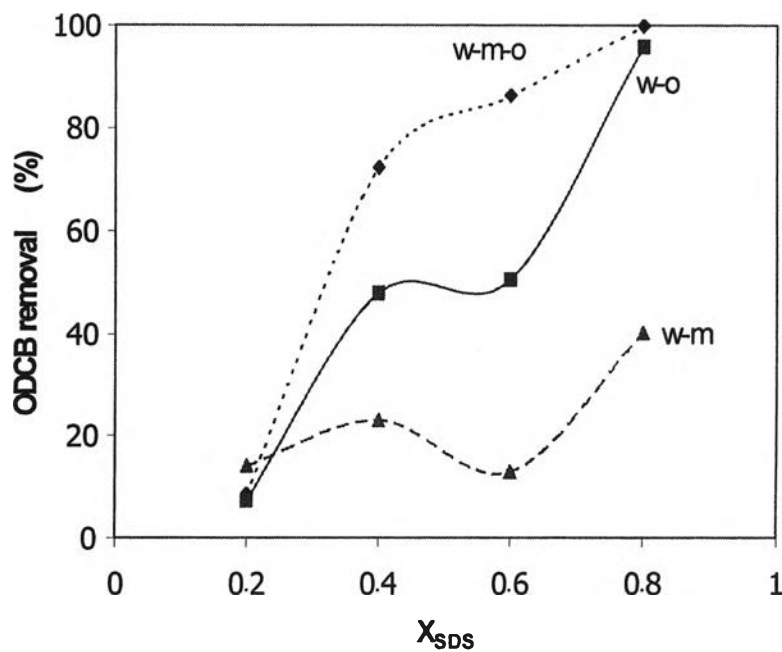


Figure 3.14 Comparison of ODCB removal of w-m-o, w-o, and w-m systems at 3% by weight total surfactant concentration, without NaCl, initial oil: water ratio of 1:1, and 120 min aeration time

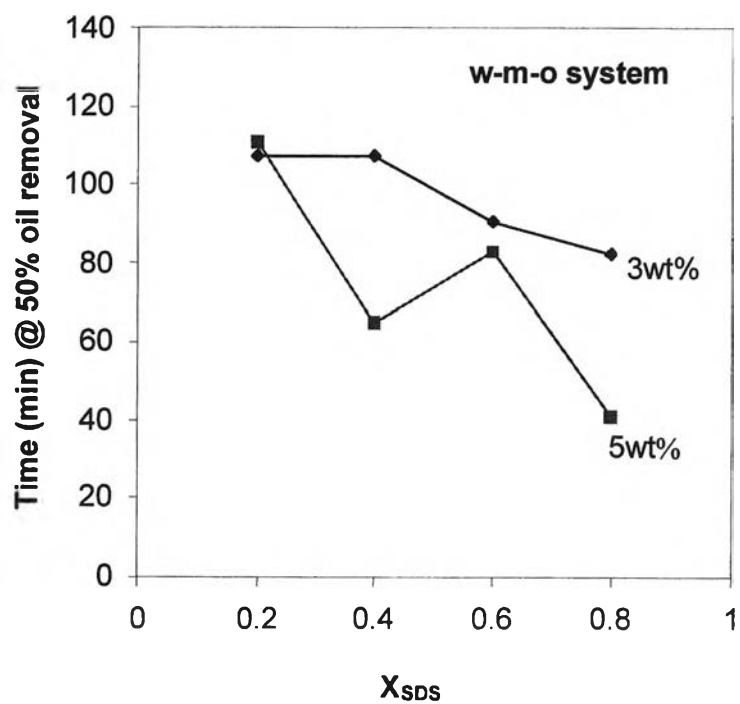


Figure 3.15 Comparison of time required to achieve 50% ODCB removal of w-m-o system at different fraction of SDS

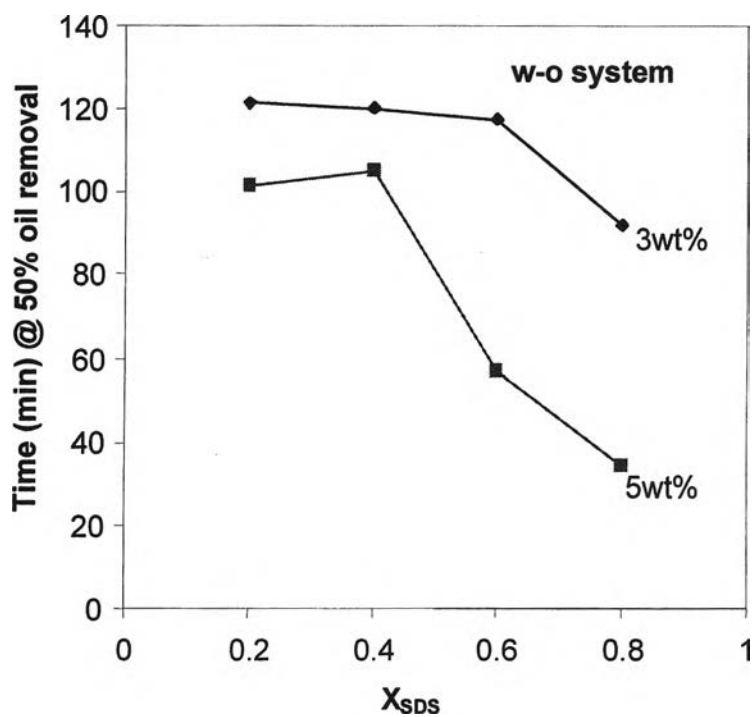


Figure 3.16 Comparison of time required to achieve 50% ODCB removal of w-o system at different fraction of SDS