CHAPTER IV
RESULTS AND DISCUSSION

4.1 Phase Behaviors

The objective of this section was to investigate the effect of surfactant concentration and NaCl concentration, where the minimum surfactant concentration can form the middle phase in microemulsion systems, or critical microemulsion concentration. Alfoterra 145-5PO (Branch alcohol propoxylated sulfate, sodium salt) was used as a surfactant to form microemulsions with motor oil because it has a proper HLB for the motor oil-water system and expected to form the Winsor Type III or middle phase microemulsions.

In this study, the microemulsion formation of motor oil with Alfoterra showed only two obvious phases, which were the water and oil excess phases. The layer of the middle phase was very thin, and it could not be clearly observed visually. Consequently, the measurement of the phase transformation became difficult to identify whether the system had a middle phase or not. Hence, the phase diagram of motor oil with Alfoterra was not shown here. The potential use of electrical conductivity measurement to characterize the microemulsion system was investigated. The electrical conductivity of the microemulsion was immediately measured, under gentle magnetic stirring, with a platinized Pt cell. Under these conditions, the obtained value remained constant for a long time, and was found to be relatively steady (± 5%). In addition, the IFT of the system was measured by the spinning drop tensiometer to examine the existence of the Winsor Type III microemulsions. The diagrams of IFT as a function of surfactant concentration and salinity are illustrated here.

4.1.1 Effect of Surfactant Concentration on IFT

Figure 4.1 illustrates the effect of surfactant concentration on the ultra-low IFT when salinity is 5 wt.% and an oil to water initial volumetric ratio is 1:1.

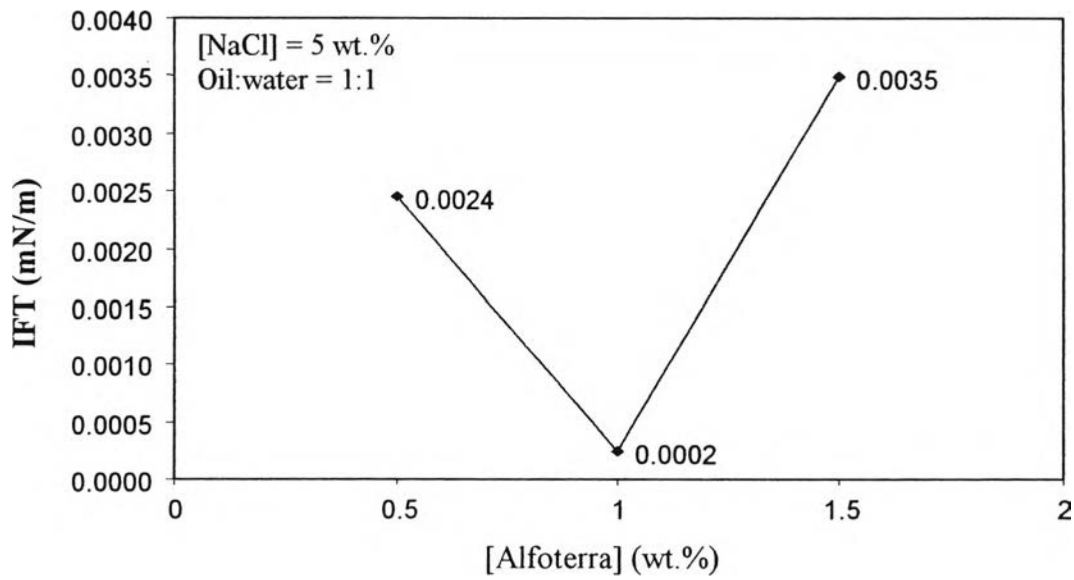


Figure 4.1 IFT as a function of Alfoterra concentration at 5 wt.% NaCl with oil to water ratio = 1:1, and 30 °C.

From Figure 4.1, the IFT of the system decreases rapidly when Alfoterra concentration increases from 0.5 to 1.0 wt.%. And then, it increases with the increase in the Alfoterra concentration from 1.0 to 1.5 wt.%. This is because the repulsive force between the anionic head groups of Alfoterra increases with the increase in the Alfoterra concentration. Therefore, micelle is difficult to form leading to lower oil solubilization, but higher IFT as shown by Equation (4.1), Chun-Huh's equation.

$$\gamma \;\alpha\; SP^{-2} \qquad (4.1)$$

where γ is the interfacial tension and SP is the solubilization parameter.

The minimum IFT of 2 x 10^{-4} mN/m at 1.0 wt.% Alfoterra is considered to be in the range of the ultra-low IFT (10^{-2}-10^{-4} dyne/cm) which is typically observed in a system with the middle phase microemulsion formation.

Consequently, it can be concluded that the phase behavior study of the motor oil system by using Alfoterra as a surfactant can form the middle phase or Winsor Type III microemulsion.

4.1.2 Effect of NaCl Concentration on IFT

Figure 4.2 shows IFT as a function of NaCl concentration or salinity scan at 0.5 wt.% Alfoterra, and an oil to water ratio of 1:1. From the result, the minimum IFT was found at 5 wt.% NaCl. At free-NaCl concentration, the repulsive force between anionic head groups is high leading to a very low aggregation number and a very small size of micelles, so the amount of solubilized oil in the inner core of micelles is low resulting in a high IFT value. When NaCl is added into the system, it reduces the repulsive force between anionic head groups resulting in increasing the aggregation number, so the amount of solubilized oil into the inner core micelles increases leading to the reduction of IFT. At very high NaCl concentrations, the charge at the head group of surfactants is neutralized, so the distance among surfactant molecules in the micelle becomes very close resulting in lowering the aggregation number, so the amount of solubilized oil in the inner core of micelle is low leading to higher IFT.

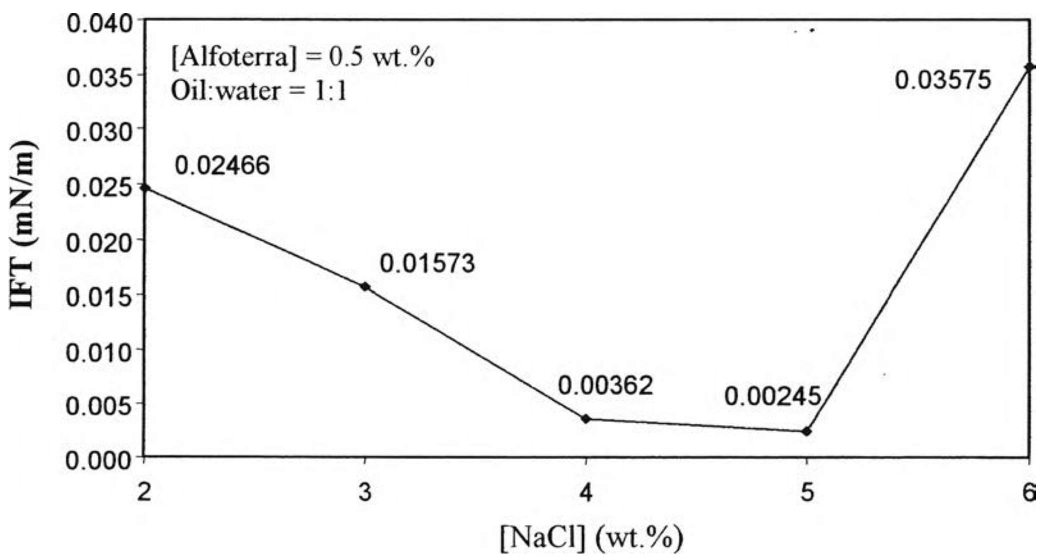


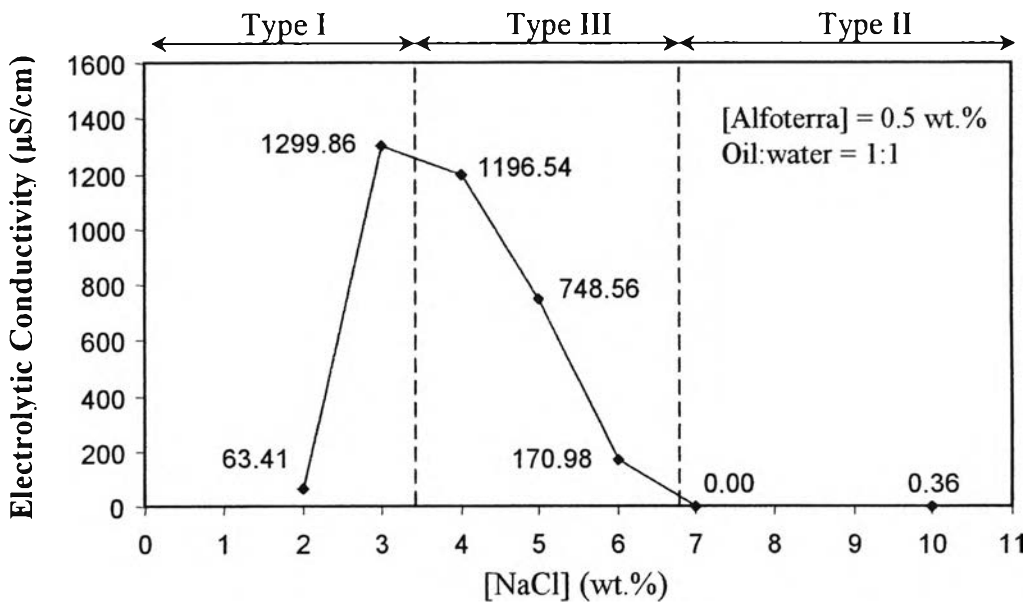
Figure 4.2 IFT as a function of salinity at 0.5 wt.% Alfoterra, and an initial oil to water ratio = 1:1.

4.1.3 Microemulsion Diagram

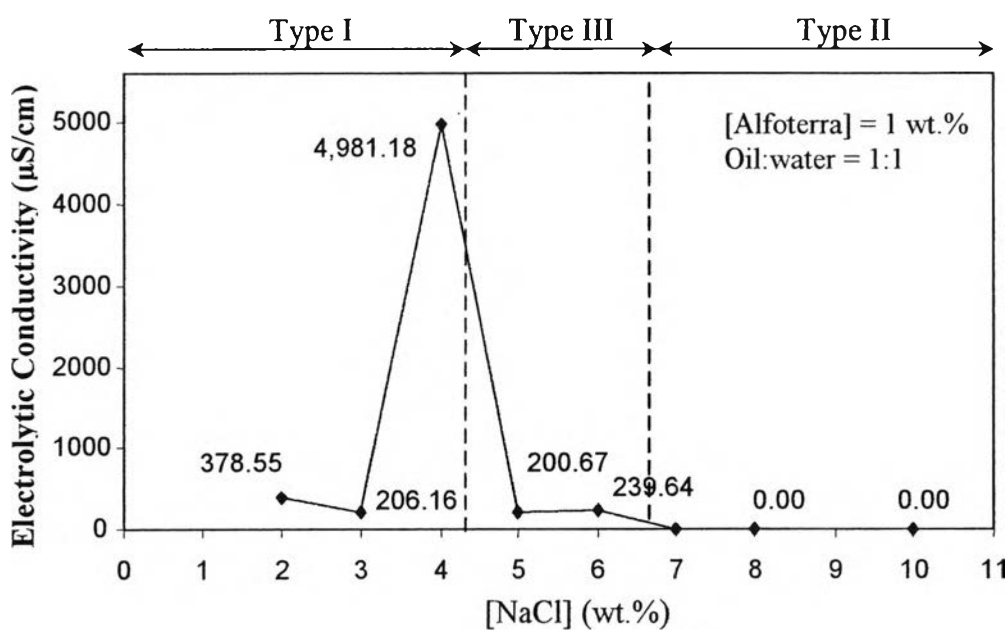
Figure 4.3 shows the electrolytic conductivity variation versus the salinity of the aqueous phase, all other parameters being held constant. At low salinities or Type I region, the conductivity increases steadily with salinity. This is because the microemulsion consists of brine droplet dispersed in aqueous solution which is the continuous phase. At high salinities or Type III region, on the other side, the conductivity is lower than Type I region, and thus essentially zero on the illustrated scale because the brine droplet dispersed in oil phase which is the continuous phase. As far as the Type III region is concerned, the conductivity exhibits in the mid-range.

While Figure 4.2 shows a salinity scan for one concentration of surfactant, Figure 4.4 shows the microemulsion diagram, sometimes referred to as the fish diagram due to its shape, which performs the regions of surfactant and NaCl concentrations that produce a given type of microemulsion phase. The region labeled as 'I' corresponds to a two phase system (excess oil phase and oil-in-water microemulsion), the region 'III' enclosed by the phase boundaries has three phases in equilibrium (excess oil, water and middle phase) and the region 'II' has two phases (excess water and water-in-oil microemulsion). At a fixed Alfoterra concentration (e.g., 0.5 wt.%), the microemulsion transitioned from a Winsor Type I to III to II microemulsions as the NaCl concentration increased.

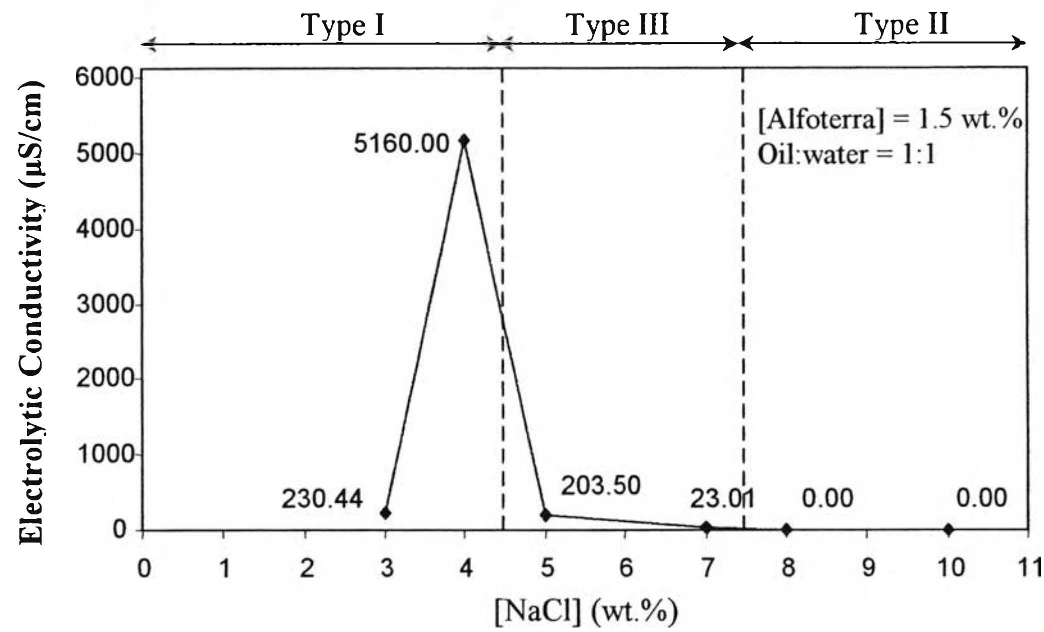
As mentioned before, in this study, the minimum surfactant concentrations were concerned. Hence, Alfoterra concentrations were selected at 0.5, 1 and 1.5 wt.% for the froth flotation experiments.



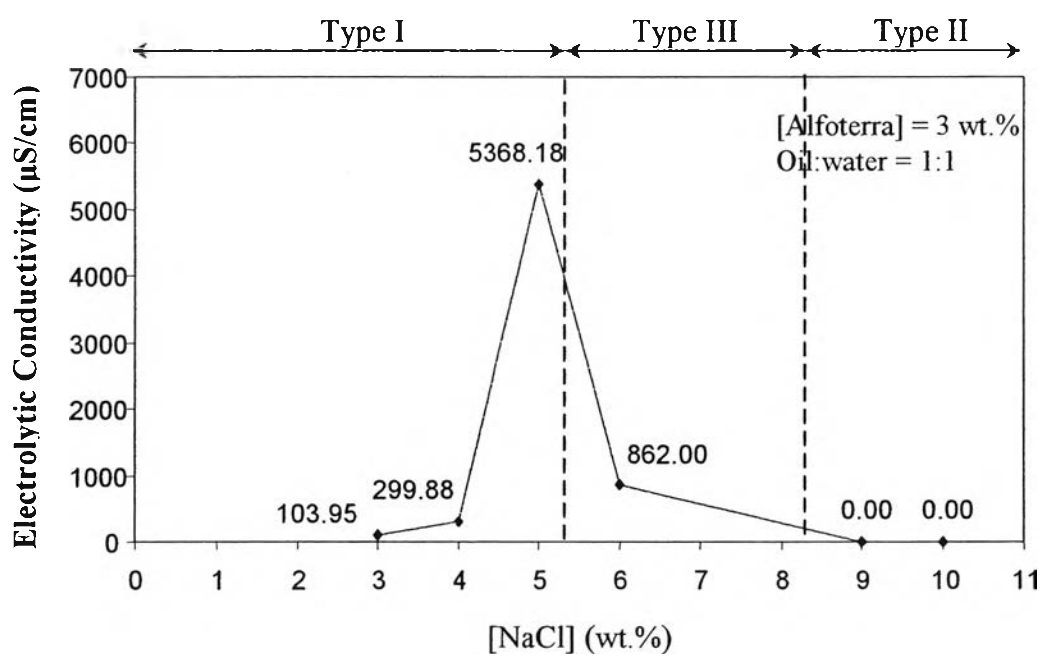
(a) 0.5 wt.% Alfoterra



(b) 1 wt.% Alfoterra



(c) 1.5 wt.% Alfoterra



(d) 3 wt.% Alfoterra

Figure 4.3 Electrolytic conductivity of microemulsion system at different NaCl concentration.

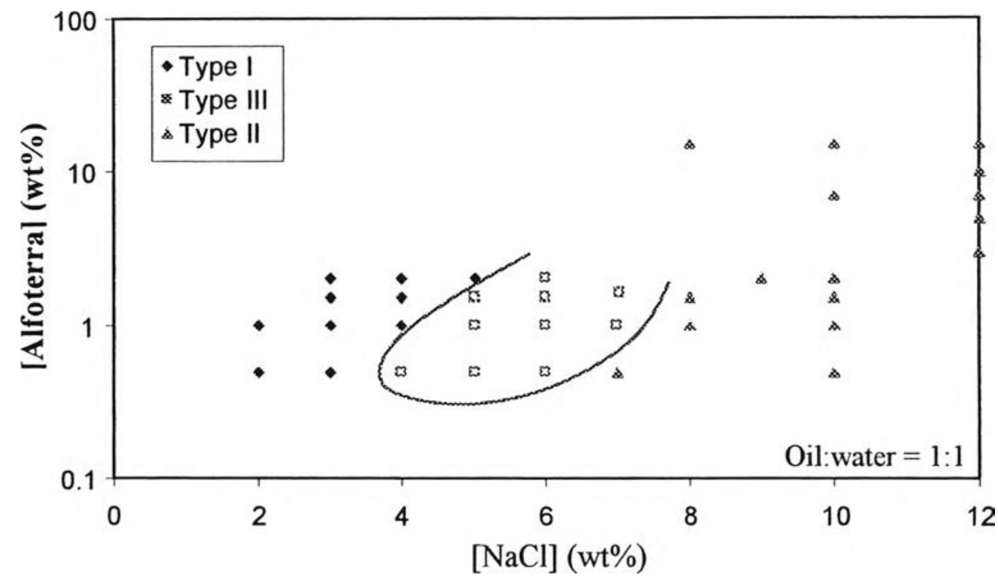
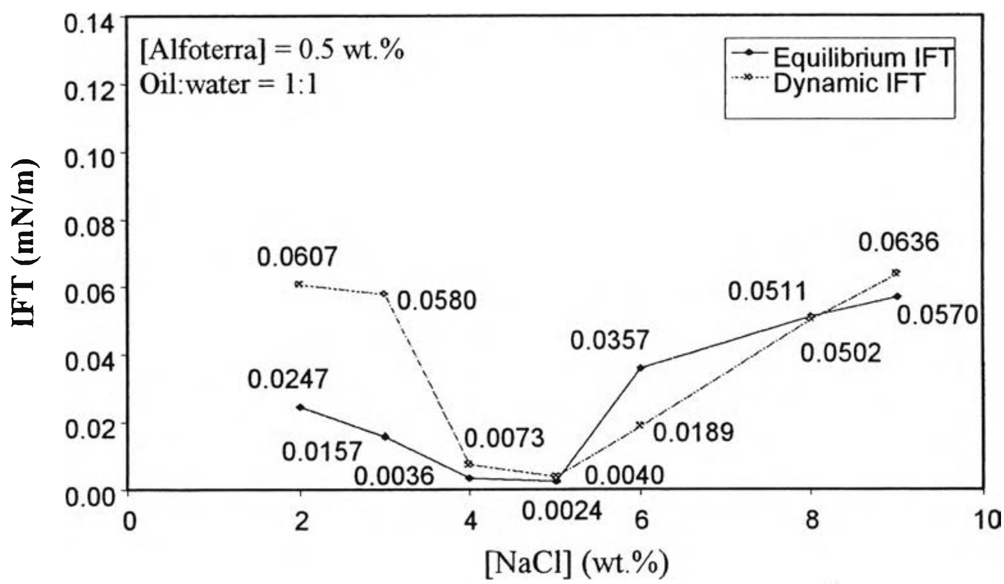


Figure 4.4 Microemulsion diagram of Alfoterra with motor oil at different NaCl concentration.

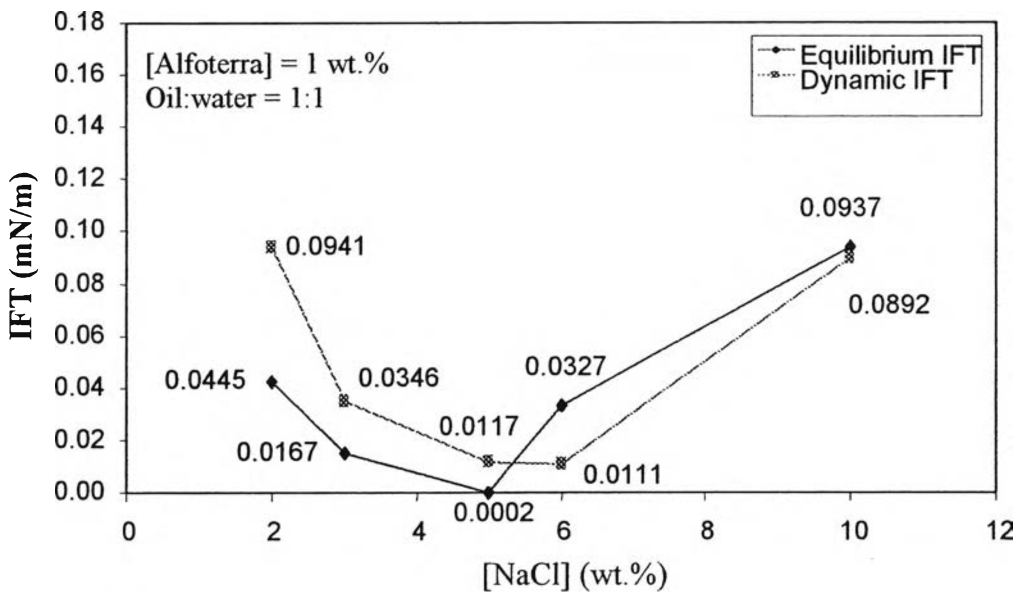
4.2 Interfacial Behaviors

Many of the industrial operations involve the liquid-fluid interfaces, for which the composition is constantly refreshed and does not reach equilibrium. The importance of such dynamic interfacial tensions is increasingly recognized to be essential to the understanding and control of interfacial processes. Hence, This research is to investigate the relationship between a non-equilibrium system in a column and an equilibrium system in the microemulsion formation.

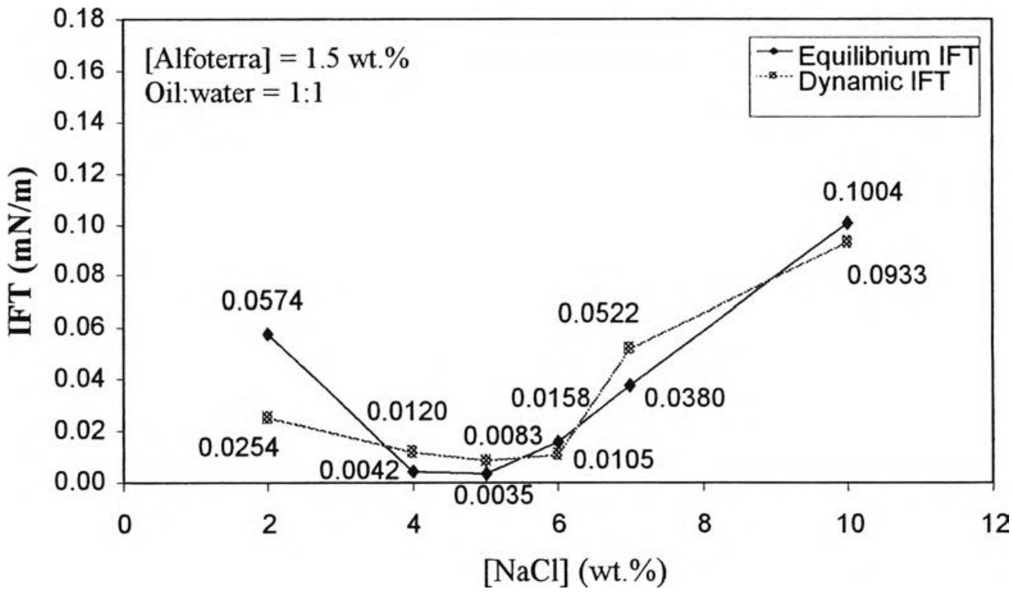
Figure 4.5 exhibits the equilibrium IFT and the dynamic IFT at 30 min, which is the hydraulic retention time for running the froth flotation experiments, at different NaCl concentration. From the results, the differences between the equilibrium IFT and the dynamic IFT are negligible because the values are in the same order of magnitude. Hence, it is insignificant on the froth flotation performance.



(a) 0.5 wt.% Alfoterra



(b) 1 wt.% Alfoterra



(c) 1.5 wt.% Alfoterra

Figure 4.5 Comparison between equilibrium IFT and dynamic IFT as a function of salinity at different Alfoterra concentration, and an initial oil to water ratio = 1:1.

4.3 Froth Flotation

Both oil removal and enrichment ratio are significant parameters to indicate the performance of a froth flotation process. In addition, the surfactant removal, foam wetness, and foam flow rate should be determined and correlated with the froth flotation performance. Generally, high oil removal efficiency is a vital requirement for an effective froth flotation process but it is not the sole factor. If oil and water are present in the froth with the same proportion as in the influent, the selectivity and separation of oil from water do not occur. Hence, for effective separation, the concentration of oil in the overhead froth has to be much higher than that in the feed. Consequently, in this study, the separation efficiency is indicated by the enrichment ratio, which is defined as the ratio of oil concentration in the overhead froth to that in the feed. In order to achieve the separation, the enrichment ratio must be greater than one. Moreover, the higher the enrichment ratio, the better the separation is.

4.3.1 Effect of Surfactant Concentration

As shown in Figure 4.6, for the Alfoterra concentration in the range of 0.3 to 0.5 wt.%, the oil removal increases because there is more foam to produce with increasing surfactant concentration as shown in Figure 4.7. Then, the oil removal decreases as the Alfoterra concentration increases from 0.5 to 1.0 wt.%. This may be because at higher Alfoterra concentration, there is more water in the foam lamellae also known as wet foam. Consequently, foam with higher Alfoterra concentration is heavier than that with lower Alfoterra concentration leading to the collapse of foam much easier. When the Alfoterra concentration further increases to 1.5 wt.%, the oil removal increases again because the rate of foam production increases as shown in Figure 4.7. Even though the increase in the Alfoterra concentration increases the thickness of foam lamella leading to the collapse of the foam, there is more easily to balance between the ability of the foam formation due to the high concentration of surfactant and the foam collapse due to the wet foam.

The effect of Alfoterra concentration on the enrichment ratio of motor oil is shown in Figure 4.8. As the Alfoterra concentration increases from 0.3 wt.% to 0.5 wt.%, the enrichment ratio slightly decreases because the concentration of surfactant at the foam decreases with increasing feed Alfoterra concentration. Hence, the foam lamellae with higher surfactant concentration becomes thicker than that with lower surfactant concentration leading to a large amount of water in the foam lamellae, so 0.5 wt.% Alfoterra results in the low enrichment ratio of motor oil. However, when the Alfoterra concentration further increases, the enrichment ratio slightly increases. This is because increasing surfactant concentration increases the hydrophobic region. Thus, the amount of oil content in the foam increases.

The effect of Alfoterra concentration on the surfactant removal is shown in Figure 4.9. The increase in the Alfoterra concentration from 0.3 to 0.5 wt.% resulted in the increase in the surfactant removal. But the surfactant removal decreases when the Alfoterra concentration further increases to 1.0 wt.%. The surfactant removal increases again with 1.5 wt.% Alfoterra. This result is related to the effect of Alfoterra concentration on the oil removal and the foam production rate as described before.

As shown in Figure 4.10, the enrichment ratio of the surfactant increases when the Alfoterra concentration increases from 0.3 to 1.0 wt.% and then slightly decreases. This is related to the result of enrichment ratio of motor oil as shown in Figure 4.8. This reason can be explained as described in the effect of Alfoterra concentration on the enrichment ratio of motor oil.

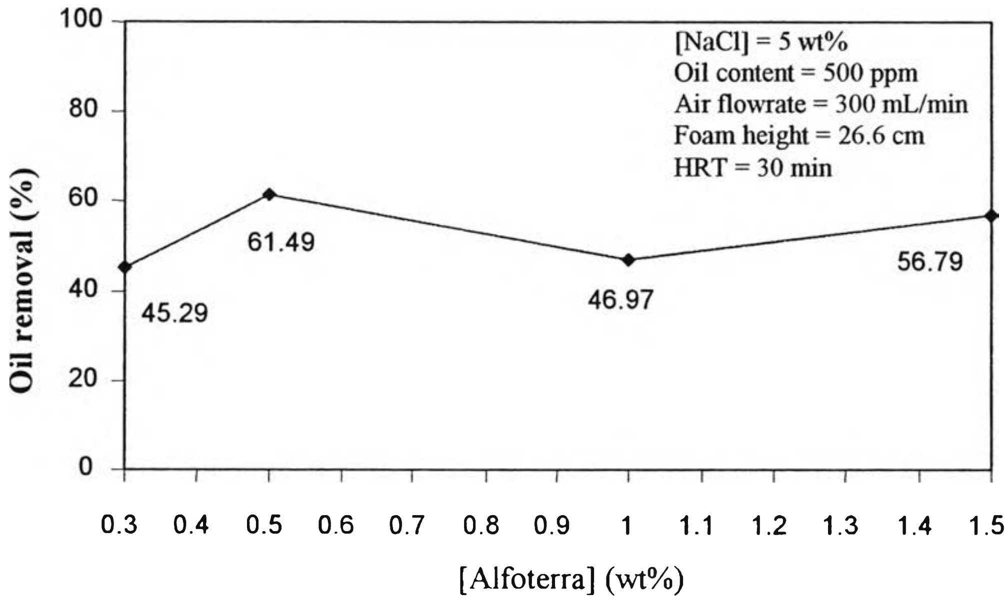


Figure 4.6 Oil removal efficiency at different Alfoterra concentration.

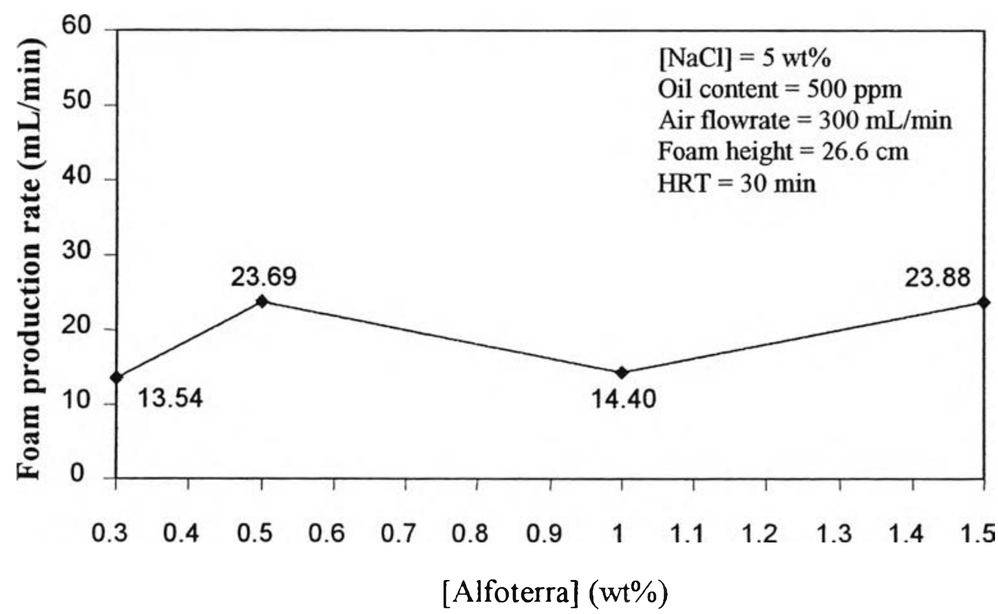


Figure 4.7 Foam production flow rate at different Alfoterra concentration.

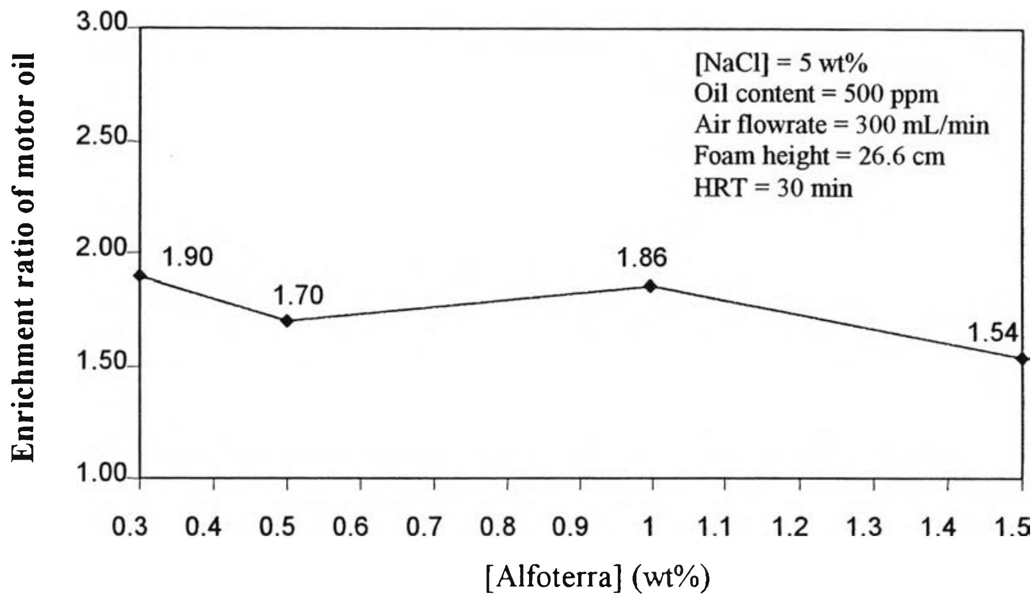


Figure 4.8 Enrichment ratio of motor oil at different Alfoterra concentration.

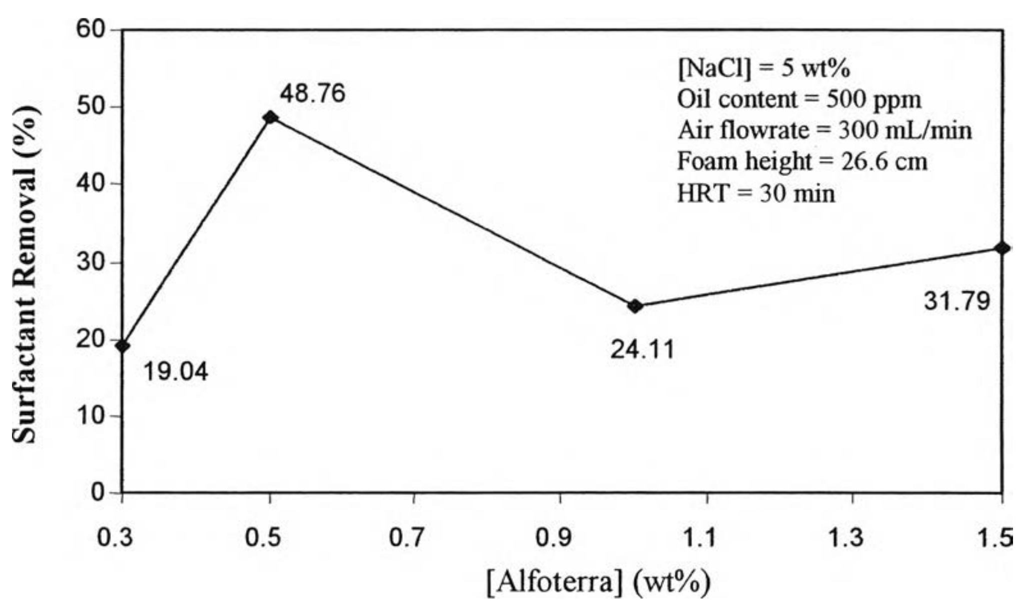


Figure 4.9 Surfactant removal at different feed Alfoterra concentration.

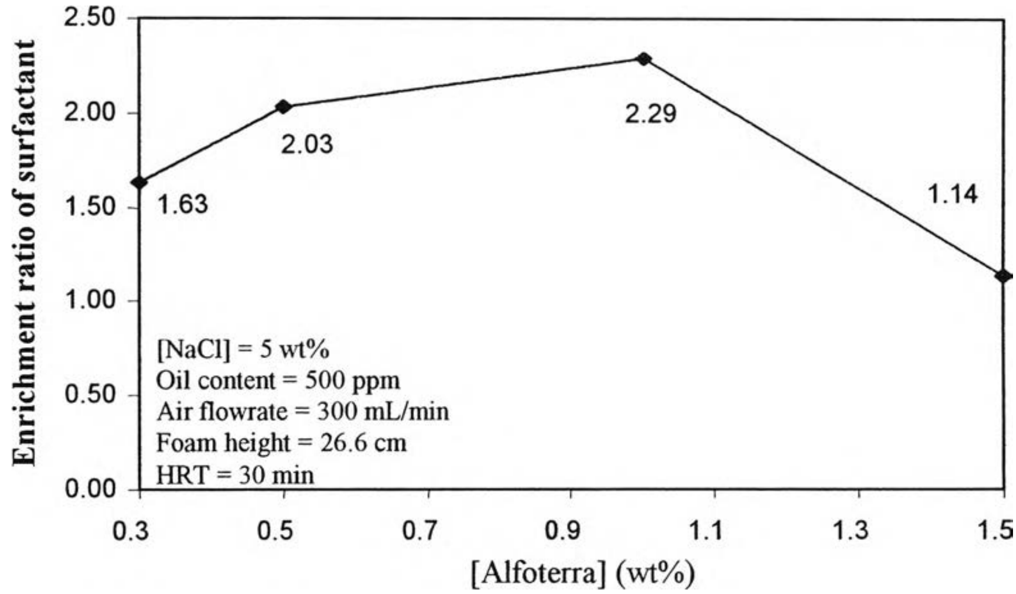


Figure 4.10 Enrichment ratio of surfactant at different feed Alfoterra concentration.

4.3.2 Effect of Hydraulic Retention Time (HRT)

From Figure 4.11, oil removal decreases when HRT increases. Even though a higher represents a longer residence time for the solution to be contact with air bubbles, a lower amount of surfactant can be carried into the column resulted in lower foam to produce with increasing HRT as shown in Figure 4.12.

Figure 4.13 shows the effect of HRT on the enrichment ratio of oil. As the HRT increases from 30 min to 45 min, the enrichment ratio slightly increases. This is because a high HRT represents a lower feed flow rate resulting in more time of oil stay in the column as well as more time to be contacted and attached to the air bubbles and the froth at the top of the column. Therefore, in the collapsed froth contains a higher amount of oil and smaller water content with increasing HRT. However, when the HRT further increases, the enrichment ratio decreases. This may be because an increase in the HRT corresponds to a longer time for the foam rises to the top of the column leading to collapse of the foam.

The effect of HRT on the surfactant removal is shown in Figure 4.14. With increasing HRT in the range 30 to 45 min, the effect of HRT on the surfactant removal is insignificant. The surfactant removal slightly decreases when HRT further increases. This result is related to the effect of HRT on the oil removal and the foam production rate as described before.

As shown in Figure 4.15, the enrichment ratio of the surfactant decreases when the HRT increases from 30 to 45 min and then decreases. This is related to the result of enrichment ratio of motor oil as shown in Figure 4.13. This reason can be explained as described in the effect of HRT on the enrichment ratio of motor oil.

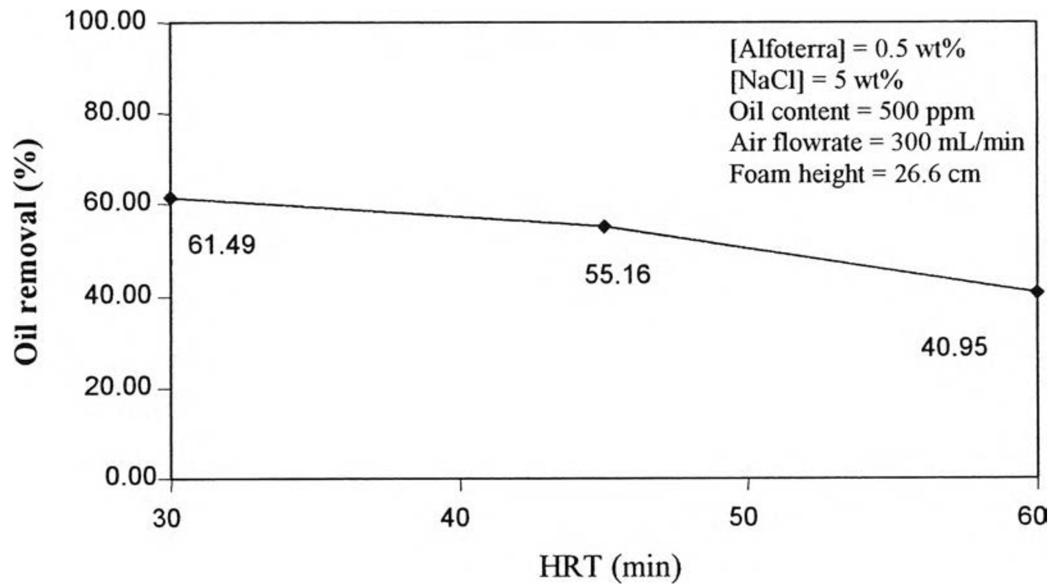


Figure 4.11 Oil removal efficiency at different HRTs.

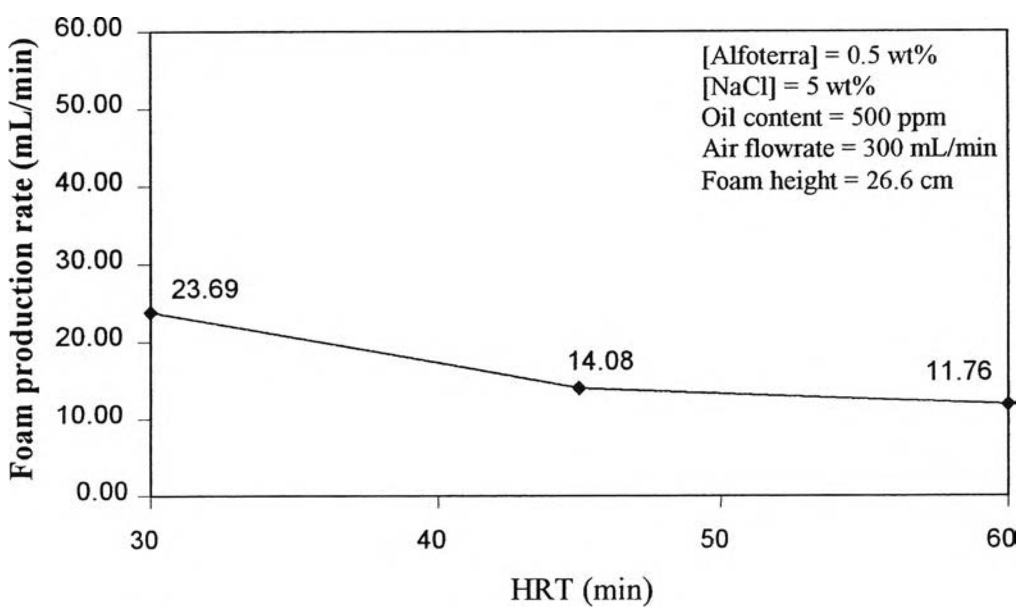


Figure 4.12 Foam production flow rate at different HRT.

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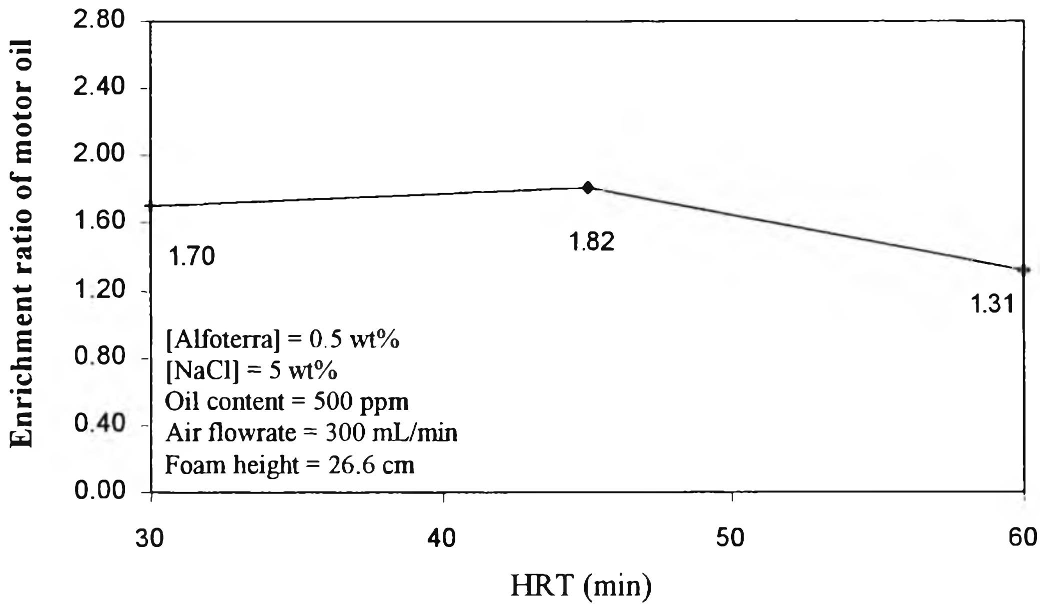


Figure 4.13 Enrichment ratio of motor oil at different HRT.

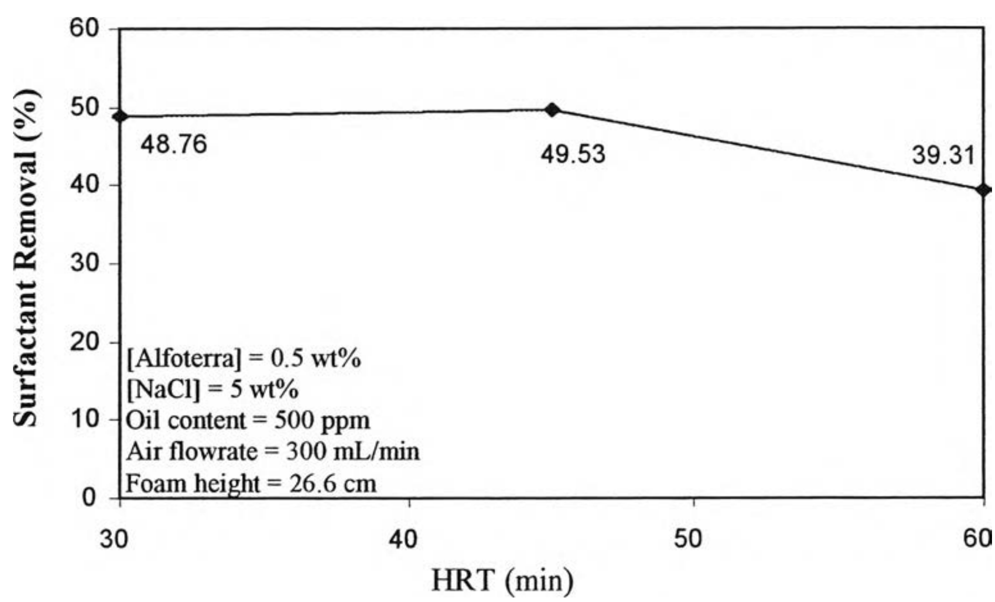


Figure 4.14 Surfactant removal at different HRT.

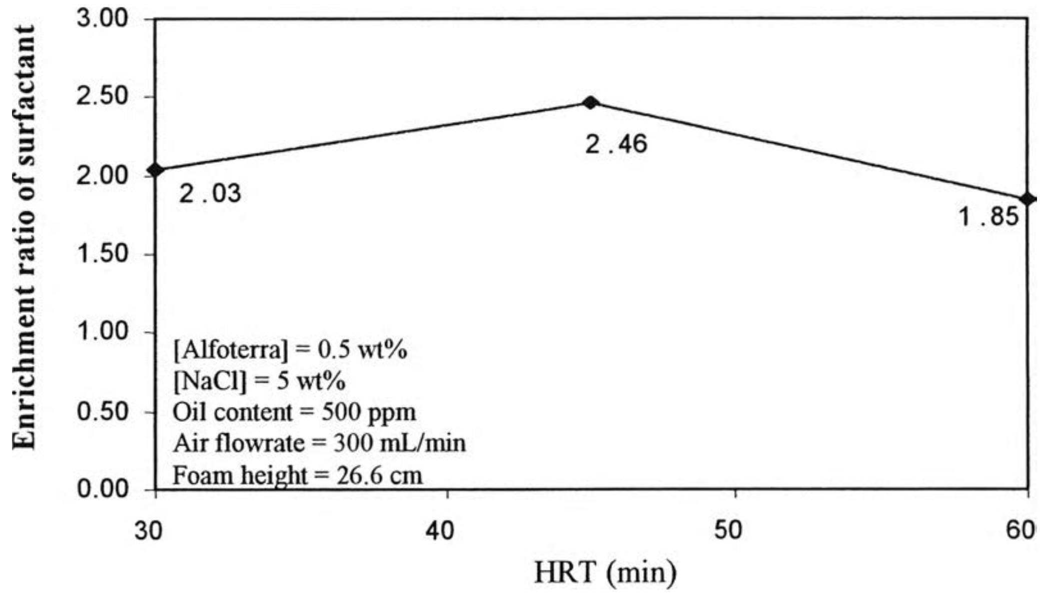


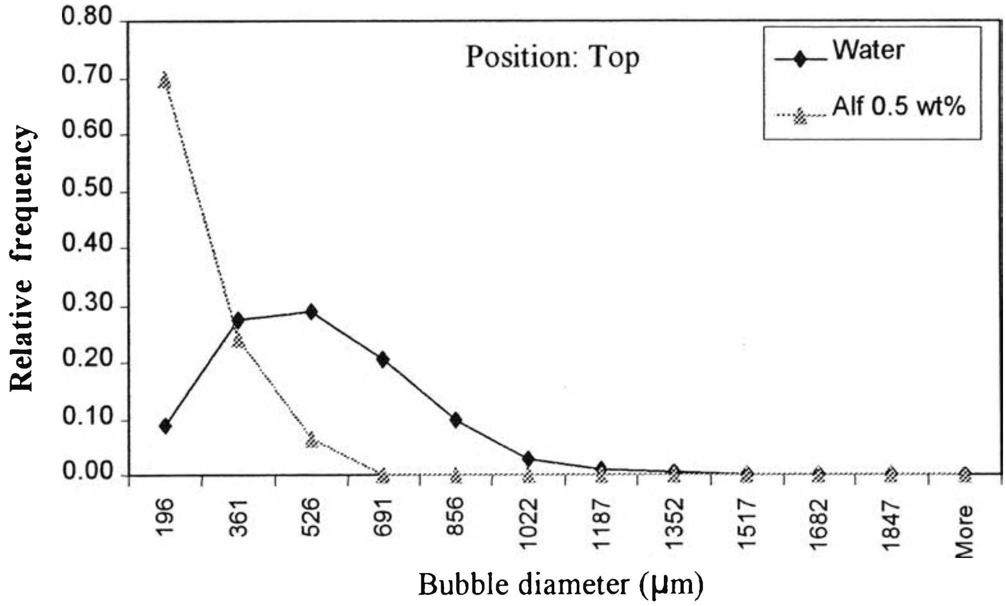
Figure 4.15 Enrichment ratio of surfactant at different HRT.

4.4 Bubble Size Distribution

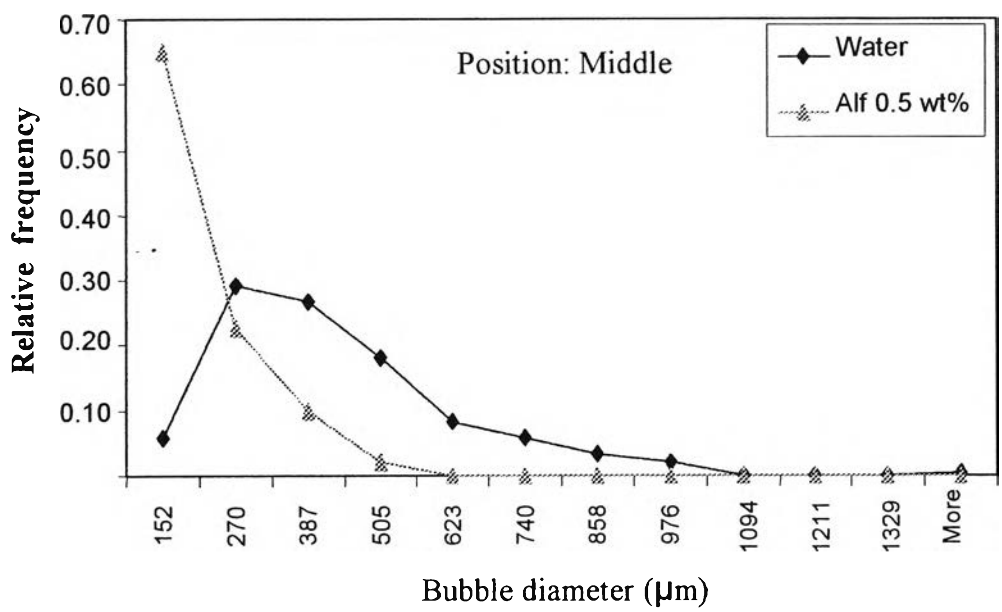
4.4.1 Effect of Surfactant Concentration

Figure 4.16 shows the comparison of bubble size distribution between a surfactant-free system (pure water) and surfactant system (Alfoterra 0.5 wt.%). It was seen that the bubble size of the surfactant-free system is greater than the bubble size of the surfactant system because of the effect of surface tension. Surfactants on the bubble surface would reduce the surface tension at the air-water interface, which would consequently reduce the holding forces during bubble formation. However, the increase in bubble size with the increase in the surfactant concentration is probably due to the property of the surfactant. The higher surfactant concentration, the better stability of bubbles will be. Hence, the high surfactant concentration resulted in bigger bubbles being formed as shown in Figure 4.17.

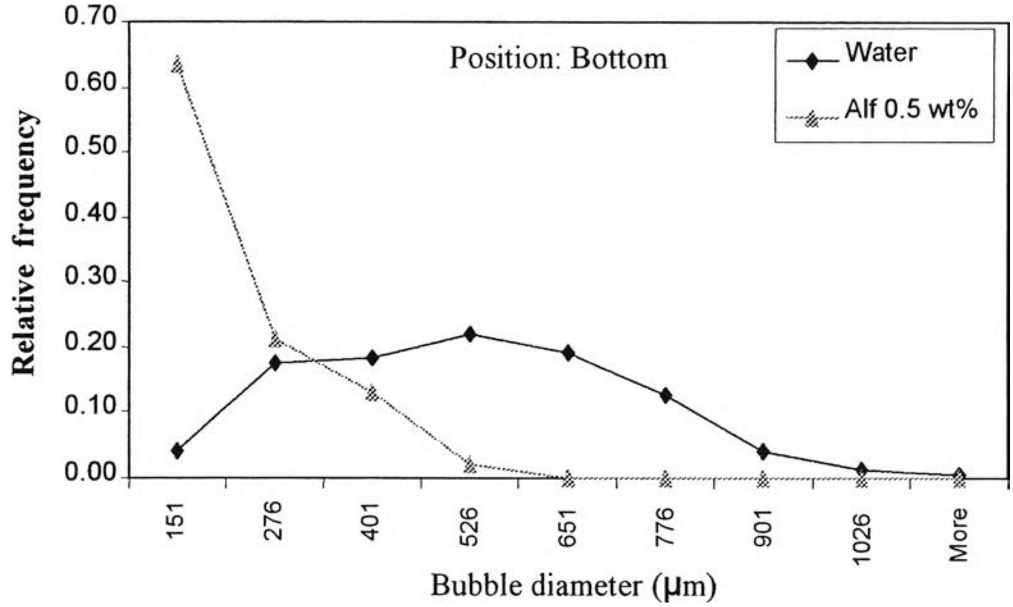
Because of the limitation of the size of sinter glass disc (16-40 μm), The bubble size can only be in this range. In addition, the bubble size between 16 μm to the minimum size of each system can be negligible because there are free of that size.



(a) Top of the column

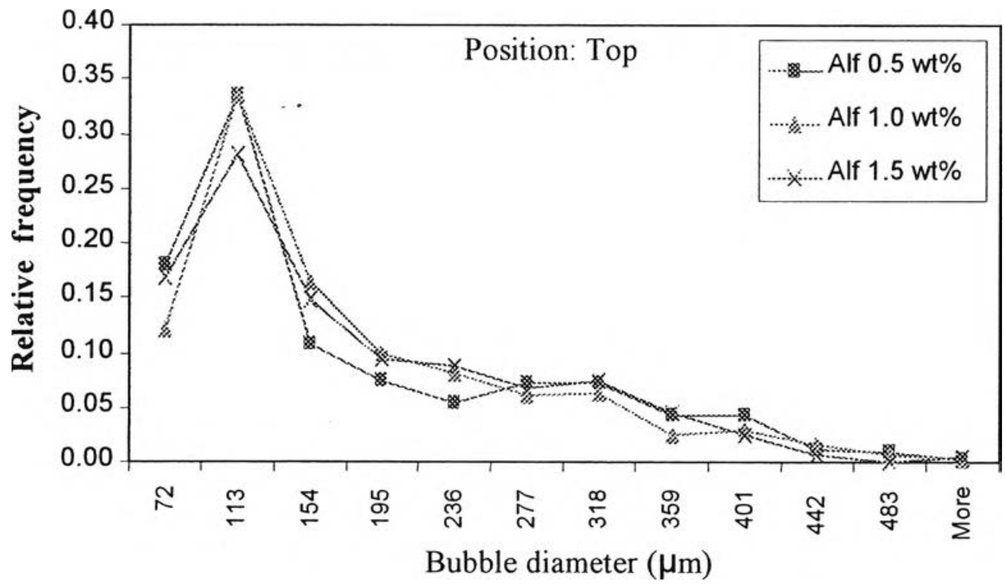


(b) Middle of the column

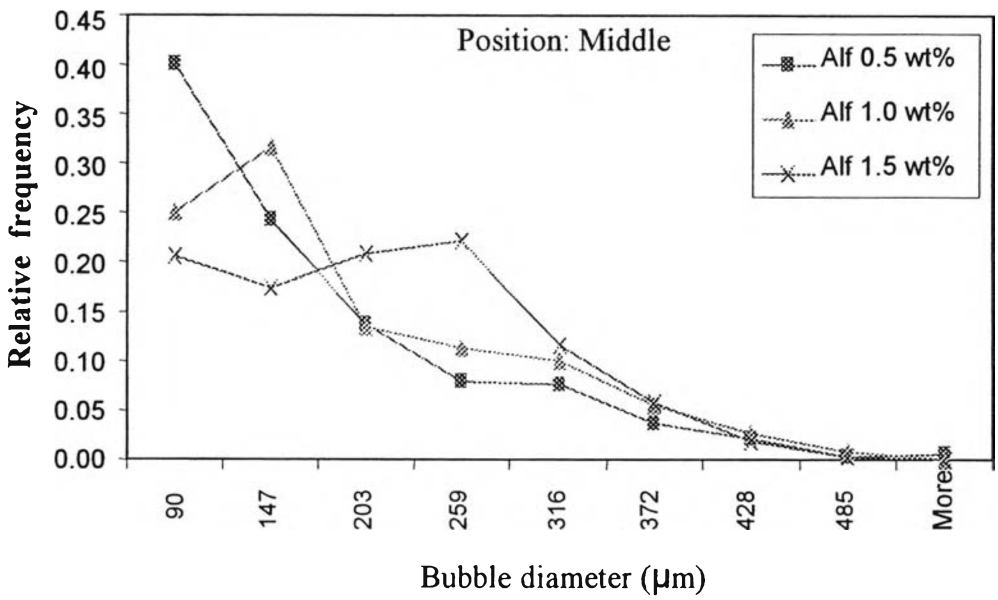


(c) Bottom of the column

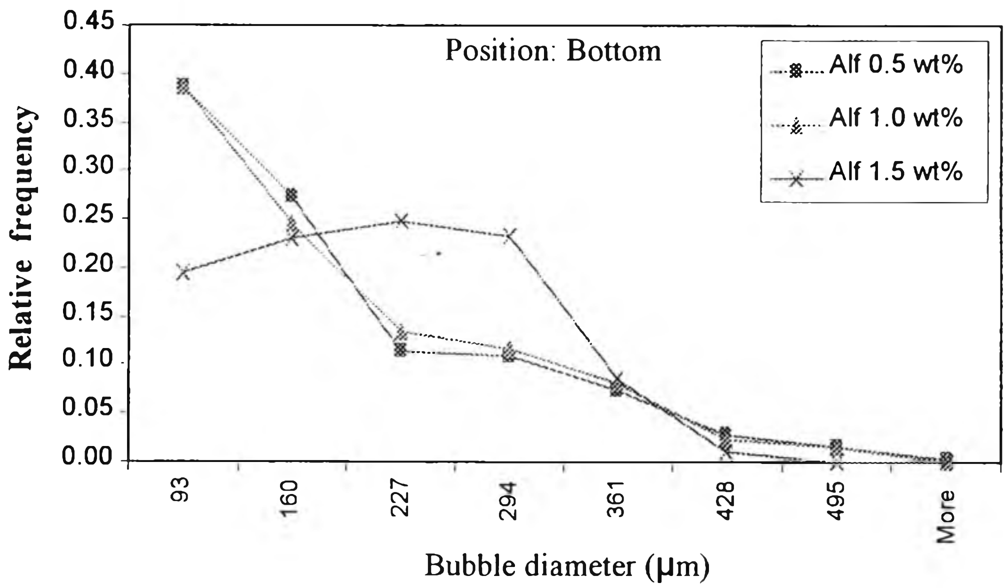
Figure 4.16 Bubble size distribution between the surfactant-free system and the surfactant system



(a) Top of the column



(b) Middle of the column

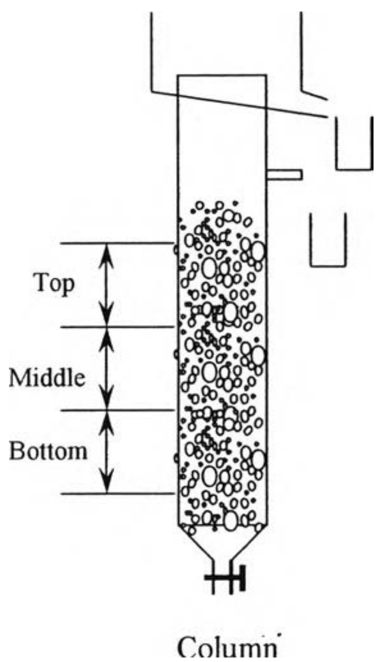


(c) Bottom of the column

Figure 4.17 Bubble size distribution at different conditions.

4.3.2 Effect of Column Height

The bubble size distribution was obtained in three axial positions (bottom, middle and top of the column) as shown in Figure 4.18. Typical results for these positions are presented in Figures 4.19 and 4.20. It was seen that the bubble sizes at the bottom of the column are greater than those at the middle and the top of the column for the surfactant-free system as shown in Figure 4.19. Breakage seems to be the dominant phenomenon since the bubble size decreases as the height increases.



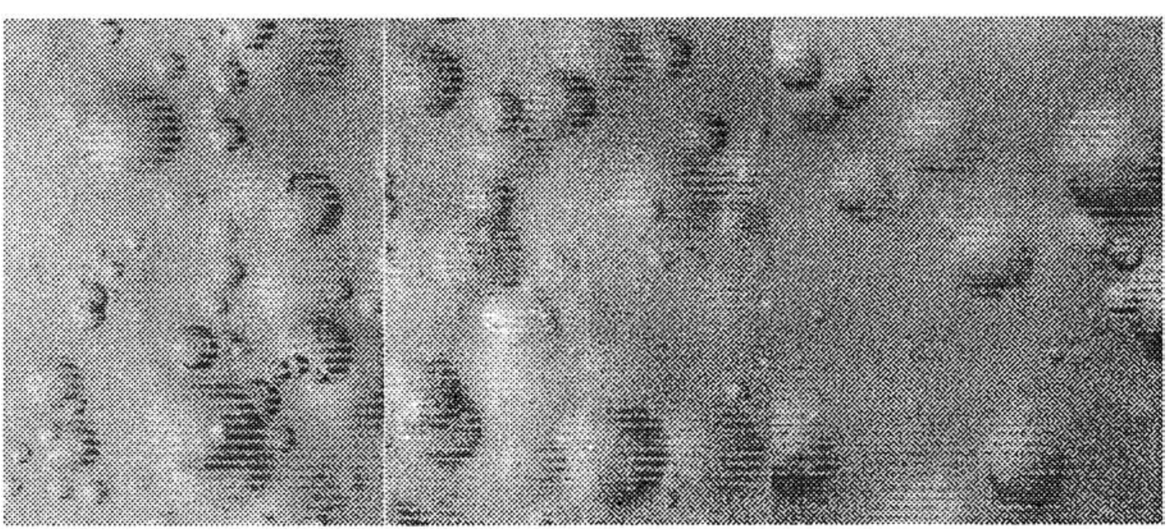


Figure 4.18 Photograph taken from different position of the column.

Figure 4.20 shows the bubble size distribution at 0.5 wt.% Alfoterra. The bubble diameter increases with the increase in the distance from the bottom of the column due to the coalescence of smaller bubbles. The coalesced bubbles at the bottom go up due to their buoyancy and accumulate at the middle and the top of the column. In addition, because of the surfactant property as mentioned in the effect of surfactant concentration on the bubble size distribution, the bubbles would not break when they ascend through the top of the column.

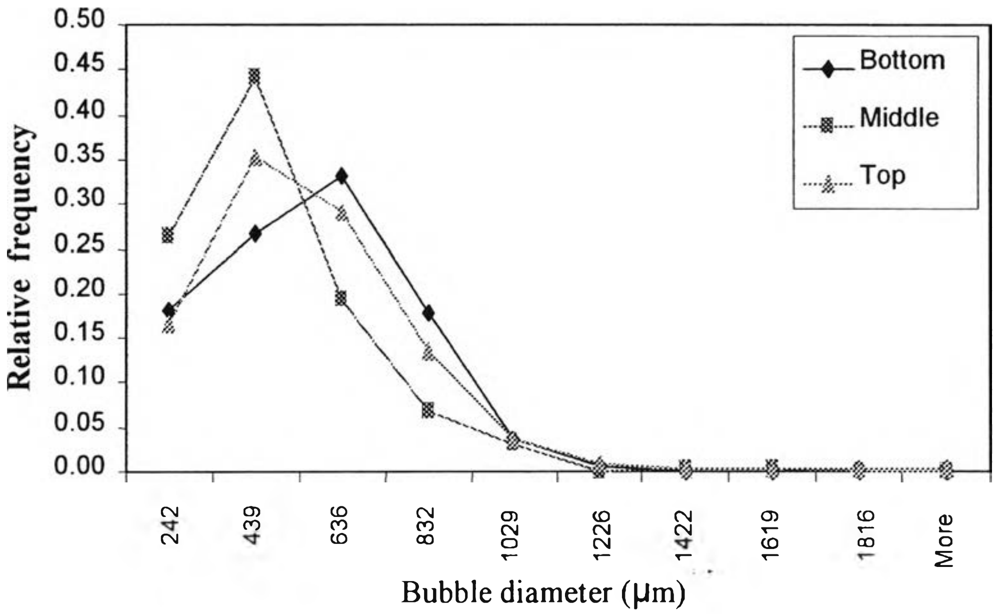
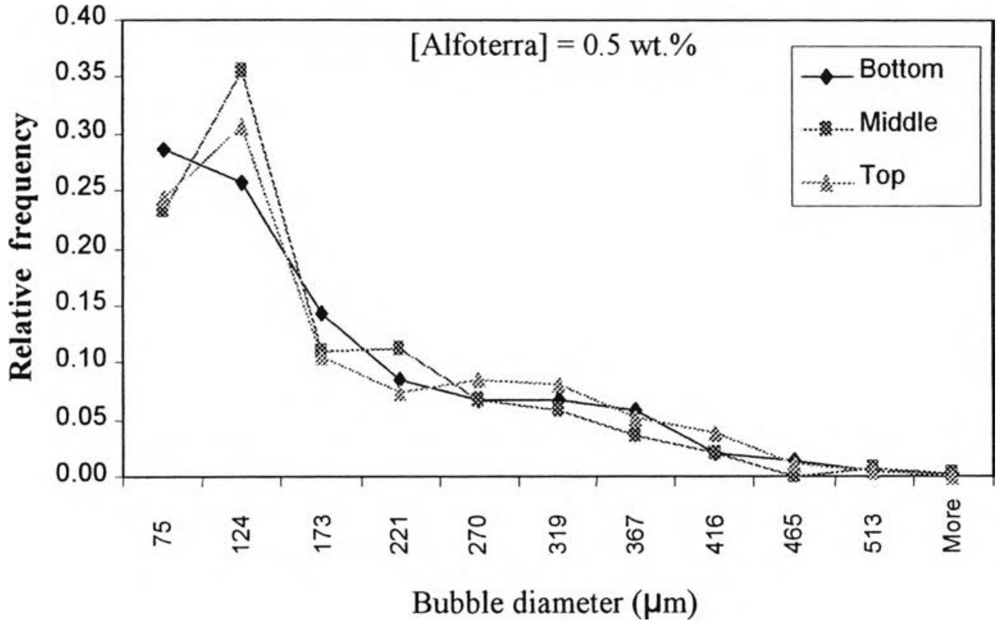
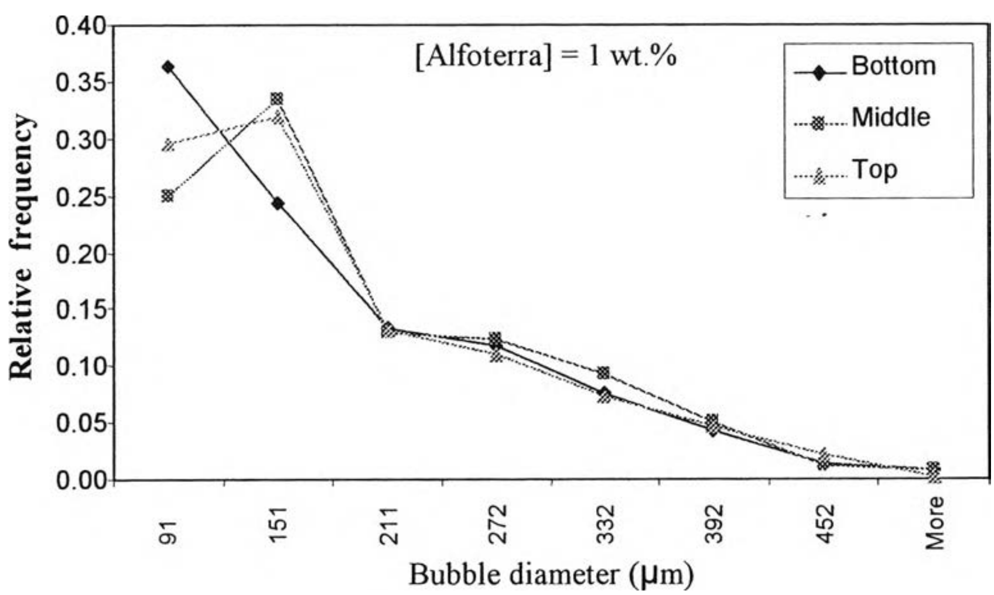


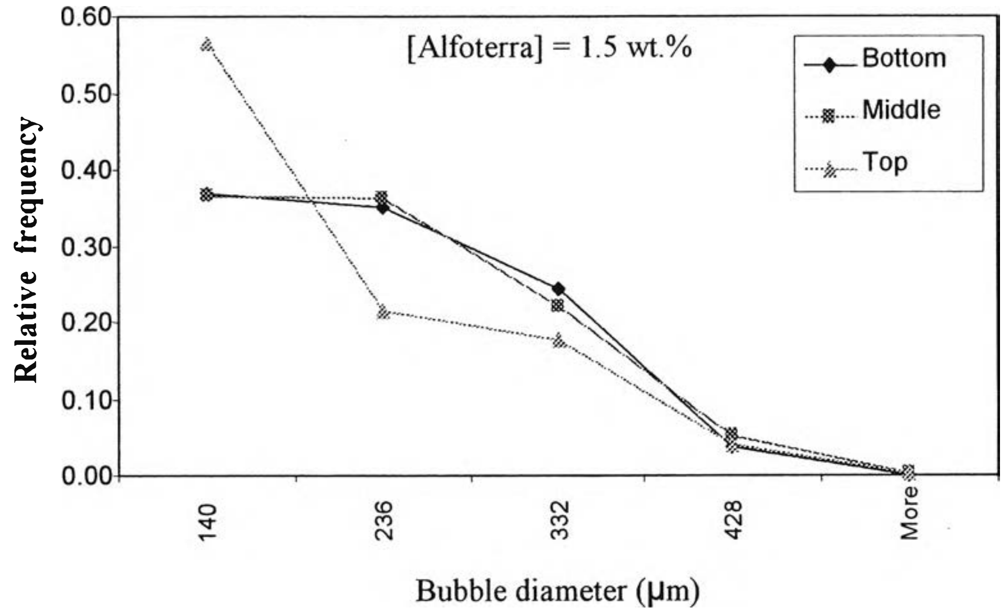
Figure 4.19 Bubble size distribution of surfactant-free system at different location.



(a) 0.5 wt.% Alfoterra



(b) 1 wt.% Alfoterra



(c) 1.5 wt.% Alfoterra

Figure 4.20 Bubble size distribution of Alfoterra system at different location.