CHAPTER IV
RESULTS AND DISCUSSION

4.1 Phase Behavior Results

In all experiments, the surfactant and NaCl concentrations are expressed in weight percent (wt.%) per volume of the aqueous phase consisting of water, salt, and surfactant (not including oil).

As mentioned before, the objective of this study was to investigate the relationship between the efficiency of froth flotation and the ultra-low interfacial tension (IFT) of water and cutting oil. Alfoterra 145-3PO Sulfate (Branch alcohol propoxylated sulfate, sodium salt), which is an extended surfactant, was used as a surfactant to form microemulsions with cutting oil because Alfoterra have a proper HLB for the cutting oil-water system and is expected to form the Winsor Type III or middle phase microemulsion. The use of extended surfactants has been repeated to form microemulsions with a variety of oils without added alcohol (cosurfactant) at room temperature (Perez *et al.*, 1995). The main purpose of this section was to establish the microemulsion diagram (fish diagram) of this system by plotting the surfactant concentration versus salinity. The fish diagram is generally used to determine a minimum surfactant concentration required to form a Winsor Type III microemulsion which is known as the critical microemulsion concentration (CμC).

In this study, the microemulsion formation of cutting oil with Alfoterra showed only two obvious phases, which were the water and oil 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 cutting oil with Alfoterra was not shown here. In order to characterize the micromulsion type for the cutting oil system, the measurement of electrolytic conductivity was used to determine the microemulsion type (Salager,2000 and Salager *et al.*,1982). For each condition, the electrolytic conductivity was measured, under gentle magnetic stirring, by using a conductivity meter (Eutech Instruments, CON11&CON110) at room temperature (26±1°C). Under these conditions, the obtained value remained constant for a long time, and was found to be relatively steady (± 5%). High conductivity indicates a Winsor Type I or III microemulsion while a low value implies a Winsor Type II microemulsion (Salager *et al.*, 1982). Moreover, the IFT of the system at different conditions were measured by the spinning drop tensiometer in order to localize precisely the microemulsion phase boundary at very low surfactant concentrations. The conductivity and the IFT results were used to plot the fish diagram where Winsor Type I, Type II, and Type III microemulsions exist. The diagrams of IFT as a function of surfactant concentration, salinity, and oil to water ratio are illustrated here.

4.1.1 Microemulsion Phase Diagram

The phase transformation in the system from Winsor Type I to Type III to Type II can be achieved by progressively changing in many parameters. The microemulsion diagram studied is generally carried out by doing the salinity scan and the surfactant scan, as illustrated in Figure 4.1. Figure 4.1 shows the microemulsion phase diagram, sometimes referred to as the fish diagram due to its shape, which shows the regions of surfactant and NaCl concentrations that produce a given type of microemulsion. This diagram was constructed by using the visual observation at very high surfactant concentrations and the IFT and conductivity data at low surfactant concentrations. The region labeled as 'Winsor Type I' corresponds to a two phase system in equilibrium (excess oil phase and oil-in-water microemulsion), the region 'Winsor Type III' enclosed by the phase boundaries has three phases in equilibrium (excess oil, water and middle phase) and the region 'Winsor Type II' has two phases (excess water and water-in-oil microemulsion). At a fixed Alfoterra concentration (e.g., 0.3 wt.% Alfoterra), the microemulsion transitioned from a Winsor Type I to Type III to Type II microemulsion as the NaCl concentration increased.

As mentioned before, the most importance of the fish diagram for this study is the lowest surfactant concentration to form a Winsor Type III microemulsion. Figure 4.1 shows the minimum surfactant concentration to form a Winsor Type III microemulsion at 0.23 wt.% Alfoterra. To find the exact value of the critical microemulsion concentration (CμC), the IFT between cutting oil and equilibrium surfactant solution having different concentration at 13 wt.% NaCl (optimum salinity) was plotted against the surfactant concentration, as shown in Figure 4.2. The plot showed two sharp drops of the IFT. The first sharp decrease in the system IFT corresponds to the adsorption of the surfactant at the oil-water interface, which occurs at concentration less than the CMC. The second one corresponds to the change in the curvature of the micelles which ends at the point where the first droplet of microemulsion forms, known as the CμC. As the result, the CMC and the CμC were found at 0.05 and 0.3 wt.% Alfoterra at 13 wt.% NaCl, respectively. Hence, Alfoterra concentrations were selected at 0.1, 0.3, and 0.5 wt.% which represent the Winsor Type I, Type III, and Type II, respectively, for running the froth flotation experiments.

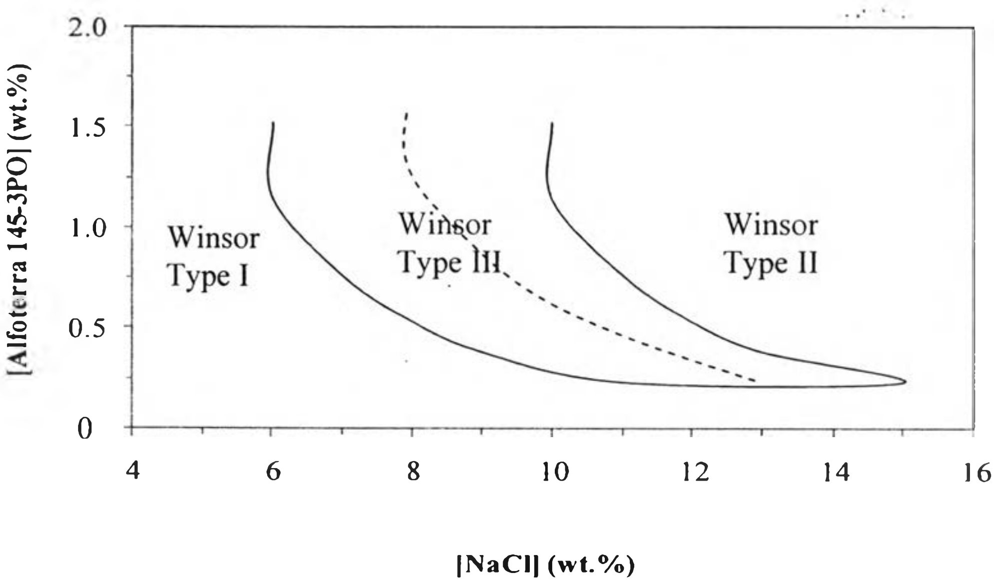

Figure 4.1 Microemulsion phase diagram of Alfoterra with cutting oil at different NaCl concentrations and oil-to-water ratio of 1:1 (v:v).

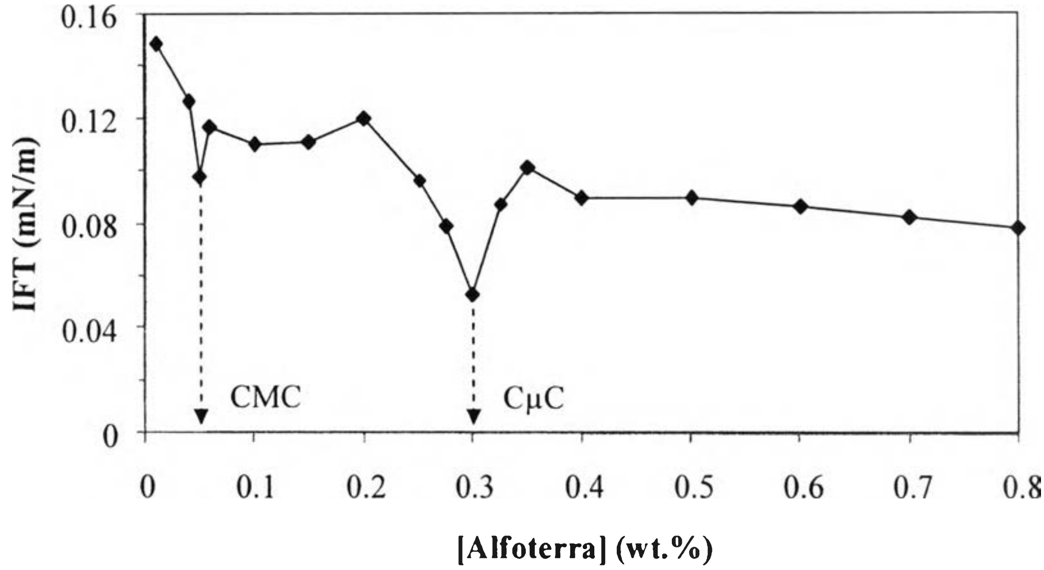

Figure 4.2 IFT as a function of surfactant concentration at the optimum NaCl concentration of 13 wt.% with an oil-to-water ratio of 1:1 (v:v), and 30°C.

4.1.2 Effect of Surfactant Concentration on IFT

Figure 4.3 illustrates the effect of surfactant concentration on IFT at 13 wt.% NaCl and an oil-to-water initial volumetric ratio of 1:1. The IFT of the system decreases rapidly when Alfoterra concentration increases from 0.2 wt.% to 0.3 wt.%. Beyond 0.3 wt.% Alfoterra, it gradually increased with increasing Alfoterra concentration from 0.3 wt.% to 0.35 wt.%. This is because at low Alfoterra concentrations, the surfactant adsorption at the interface between the two phases increases with increasing surfactant concentration. At high Alfoterra concentrations, most surfactant molecule move to the oil phase corresponding to the phase transformation from Winsor Type III to Winsor Type II microemulsion. The minimum IFT around 5.27 x 10^{-2} mN/m was found at 0.30 wt.% Alfoterra is considered to be in the range of the ultra-low IFT (10^{-2}-10^{-3} mN/m).

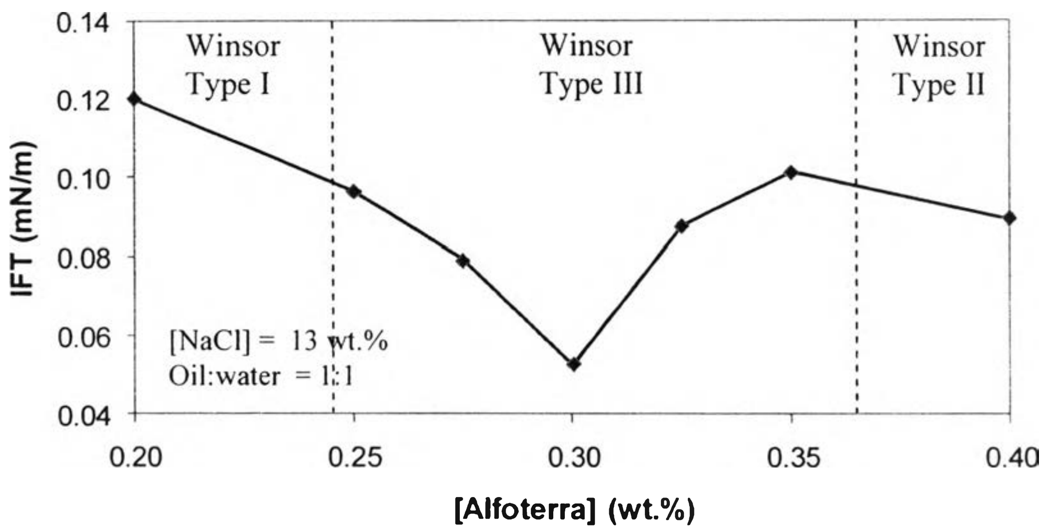

Figure 4.3 IFT as a function of Alfoterra concentration at 13 wt.% of NaCl with oil-to-water ratio of 1:1 (v:v), and 30°C.

4.1.3 Effect of NaCl Concentration on IFT

Figure 4.4 shows the IFT as a function of NaCl concentration or salinity scan at 0.3 wt.% of Alfoterra, and an oil-to-water ratio of 1:1. From the result, the minimum IFT was found at 13 wt.% NaCl concentration, known as the optimum salinity. 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 oil solubilized 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 of surfactant resulting in increasing of aggregation number, so the amount of oil solubilized into the inner core micelles increases leading to the reduction of IFT as well as the increasing surfactant adsorption at the interface between the two phases, leading to lower IFT. At very high NaCl concentrations, an increase in NaCl results in the salting out effect, pushing the surfactant out from the aqueous phase and so more surfactant solubilizes into the oil phase.

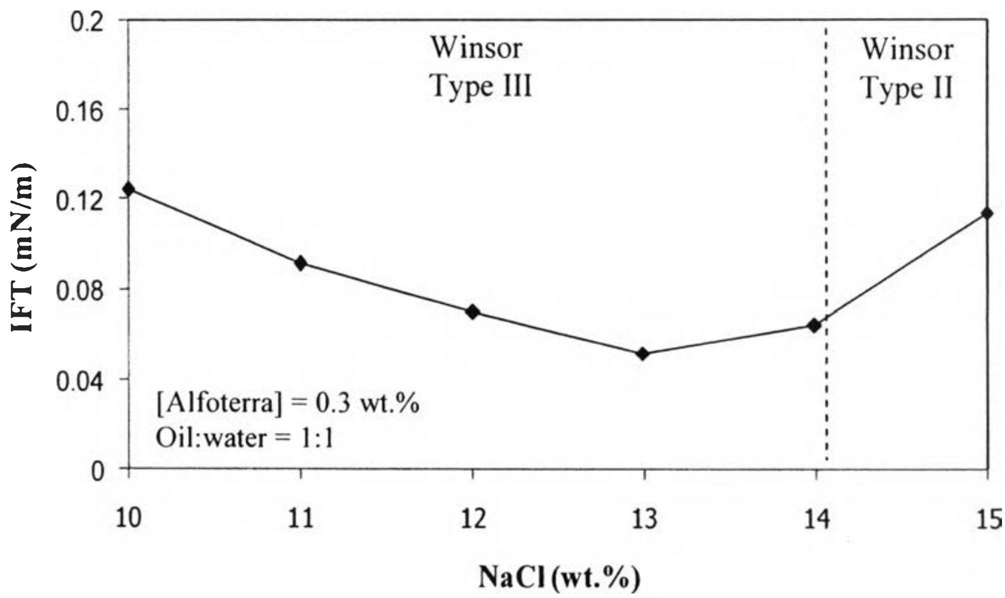

Figure 4.4 IFT as a function of salinity at 0.3 wt.% of Alfoterra with oil-to-water ratio of 1:1 (v:v), and 30°C.

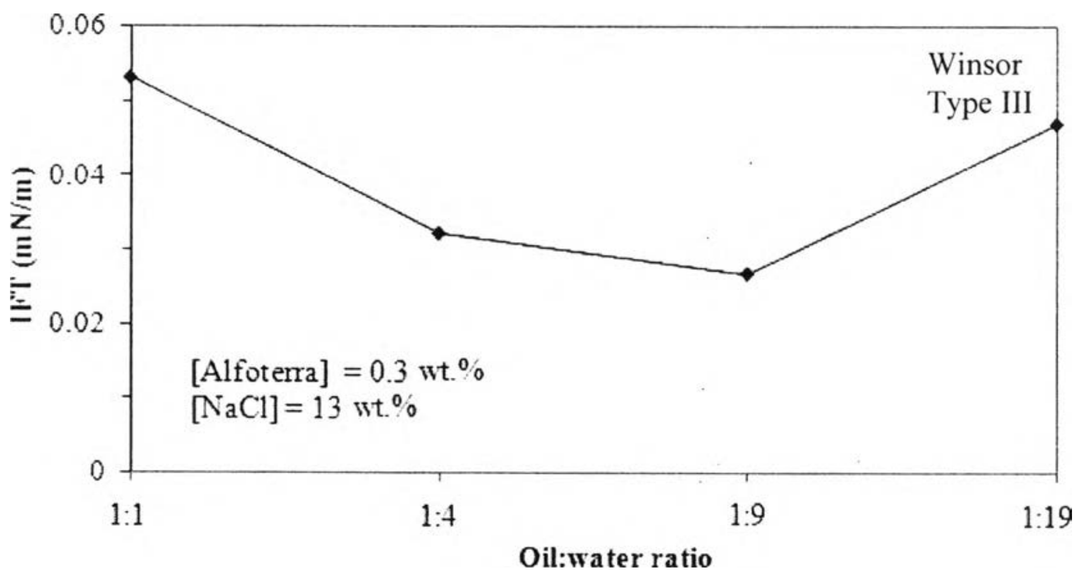

Figure 4.5 IFT as a function of oil-to-water ratio at 0.3 wt.% Alfoterra, 13 wt.% NaCl, and 30°C.

4.1.4 Effect of Oil-to-Water Ratio on IFT

As mentioned before, the optimum NaCl concentration of 13 wt.% provides a minimum IFT, so 13 wt.% NaCl was selected to study the effect of oil-to-water ratio on the IFT. Figure 4.5 illustrates the IFT as a function of oil-to-water ratio at 0.3 wt.% of Alfoterra and 13 wt.% of NaCl. From the result, the IFT appeared to be independent on the oil-to-water ratio. This may be due to the same solubilization power of each system because it contains nearly the same Alfoterra and NaCl concentrations.

4.1.5 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 investigated the relationship between non-equilibrium system in column and equilibrium system in microemulsion formation. Figure 4.6 shows a comparison between the equilibrium IFT and the dynamic IFT at 20 min, which corresponds to the hydraulic retention time used 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 of them are in the same order of magnitude. Therefore, the equilibration condition is insignificant on the froth flotation performance.

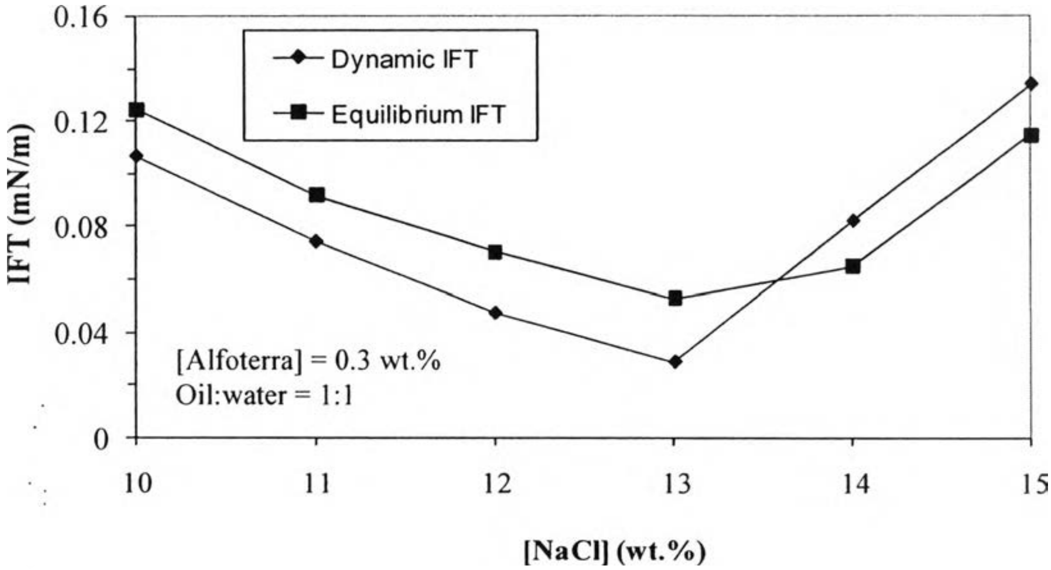

Figure 4.6 Comparison between equilibrium IFT and dynamic IFT as a function of salinity at 0.3 wt.% of Alfoterra, and an initial oil-to-water volumetric ratio of 1:1.

4.2 Froth Flotation Performance

The significant parameters that indicate the performance of the froth flotation process are the removal and enrichment ratio of oil. In addition, the removal and enrichment ratio of surfactant, foam production rate, foam wetness, foam stability, and foamability should be determined and correlated with the froth flotation performance. In general, high oil removal efficiency is a vital requirement for an effective froth flotation operation but it is not the sole factor. If oil and water are present in the froth with the same proportions as those in the influent, the selective separation of oil from water does 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 concentration of oil in the overhead froth to that in the feed solution. In order to achieve the separation, the enrichment ratio must be greater than one. Moreover, the higher the enrichment ratio, the better the separation.

4.2.1 Effect of Surfactant Concentration on the Froth Flotation Performance

Figure 4.7 illustrates the oil removal as a function of surfactant concentration and microemulsion type. The oil removal increased with increasing Alfoterra concentration from 0.1 wt.% to 0.3 wt.% because there is more foam to be produced (see Figure 4.8). Therefore, the oil is removed from the solution more efficiently. When the Alfoterra concentration further increased from 0.3 wt.% to 0.5 wt.%, the oil removal was nearly unchanged. A possible explanation for this is the foam wetness effect. As shown in Figure 4.9, when the Alfoterra concentration increases from 0.3 wt.% to 0.5 wt.%, the foam wetness increases slightly. This may be because at a high Alfoterra concentration, there is more water in the foam lamellae which known as wet foam.

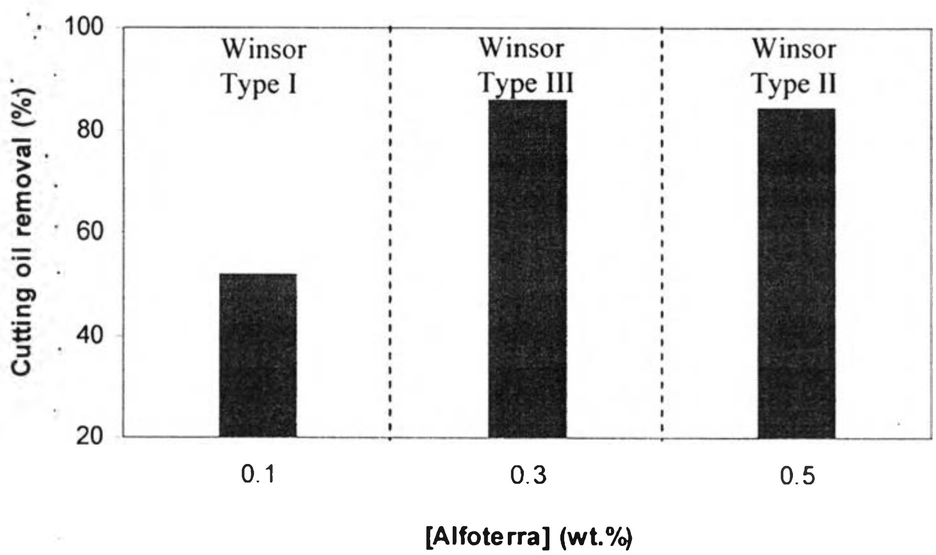

Figure 4.7 Cutting oil removal efficiency at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed Alfoterra concentrations.

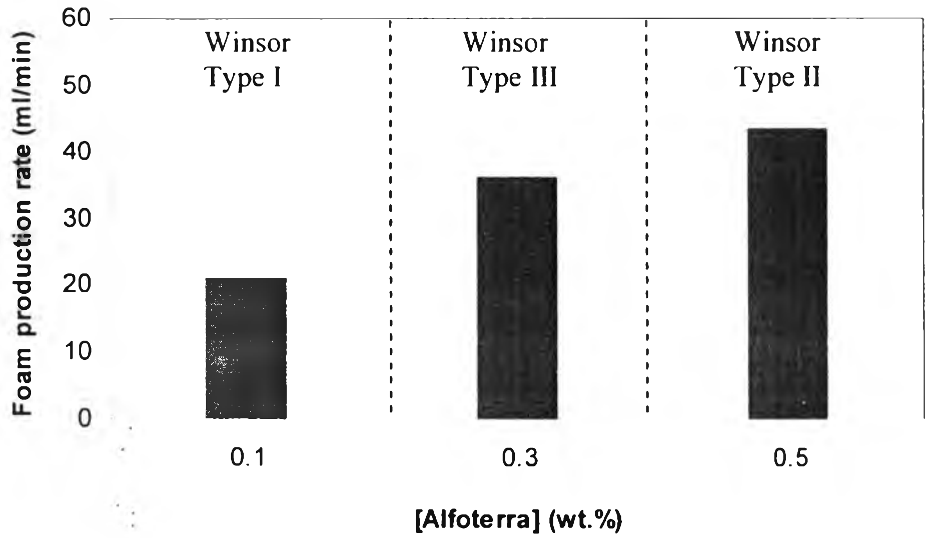

Figure 4.8 Foam production rate at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed Alfoterra concentrations.

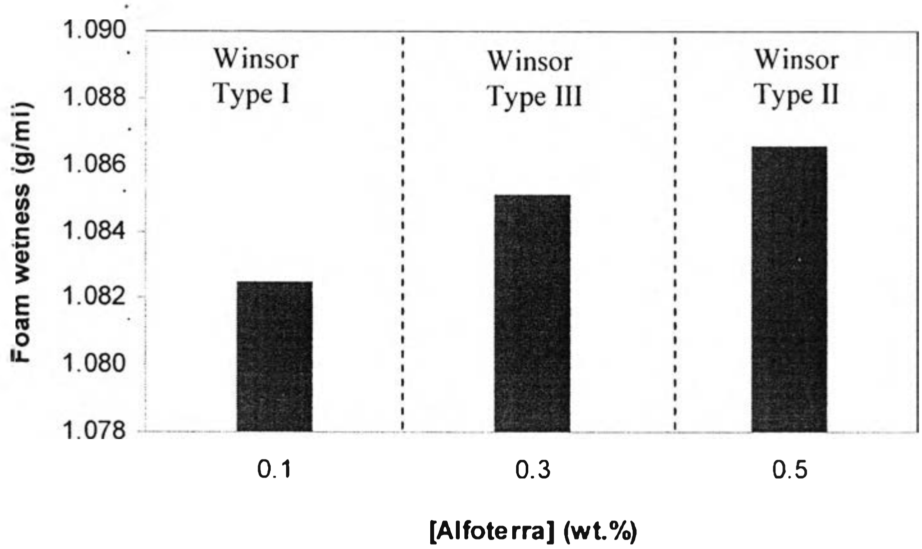

Figure 4.9 Foam wetness at 13 wt.% NaCl, 500 ppm oil content. 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed Alfoterra concentrations.

The effect of Alfoterra concentration on the enrichment ratio of cutting oil is shown in Figure 4.10. As the Alfoterra concentration increased from 0.1 wt.% to 0.3 wt.%, the enrichment ratio gradually increased because the foam stability and foamability of the system increase with increasing Alfoterra concentration as shown in Figure 4.11 and 4.12, respectively. However, when the Alfoterra concentration further increased to 0.5 wt.%, the enrichment ratio slightly decreased because the foam stability and foamability of the system decrease with increasing Alfoterra concentration, as shown in Figures 4.11 and 4.12, respectively. In addition, increasing surfactant concentration increases the hydrophobic region, so the amount of oil content in the foam increases. The combined effect between the increase in the hydrophobic region and the decrease in the foam stability and foamability leads to the insignificant change in the enrichment ratio when increase Alfoterra concentration increases from 0.3 wt.% to 0.5 wt.%.

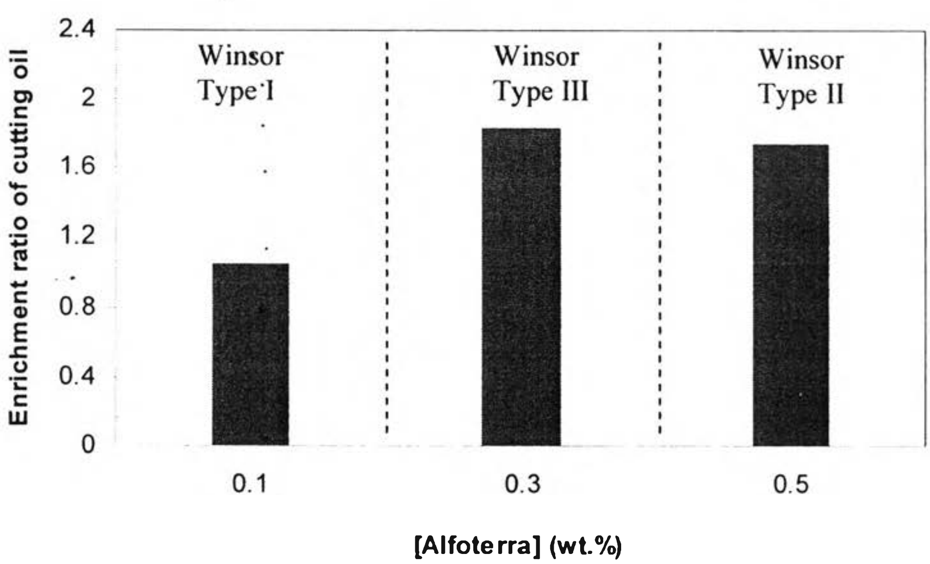

Figure 4.10 Enrichment ratio of cutting oil at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed Alfoterra concentrations.

The effect of Alfoterra concentration on the surfactant removal is shown in Figure 4.13. Increasing Alfoterra concentration from 0.1 wt.% to 0.3 wt.% resulted in an increase in the surfactant removal. Conversely, when the Alfoterra concentration further increased from 0.3 wt.% to 0.5 wt.%, the surfactant removal slightly decreased. This result relates to the effect of Alfoterra concentration on the oil removal, as shown in Figure 4.7. Again, the explanation is that as increase Alfoterra concentration, the foam production rate increases resulting in the increase of the surfactant removal. At the same time, the increase in foam wetness results in more water in the foam lamellae and less surfactant removal at 0.5 wt.% Alfoterra as well as the effect of Alfoterra concentration on the oil removal, as described before.

As shown in Figure 4.14, the enrichment ratio of surfactant increases slightly with increasing Alfoterra concentration from 0.1 wt.% to 0.3 wt.% and then decreases when Alfoterra concentration increases from 0.3 wt.% to 0.5 wt.%. The results can be explained as described in the effect of Alfoterra concentration on the enrichment ratio of cutting oil.

From the results, the system that gives the highest removal and enrichment ratio of both cutting oil and surfactant was found at 0.3 wt.% Alfoterra and 13 wt.% NaCl which is in the Winsor Type III microemulsion region (see Figure 4.4). However, the salinity of the system is very high, it is more applicable if it can be reduced whereas the oil removal is still high. hence, the purpose of next experiment was to minimize the NaCl concentration for the froth flotation operation to remove cutting oil.

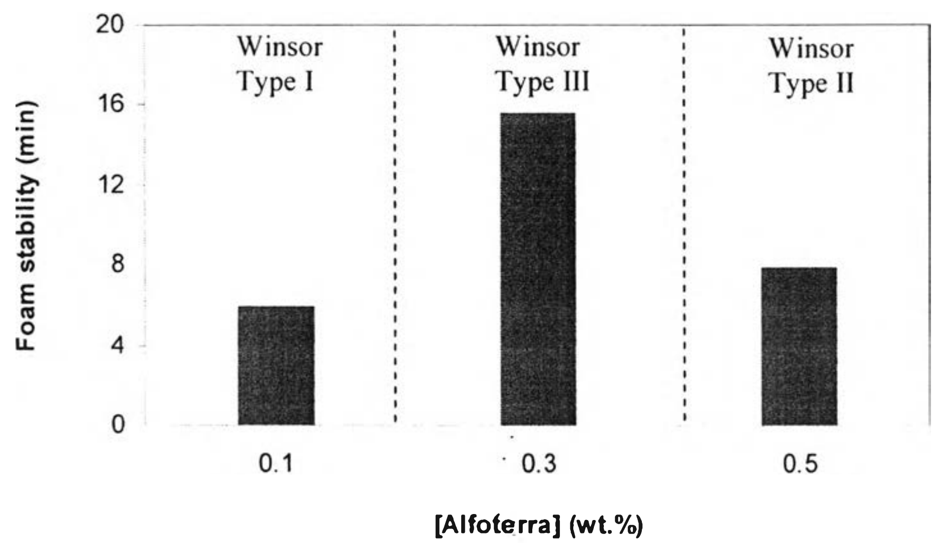

Figure 4.11 Foam stability of the system at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, and different feed Alfoterra concentrations.

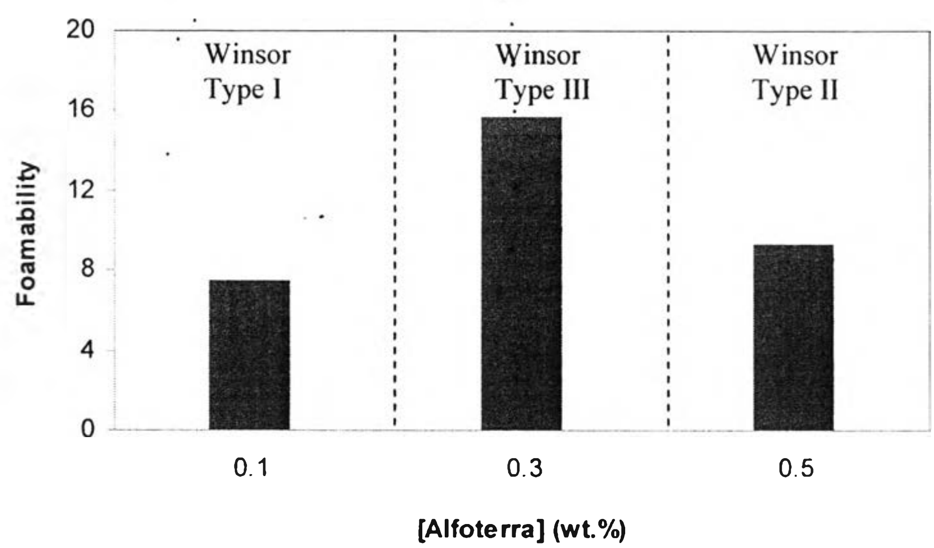

Figure 4.12 Foamability of the system at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, and different feed Alfoterra concentrations.

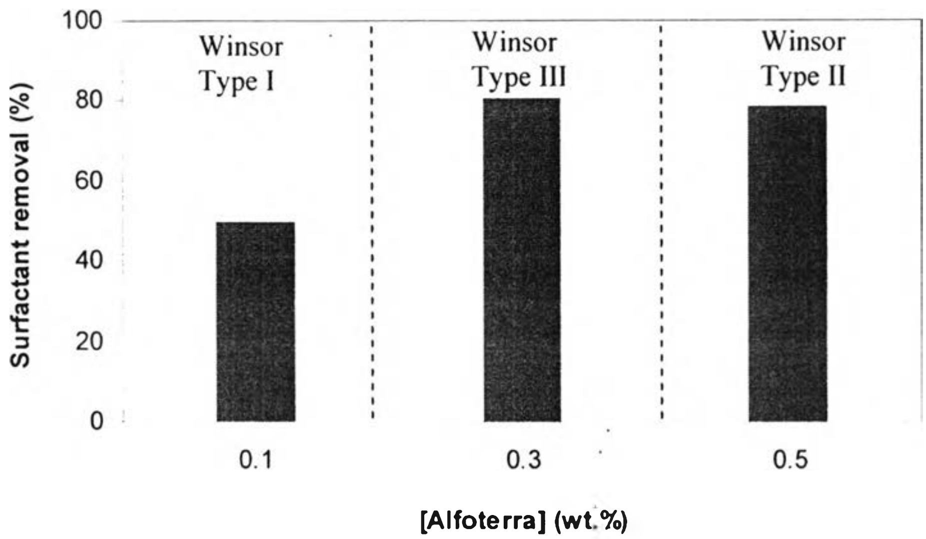

Figure 4.13 Surfactant removal efficiency at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed Alfoterra concentrations.

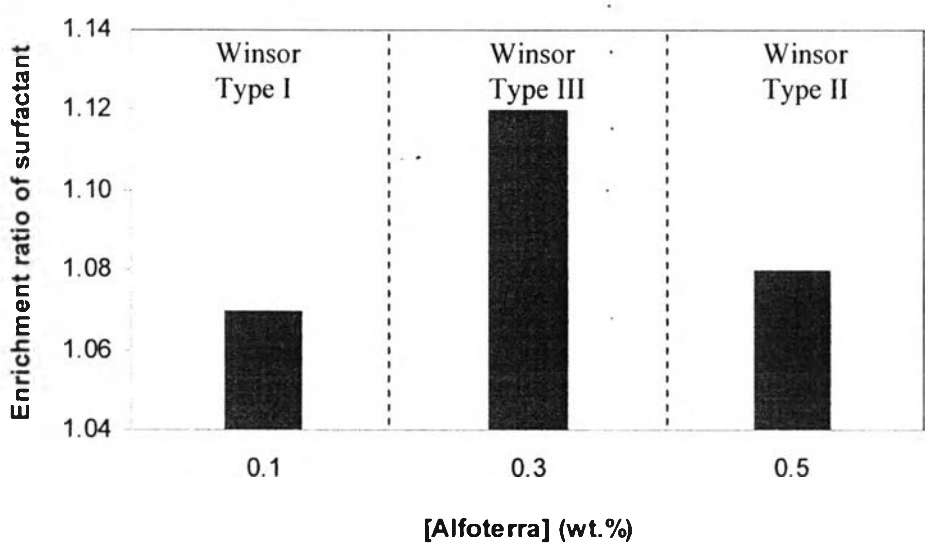

Figure 4.14 Enrichment ratio of surfactant at 13 wt.% NaCl, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed Alfoterra concentrations.

4.2.2 Effect of NaCl Concentration on the Froth Flotation Performance

It has been known that salinity is one of operational parameters affecting froth flotation operation. The effect of NaCl concentration on the performance of froth flotation was carried out by varying NaCl concentration in the range of 6 wt.% to 13 wt.% at 0.3 wt.% Alfoterra. Figure 4.15 shows the increase in the NaCl concentration from 6 wt.% to 13 wt.% resulting in the increase in the cutting oil removal. This is due to the increase in foam production rate (as shown in Fig 4.16) and the decrease in the repulsive force between the anionic head groups of the surfactant. There is more foam to be produced therefore, the surfactant can carry oil and remove it from the solution more efficiently.

For effective separation, the overhead froth should have a higher cutting oil concentration than that in the feed. Here, the separation efficiency of the froth flotation is indicated by the enrichment ratio. Figure 4.18 illustrates the effect of NaCl concentration on the enrichment ratio of cutting oil, An increase in the NaCl concentration from 6 wt.% to 10 wt.% gradually increased the enrichment ratio of cutting oil. This is because the reduction of repulsive force between the anionic head groups of the surfactant by the Na counterion of added NaCl and so more foam is produced. As a result, more oil is removed. Moreover, both foam stability and foamability also increase with icreasing NaCl concentration. As the NaCl concentration further increased, the enrichment ratio of cutting oil slightly decreased due to the decrease in both foam stability and foamability and the increase in foam wetness, as shown in Figures 4.19, 4.20, and 4.17, respectively.

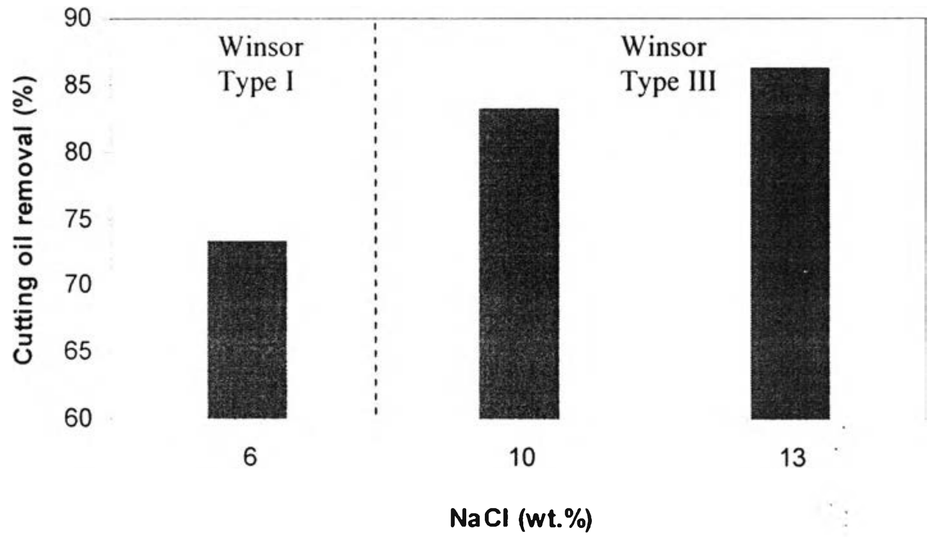

Figure 4.15 Cutting oil removal efficiency at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed NaCl concentrations.

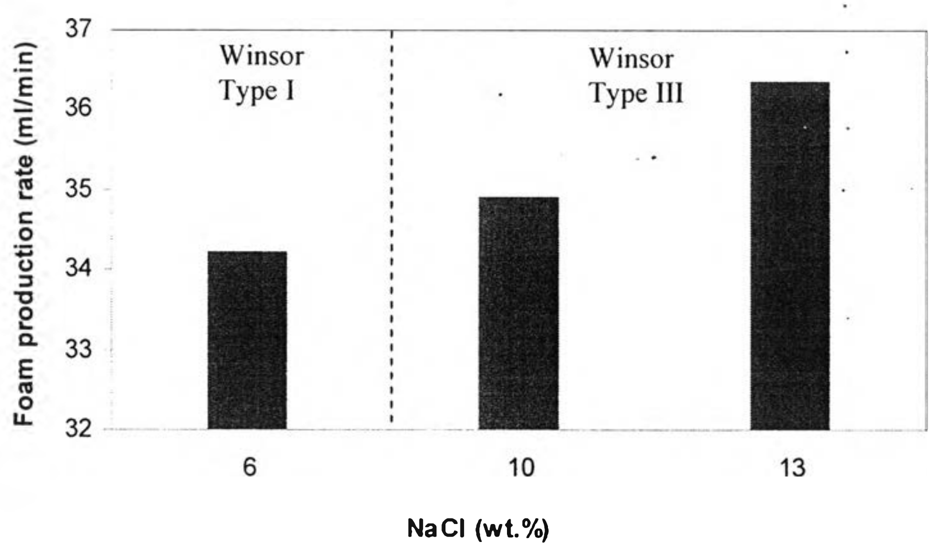

Figure 4.16 Foam production rate at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed NaCl concentrations.

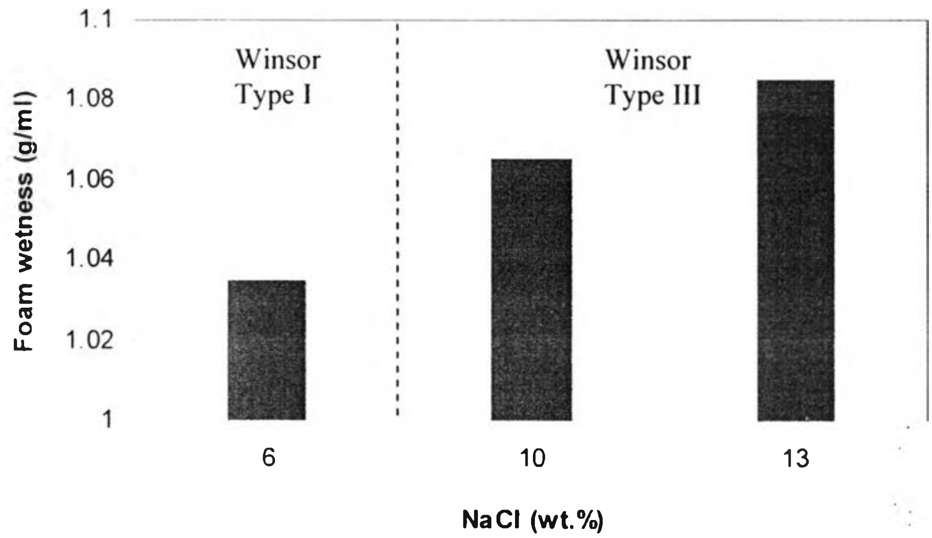

Figure 4.17 Foam wetness at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed NaCl concentrations.

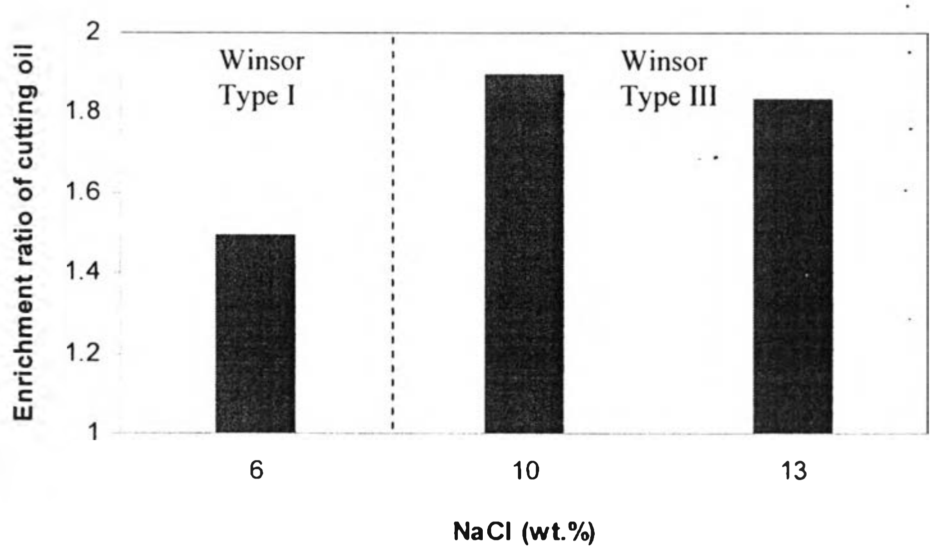

Figure 4.18 Enrichment ratio of cutting oil at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed NaCl concentrations.

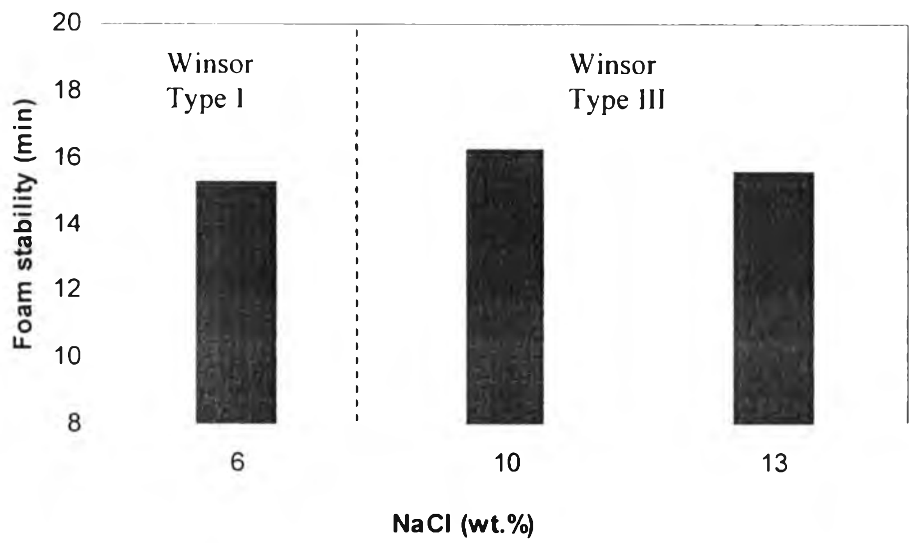

Figure 4.19 Foam stability of the system at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, and different feed NaCl concentrations.

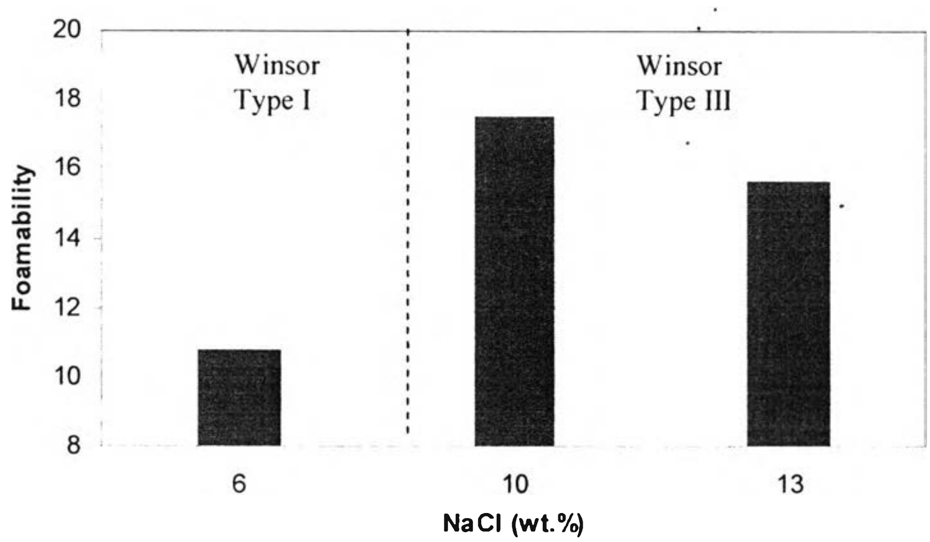

Figure 4.20 Foamability of the system at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate. and different feed NaCl concentrations.

The effect of NaCl concentration on the surfactant removal is shown in Figure 4.21. Increasing NaCl concentration from 6 wt.% to 13 wt.% results in a slight increase in the surfactant removal. This result is similar to the effect of NaCl concentration on the oil removal as described before.

As shown in Figure 4.22, the enrichment ratio of surfactant increases with increasing NaCl concentration from 6 wt.% to 10 wt.% and slightly decreases as the NaCl concentration further increase to 13 wt.%. This is because of the changing of the repulsive force between the anionic head groups of the surfactant, the foam stability, foamability and foam wetness of the system as same as the effect of NaCl concentration on the enrichment ratio of cutting oil. According to these results, a proper NaCl concentration that provided high removal efficiency and high enrichment ratio of both cutting oil and surfactant in this system was 10 wt.% which was still in the Winsor Type III microemulsion region. This optimum salinity of 10 wt.% was used for further investigation.

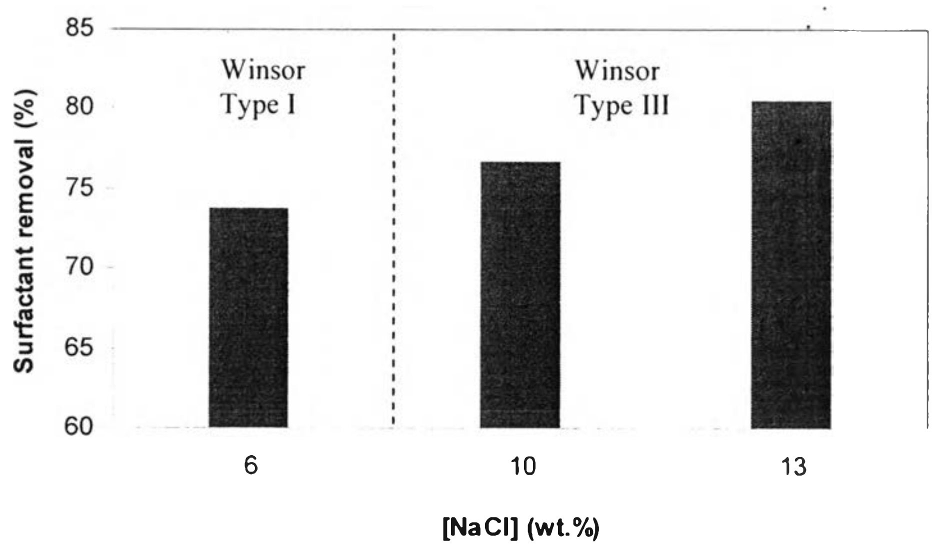

Figure 4.21 Surfactant removal efficiency at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed NaCl concentrations.

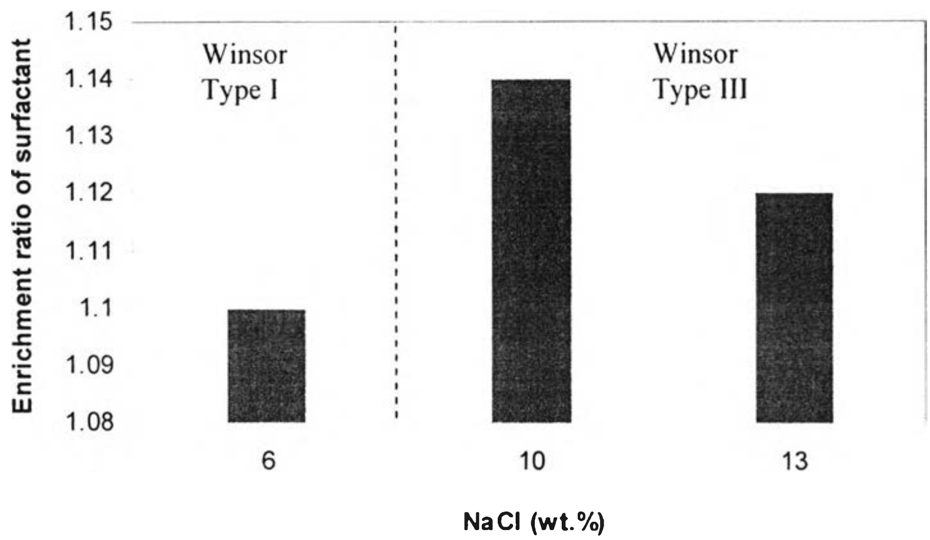

Figure 4.22 Enrichment ratio of surfactant at 0.3 wt.% Alfoterra, 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, 20 min HRT, and different feed NaCl concentrations.

4.2.3 Effect of Hydraulic Retention Time (HRT) on the Froth Flotation Performance

The term of hydraulic retention time is expressed as the holding or residence time of the liquid in the froth flotation column which is calculated from the liquid volume in the column divided by the feed flow rate. From Figure 4.23, the oil removal increases when HRT increases. This is because a higher HRT represents a longer residence time for the solution to be contact with air bubbles. As a result, a higher amount of oil can be carried out to the top of the column and a higher oil removal is obtained.

As shown in Figure 4.24, the enrichment ratio of cutting oil increases as HRT increases because a higher 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 be collected as the froth at the top of the column. Therefore, the collapsed froth was found to contain a higher amount of oil and less water content with increasing HRT. As expected, increasing HRT resulting in decreasing foam wetness (see Figure 4.25). This corresponds to the result of the enrichment ratio of cutting oil because at a higher HRT, the system simply has a longer time for allowing more water drainage for the foam produced. As a result, the foam wetness and the foam production rate decrease as shown in the Figures 4.25 and 4.26, respectively.

The effect of HRT on the removal and enrichment ratio of surfactant are shown in Figures 4.27 and 4.28, respectively. With increasing HRT in the range of 10 to 17.5 min, the effect of HRT on both removal and enrichment ratio of surfactant was insignificant but at the highest HRT of 20 min, both removal and enrichment ratio of surfactant increased remarkably. The results indicate that at a low HRT, a proper balance between the foam production rate and the rate of water drainage from the foam attributes to relatively constant values of both removal and enrichment ratio of surfactant. However, at the highest HRT, the rate of water drainage becomes prominent, resulting in both higher values of the removal and enrichment ratio of surfactant.

From the results, the froth flotation performance tended to increase with increasing HRT. However this system could not be operated at a HRT higher than 20 min because the feed solution was converted completely into froth without the treated solution coming out.

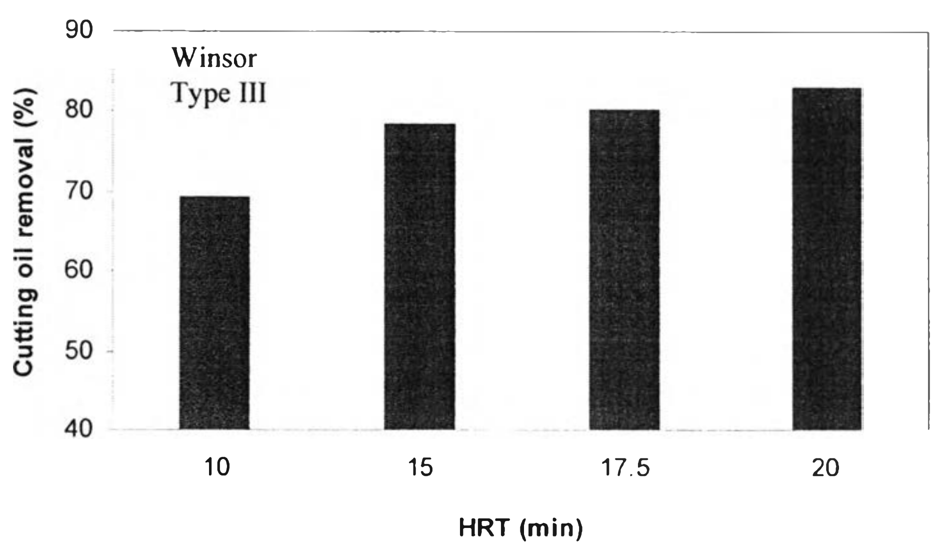

Figure 4.23 Oil removal efficiency at 0.3 wt.% Alfoterra, 10 wt.% NaCl 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, and different HRTs.

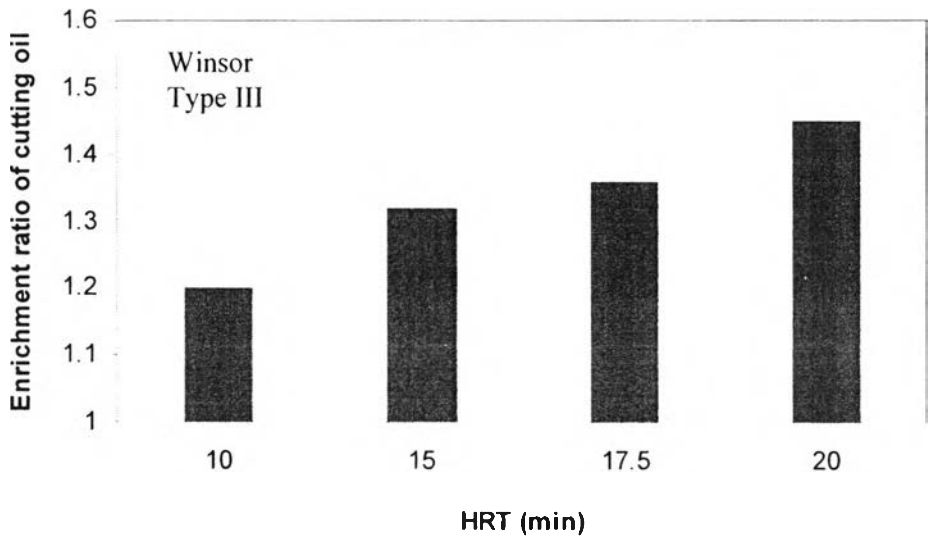

Figure 4.24 Enrichment ratio of cutting oil at 0.3 wt.% Alfoterra, 10 wt.% NaCl 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, and different HRTs.

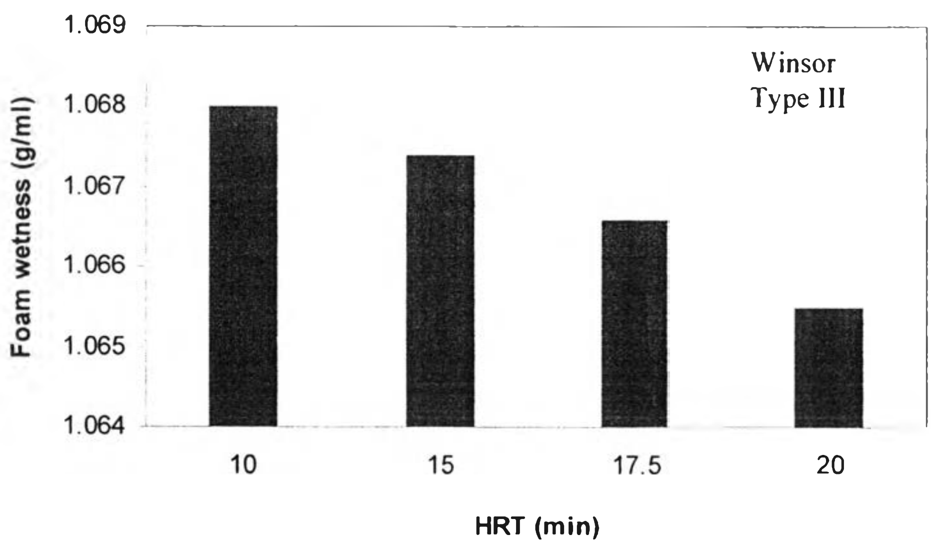

Figure 4.25 Foam wetness at 0.3 wt.% Alfoterra, 10 wt.% NaCl 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, and different HRTs.

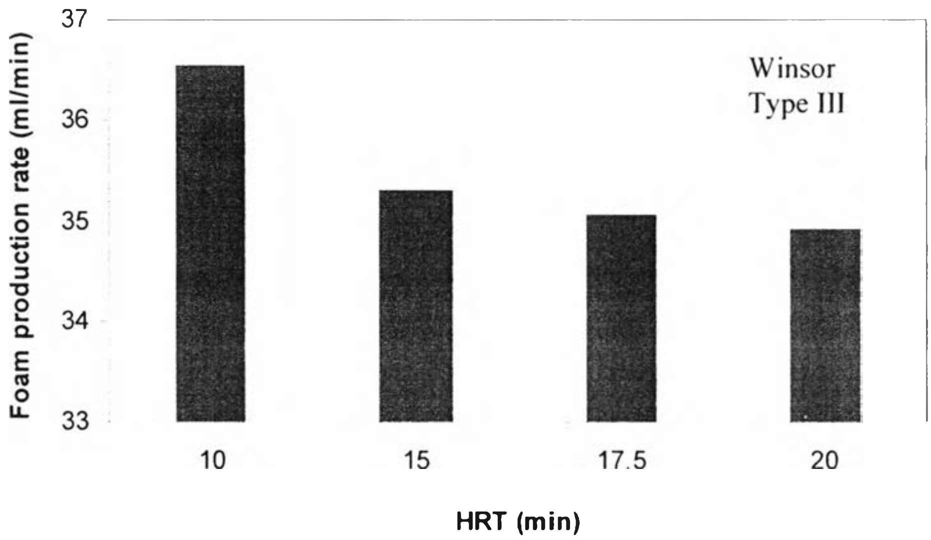

Figure 4.26 Foam production rate at 0.3 wt.% Alfoterra, 10 wt.% NaCl 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, and different HRTs.

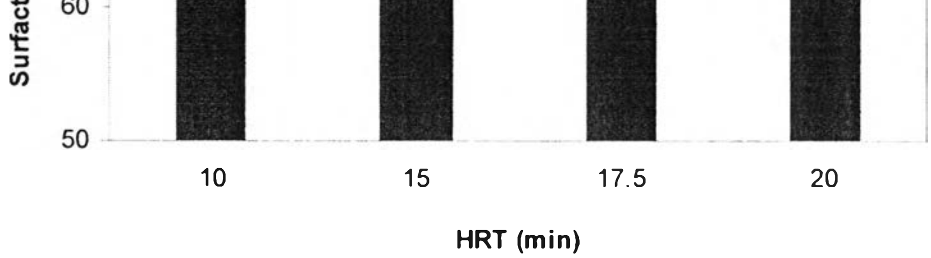

Figure 4.27 Surfactant removal efficiency at 0.3 wt.% Alfoterra, 10 wt.% NaCl 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, and different HRTs.

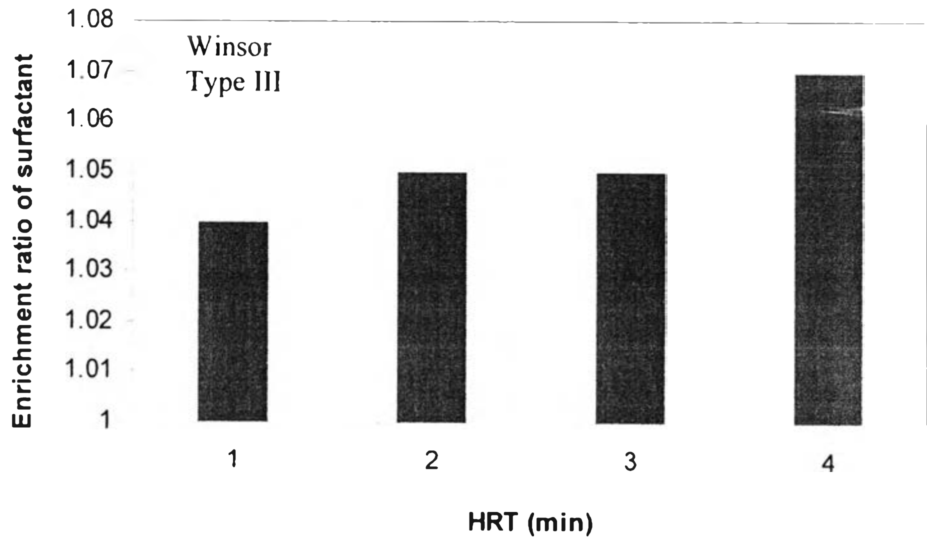

Figure 4.28 Enrichment ratio of surfactant at 0.3 wt.% Alfoterra, 10 wt.% NaCl 500 ppm oil content, 0.3 L/min air flow rate, 31 cm foam height, and different HRTs.

4.3 Bubble Size Distribution Results

The flotation process relies on the attachment of air bubbles to the dispersed oil droplets. This attachment is heavily dependent on the complex processes involving the surface characteristics of the oil droplets and their interaction with air bubbles. The air bubble size, bubble size distribution and degree of dispersion affect the performance of flotation process significantly. A range of air bubbles is beneficial because the smaller bubbles can capture the smaller oil droplets and the larger ones the larger droplets (Moosai *et al.,* 2003). In this part, the air bubble size distribution in the froth flotation column was determined to investigate the role of surfactant in the froth flotation process.

4.3.1 Effect of Added Surfactant

From the froth flotation results, the optimum conditions were 0.3 wt.% Alfoterra, 10 wt.% NaCl, and 20 min HRT. These optimum conditions were used to study air bubble size distribution in the froth flotation column. Figure 4.29 shows the comparison of the air bubble size distribution between a surfactant-free system (pure water) and a surfactant system (at the optimum conditions) at three axial positions (bottom, middle, and top of the column). From the results, the bubble sizes of the surfactant system appeared much smaller than those of the surfactant-free system. The results can be explained in that the presence of surfactant can reduce the surface tension, resulting in the enhancement of foam production and also reducing the coalescence rate of air bubbles due to the repulsion forces among the generated air bubbles.

a)

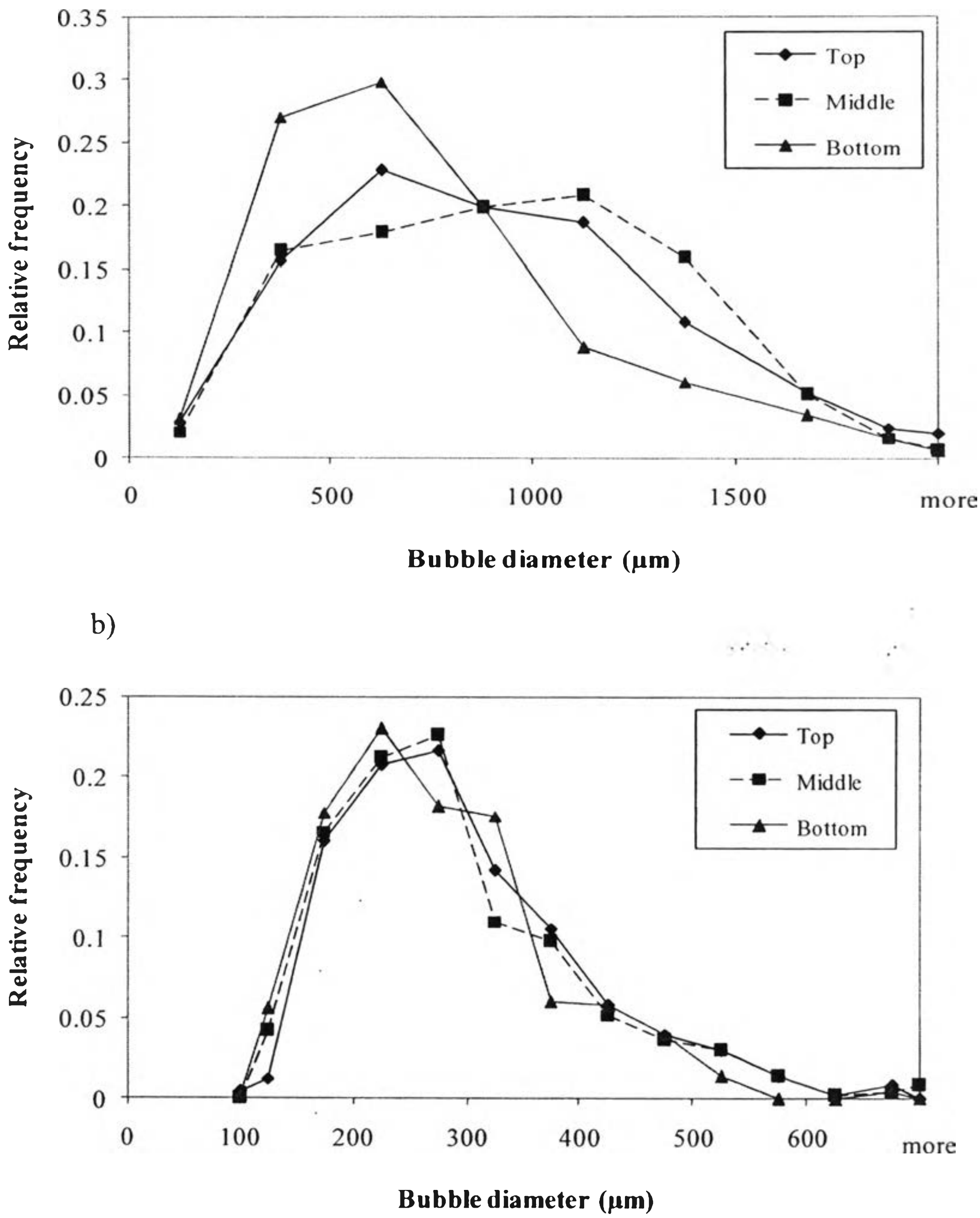

Figure 4.29 Bubble size distribution of a) surfactant-free system (pure water), b) surfactant system (optimum conditions) at different positions along the column.

4.3.2 Effect of Column Height

As can be seen in Figure 4.29, the relative frequency of the big bubbles of the surfactant-free system increased with increasing the distance from the bottom of the column and the small bubbles show a consistent reduction. Conversely, the air bubble size distribution of the surfactant system did not change as a function of column height. In the absence of surfactant, the average diameter of the air bubbles increased as a function of column height, so there is a coalescence of air bubbles in this system. On the other hand, the average diameter of the air bubbles in the presence of surfactant was found to be nearly the same for all three axial positions along the column (as shown in Figure 4.30). Hence, the presence of surfactant can greatly reduce the coalescence rate of air bubbles, leading to smaller size of the air bubbles and the air bubbles are also stabilized by the adsorbed surfactant.

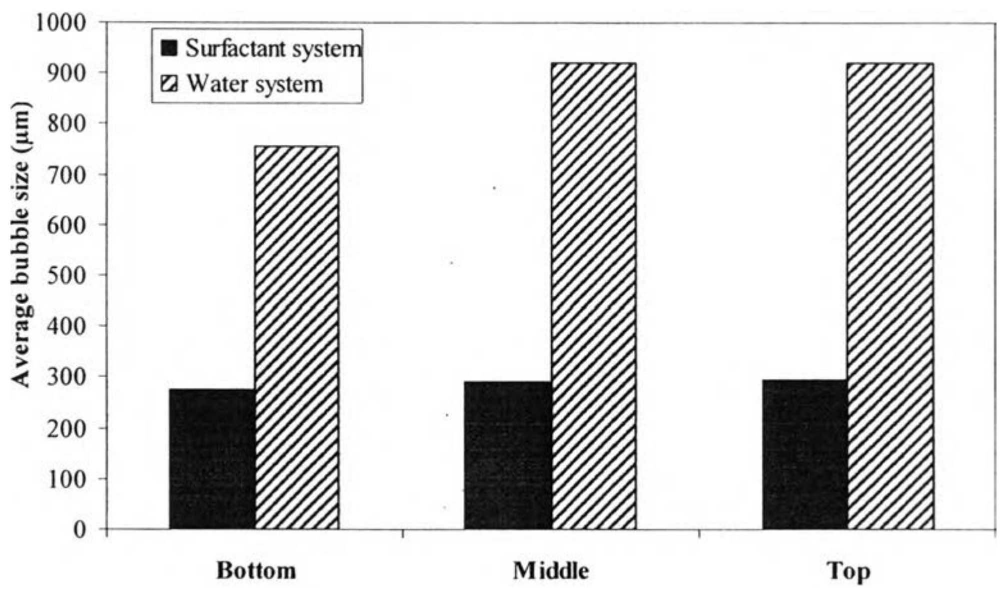

Figure 4.30 Average diameter of air bubbles of the surfactant-free system and the surfactant system (optimum conditions) at different positions along the column.