CHAPTER IV RESULTS AND DISCUSSION

4.1 Microemulsion Formation

The experimental data of microemulsion formation was shown in Appendix A.

4.1.1 Effect of type of single surfactant concentration on microemulsion formation

The effect of AOT concentration on microemulsion formation is illustrated in Figure 4.1. As AOT concentration increased, the solution still had only two phases, which were the water and excess oil phases, without the middle phase. The height or volume of each phase varied remarkably. The volume of water excess phase decreased while that of oil excess phase increased with increasing AOT concentration. Since AOT is a hydrophobic anionic surfactant having a relatively low HLB, it favors to solubilize in the oil phase leading to dispersion of water droplets in the continuous oil phase. In this case, water-in-oil microemulsion or Winsor's type II microemulsion was formed.



Figure 4.1 Relationship between volume fraction and AOT concentration with an initial oil-to-water ratio =1:1.

Figure 4.2 shows the effect of Dowfax concentration on phase behavior. As Dowfax has two hydrophilic head groups, it is a vater-soluble surfactant or a highly hydrophilic anionic surfactant having an extending high HLB solubilize more in the water phase than in the oil phase. As expected, the volume of the water excess phase increased but the volume of the oil excess phase decreased as the Dowfax concentration increased. The system contained the dispersion of oil in water phase known as oil-in-water microemulsion that is usually called Winsor's type I microemulsion. The result indicates that Dowfax surfactant can not form middle phase microemulsion.



Figure 4.2 Relationship between volume fraction and Dowfax concentration with initial oil-to-water ratio =1:1.

AMA was another anionic surfactant to be tested for microemulsion formation. AMA has a proper HLB for ethylbenzene-water system and expected to form middle phase microemulsion. Under the studied range of the AMA concentrations studied, the system was found to separate into three phases with a very small volume of middle phase. Hence, it was not possible to measure the volume of middle phase. Therefore, the measurement of interfacial tension of the water phase and the oil phase was used to confirm the existence of middle phase microemulsion. By visual observation, at a constant NaCl concentration of 3 wt %, the system exhibited Winsor's type III microemulsion in a wide range of AMA concentration. Figure 4.3 illustrates the values of interfacial tension in the range of 0.3 to 3 wt % AMA. As can be seen from Figure 4.3, the interfacial tension does not vary with AMA concentration and at the range of AMA concentrations, the interfacial tension is considerably ultra low indicating the existence of Winsor's type III microemulsion or middle phase. AMA is the only single anionic surfactant in the three studies surfactants that can form Winsor's type III microemulsion. Therefore, AMA was still used in the next studies of phase behavior of water-ethylbenzene system.



Figure 4.3 Minimum IFT at different AMA concentrations.

4.1.2 Effect of mixed surfactant concentration on microemulsion formation

As decribed before, either single AOT or Dowfax could not form Winsor's type III microemulsion with water and ethylbenzene. According to the structure of AOT, AOT has two hydrophobic tail groups so it has rather high hydrophobicity leading to solubilize in oil more than in water phase. Hence, it forms water-in-oil microemulsion or Winsor type II microemulsion. In contrast, Dowfax has two hydrophilic head groups so that it is more hydrophilic and favors to solubilize in water more than in oil phase. It will create the dispersion of oil droplets in continuous water phase, which is known as Winsor's type I microemulsion. From the difference in the properties of solubilization of them, it is believed that a proper ratio of AOT and Dowfax should enhance the solubilization of both oil and water resulting in forming middle phase microemulsion. Hence, a mixed surfactant system of AOT and Dowfax was further investigated in this study.

4.1.2.1 The effect of AOT concentration

In order to study the effect of AOT concentration of the mixed surfactant system on microemulsion formation, a Dowfax concentration was fixed at 2 wt % then varied a AOT concentration was varied from 3 to 5 wt %. The result is shown in Figure 4.4 (a)-(c). By observing Figure 4.4, as AOT concentration increases, the volume of middle phase increases but the range of salinity for the formation of middle phase becomes narrow. Increasing surfactant concentration is known to be one of methods for promoting phase change (Bourrel and Schechter, 1988). It is interesting to note that the amount of surfactant required dissolving equal volume of oil and water results in maximizing volume of middle phase. Another finding is that when AOT concentration was increased, the formation of Winsor's type III microemulsion was found at a lower salinity, which will be further explained in section 4.1.3. In comparison between single AOT system and the mixed surfactant (AOT and Dowfax) system, it was clearly seen that a larger volume of middle phase was achieved by using the mixed surfactant system, since this surfactant mixture provides proper balance between hydrophilicity and lipophilicity promoting both the solubilization of oil (by AOT) and the solubilization of water (by Dowfax). Hence, the mixture of AOT and Dowfax surfactants has a synergism to form middle phase microemulsion.

4.1.2.2 The effect of Dowfax concentration

Figure 4.5 shows the effect of Dowfax concentration on microemulsion formation under the mixed surfactant system. The Dowfax concentration was varied from 0.25 to 2 wt % while the concentration of AOT was fixed constant at 3 wt %. The reason for fixing an AOT concentration at 3 wt % was that it was the lowest AOT concentration to form middle phase microemulsion. For

0.25 to 1 wt % Dowfax concentration as shown in Figure 4.5 (a)-(d), the volume fraction of oil excess phase is slightly higher than the volume fraction of water excess phase indicating that the system forms Winsor's type II microemulsion due to the low HLB value of AOT. When Dowfax concentration was increased to 2 wt % (Figure 4.5 (e)), the solution turned into three phases, which were an excess water phase, a middle phase and an excess oil phase since the system had a proper balance between hydrophilicity and hydrophobicity of the mixed surfactant system.



Figure 4.4 Relationship between volume fraction and NaCl concentration at different AOT concentrations of the mixed surfactant system (AOT + Dowfax)



Figure 4.5 Volume fraction as a function of NaCl concentration at different Dowfax concentrations of the mixed surfactant system (AOT+Dowfax).

Consequently, the middle phase microemulsion appeared. Hence, 3 wt % AOT and 2 wt % Dowfax was selected as formulation to operate flotation experiments since it can provide a ultra low IFT.

4.1.3 Effect of NaCl on microemulsion formation of single and mixed surfactant systems

A study on the effect of adding salt on microemulsion formation was carried out in both single (AMA) and mixed surfactant (AOT and Dowfax) systems with salinity scan.

4.1.3.1 Microemulsion formation with single surfactant system

For the single surfactant system, the AMA concentration was varied in the range of 0.3-3. wt % with salinity scan to form microemulsion with ethylbenzene since Winsor's type III microemulsion was formed in this range. Due to the single AMA system created a very thin layer of middle phase and so the measurement of interfacial tension was employed to rectify the existence of middle phase. Figure 4.6 depicts the value of interfacial tension between an excess water and excess oil phase as a function of salinity at different AMA concentrations. The results showed that for a NaCl concentration, greater than 2 wt % the system had a relatively high interfacial tension value because it formed Winsor's type I microemulsion. For anionic surfactant, it is known that an increased in the salt concentration resulted in increasing the solubilization of oil. As expected, the system transformed from Winsor's type I to type III microemulsion as adding NaCl in the range of 3 to 4 wt %. The interfacial tension reached the minimum point at 3 wt % NaCl concentration. This NaCl concentration of 3 wt % is classified as the optimum point due to this ultra low interfacial tension. A further increase in salinity resulted in increasing the interfacial tension indicating that the system transformed from type III to type II microemulsion. The values of the minimum interfacial tension of 1, 2, and 3 wt% AMA system were 0.023, 0.039, and 0.036 mN/m, respectively. The lowest interfacial tension was found at 1 wt% AMA. However, for the single AMA system, the minimum interfacial tension value did not vary significantly with AMA concentration. Form the result, it exhibited that the existence of ultra low interfacial tension is definitely correlated to phase behavior, in particular to the existence of Winsor's type III microemulsion. Therefore, all of four AMA concentrations were selected to operate the froth flotation experiment.



Figure 4.6 Interfacial tension as a function of salinity at different AMA concentrations with initial oil-to-water ratio = 1:1.

4.1.3.2 Microemulsion formation with mixed surfactant system

As mentioned before, the mixed surfactant system (AOT and Dowfax) could form Winsor's type III microemulsion with an appropriate range of salinity. In order to enlarge the middle phase, another experiment was further conducted with higher AOT concentrations. Figure 4.7 illustrates the phase behavior of ethylbenzene with a Dowfax concentration of 2 wt % and different AOT concentrations. For any given compositions of the mixed surfactants with low salinity, the system was oil in water microemulsion or Winsor's type I microemulsion. When NaCl was continuously added, the system transferred from Winsor's type I to Winsor's type III microemulsion since the increasing salinity results in more surfactant moving out from the water phase to the oil phase. At a very high salinity, addition of salt caused disappearance of the middle phase and the inversion from Winsor's type III to Winsor's type II microemulsion.

As can be seen in Figure 4.7, an increase in AOT concentration affects remarkably the formation of middle phase at a the lower salinity. For the second mixed surfactant concentration, which was 4 wt% AOT and 2 wt% Dowfax, the middle phase appeared at 2.5 wt % NaCl. When NaCl was greater than 5 wt%, the disappearance of middle phase was observed as a result that the system transferred from Winsor type III to Winsor type II microemulsion. For the last mixed surfactant concentration (AOT 5 wt%, Dowfax 2 wt%), it was observed that the salinity was scan a lower salinity about 1.7 wt% was enough for the formation of the middle phase microemulsion. It was interesting to point out that an increase in the mixed surfactant concentration led to lowering salinity to promote the formation of middle phase microemulsion since increasing mixed surfactant concentration directly promotes solubilization of oil and water leading to the phase transformation. Therefore, a low salinity is needed to accelerate the formation of middle phase.

From the results, it can be concluded that for the mixed surfactants, a small amount of salt will promote the formation of middle phase microemulsion since NaCl reduces the repulsive force between the charged ionic surfactant head groups which can lead to decreasing the CMC and increasing the aggregation number (or decreasing HLB). Consequently, more oil can be solubilized into the inner core of micelles resulting in changing the structure of micelles from spherical to bicontinuous structure, a shift from Winsor's type I to Winsor's type III. But at a high NaCl concentration, it resulted in transformation from Winsor's type III to Winsor's type II microemulsion became more surfactants will be formed to move from the aqueous phase to the oil phase which enhance the formation of an water in oil microemulsion.

As one knows the unique properties of microemulsion are high solubilization and ultra-low interfacial tension. The solubilization is defined as a volume of either oil or water dissolved per unit mass of surfactants. Figure 4.8 shows the solubilization parameter of both oil and water as a function of salinity at different mixed surfactant concentrations. At low salinity, the system was Winsor's type I microemulsion, the volume of oil dissolved in the aqueous micellar phase was very small but the solubility parameter of water was very high.



Figure 4.7 Volume fraction as a function of NaCl concentration at different mixed surfactant concentration, initial oil-to-water ratio = 1:1, (a)-3 wt % AOT, 2 wt % Dowfax, (b)-4 wt %AOT, 2 wt % Dowfax, (c)-5 wt % AOT, 2 wt %Dowfax.



Figure 4.8 Solubilization parameter as a function of salinity of different mixed surfactant concentrations, (a)3 wt% AOT and 2 wt% Dowfax, (b)4 wt% AOT and 2 wt% Dowfax, (c)5 wt% AOT and 2 wt% Dowfax.

An increase in the electrolyte concentration resulted in increasing in the solubilization of oil (SP_o). For the solubilization of water (SP_w) in Winsor's type I, very little water presents in the excess oil phase and virtually all water is in the aqueous micellar phase. SP_w is therefore essentially constant as long as Winsor's type I exists. When the system further move from Winsor's type I to type III region, both water and oil will be moved into the middle since all surfactant molecules present in the middle phase. As a result, SP_w decreases but SP_o increases gradually with increasing salinity. As salinity further increased, the system transferred from Winsor's type III to type II microemulsion. The value of SP_o increased while the values of SP_w decreased. The NaCl concentration at the interception of SP_w and SP_o is classified as the optimum salinity. At this optimum salinity, the equal volume of oil and water are solubilized. As expected, the optimum salinity of the studied systems was found in Winsor's type III region. It means that the formation of Winsor's type III microemulsion could enhance the solubilization of oil and water. As can be seen in Figure 4.8, the optimum salinity decreases with increasing AOT concentration since adding AOT reduces a HLB of this system leading to lowering salinity required to shift the system from Winsor's type I to type III. Interestingly, as shown in Figure 4.8 the three studied systems have a similar value of optimum solubilization parameter of 15 ml/g surfactants.

The interfacial tension (IFT), which was measured by using a spinning drop tensiometer, is another interesting property. The interfacial tension is inversely proportional to the solubilization. In this study, the measurement of interfacial tension was done in the region of Winsor's type III microemlusion by measuring interfacial tension of the excess oil phase and the middle phase ($\gamma_{o,m}$) and the interfacial tension of the excess water phase and the middle phase ($\gamma_{w,m}$). The result is shown in Figure 4.9. When the salinity was increased, the interfacial tension of the excess oil and the middle phases decreased rapidly but the interfacial tension of the excess water and the middle phase increased rapidly. The intercept of these interfacial tensions is known as the optimum salinity. Form the present study results, the minimum interfacial tension was found at the optimum salinity of all studied conditions. Interestingly, for the studied system, the optimum salinity at the

minimum IFT which corresponded to the maximum solubilization was found to decrease remarkably with increasing salinity since increasing salt directly reduces the HLB value of the system.



Figure 4.9 Interfacial tension as a function of salinity of different mixed surfactant concentrations, (a)3 wt% AOT and 2 wt% Dowfax, (b)4 wt% AOT and 2 wt% Dowfax, (c)5 wt% AOT and 2 wt% Dowfax.

4.2 Froth flotation experiment

The experimental data and calculation methods of the froth flotation experiment were shown in Appendix B. The analytical methods of each component were shown in Appendix C. The performance of froth flotation was determined by two parameters, oil removal and enrichment ratio. Moreover, the surfactant removal, foam wetness, and foam flow rate were also considered.

4.2.1 Effect of single surfactant concentration on froth flotation performance

As described before, the formation of Winsor's type III microemulsion was found at AMA concentrations in range of 0.3-3 wt % and the minimum IFT was obtained at 3 wt % NaCl concentration. Therefore, the froth flotation experiment was carried out at 0.3 to 3 wt% AMA concentrations in order to verify the relationship between interfacial tension and froth flotation operation. Figure 4.10 shows the effect of AMA concentration on oil removal. The highest oil removal (99.55%) was found in the system of 0.3 wt% AMA concentration with the shortest operation time when compared to the other systems. This result contrasts with the hypothesis that the maximum oil corresponds to the lowest interfacial tension, which was 0.023 mN/m at 1 wt% AMA concentration. It implies that there must be other factors influencing the operation of flotation operation but these two parameters are not included in this study.

Figure 4.11 shows the effect of AMA concentration on surfactant removal. For any given time of operation, an increase in initial concentration of AMA resulted in decreasing surfactant removal but increasing operational time for any desired surfactant removal efficiency. It can be explained that an increasing an amount of surfactant added causes higher water entrainment in the foam produced resulting in lower the foamstability, which will be discussed later.

As seen in Figure 4.12, the wetness of foam is increased as initial surfactant concentration increases. This is because an increase in the surfactant concentration leads to increasing in the hydrophilic region in the foam produced. Consequently, water can be retained more in the foam. At an initial AMA concentration of 0.3 wt %, the system produced the driest foam.



Figure 4.10 Dynamic removal efficiency of EB of non-equilibrium system at different AMA concentrations.



Figure 4.11 Surfactant removal of non-equilibrium system at different AMA concentrations.

Figure 4.13 illustrates the effect of initial surfactant concentration on the foam flow rate produced. The result showed that the highest foam flow rate at 0.3 wt % AMA concentration corresponded to the lowest foam wetness. From the experimental results, it can be concluded that the foamstability and foamability in term of foam wetness and foam production rate are considered the important parameters influencing the performance of froth flotation operation apart from the effect of ultra low interfacial tension.

High oil removal is a necessary need for an effective flotation operation, but it is not the sole factor to be considered. If oil and water are present in the froth in the same proportions as in the feed solution, no selectivity is present and no separation of oil and water occurs. Enrichment ratio which is defined as a ratio of the concentration of ether surfactant or oil in collapsed foam solution to that in the feed solution was determined in this work. The separation appears when the enrichment ratio is greater than one. From Figure 4.14, for any given time of operation, the enrichment ratio is increased when the initial AMA concentration decreases. As mentioned earlier, the foam produced becomes drier or contains less water with decreasing surfactant concentration which leads to increase in the enrichment ratio. The system of 0.3 wt % AMA showed the best separation but for 3 wt% AMA, the separation did not occur because the enrichment ratio was lower than one.

4.2.2 <u>Effect of mixed surfactant concentration on froth flotation</u> <u>performance</u>

As be described in the phase study, 3 wt % AOT and 2 wt % Dowfax were selected for froth flotation experiment because this system was found to form the middle phase microemulsion and to be salinity robust. Based on the pervious results (Ponstabodee, 1998), the maximum oil removal in froth flotation process corresponds to the minimum interfacial tension of the system. Therefore, this mixed surfactants on at the optimum salinity, which had the minimum interfacial tension (10⁻³ mN/m), was selected to run the flotation experiment. Unfortunately, the foam stability of this system at the optimum



Figure 4.12 Relationship between foam wetness and initial AMA concentration of non-equilibrium system



Figure 4.13 Relationship between foam flow rate and initial AMA concentration of non-equilibrium system



Figure 4.14 Relationship between enrichment ratio and AMA concentration of non-equilibrium system.

salinity was very low then the separation did not occur. The low foam stability is due to the counter ion effect of NaCl added to reduce the repulsive force of the anionic head groups of the surfactants at the foam lamella. The reduction of the repulsive force between the anionic heads of the surfactants leads to the film of foam to be collapsed easily. Lower surfactant concentrations around 0.5 wt % were also tried to run froth flotation unsuccessfully. It can be concluded that not only the interfacial tension of system plays an important role for running froth flotation process but also the stability of foam should be considered.

4.2.3 Effect of NaCl concentration on froth flotation performance

The effect of NaCl concentration on the operation of froth flotation was carried out by varying NaCl concentration at 3 wt % AMA. As shown in Figure 4.15, for non-equilibrium system at a surfactant concentration of 0.3 wt %, dynamic EB removal of the system was much higher than that with 2 wt % NaCl. When the salinity was increased to 4 wt %, the separation was not occured (no foam coming

out from the column) even though the interfacial tension at 4 wt% NaCl was significantly lower than that at 2 wt % NaCl. The higher the NaCl concentration, the lower the repulsive force between head groups of anionic surfactant is obtained. Consequently, the hydrophobic characteristic of foam surface increases leading to increase in oil attached to the air bubble. However, further decreasing repulsive force decreases foam stability since the liquid film (lamella) of the foam can easily collapse. Hence, the optimization between the hydrophobic characteristic of foam and the foam stability to obtain the maximum oil separation can be achieved by adjusting salinity. From this result, it is worth noting that interfacial tension is not the sole factor to be considered for running froth flotation.

The effect of NaCl concentration on surfactant removal is shown in Figure 4.16. The surfactant removal at 3 wt % NaCl concentration was higher and the operational time was shorter than those at 2 wt % NaCl concentration. The adding salt causes to reduce the repulsive force between anionic head groups. Therefore, more surfactant can adsorbed at the air-solution interface and then, the removal of surfactant increased.

Figure 4.17 shows the effect of adding salt on foam wetness. From the result, the foam wetness decreased with decreasing NaCl concentration. On the other hand, the foam becomes drier with increasing salinity. This is because the reduction of the repulsive force between anionic head groups leading to reduce in the thickness of foam lamella. Consequently, the amount of water in lamella is decreased and dry foam is generated. Moreover, the decreasing repulsive force also leads to more oil attached with the air bubble surfaces and thus the foam wetness decreases.

The rate of foam production or foam flow rate at two different salinity is shown in Figure 4.18. The foam flow rate was closely related to the foam wetness as the system at 3 wt % NaCl had a higher foam flow rate than that at 2 wt % NaCl. The result indicates that the foam flow rate increases with increasing NaCl concentration. The effect of salinity on the foam production rate can be explained the same as described before for the effect of salinity on the foam wetness.

The enrichment ratio is an important factor to express the separation efficiency of froth flotation. Figure 4.19 illustrates the effect of NaCl concentration

on enrichment ratio. The result showed that the enrichment ratio of the system at 3 wt% NaCl was greater than at 2 wt % NaCl. This result implies at the optimum salinity (3 wt % NaCl), the system has the lowest interfacial tension of Winsor's type III microemulsion, resulting in the success of froth flotation operation since the enrichment ratio of the system was greater than one.



Figure 4.15 Dynamic removal efficiency of EB of non-equilibrium system at different NaCl concentration.



Figure 4.16 Surfactant removal of non-equilibrium system at different NaCl concnentration.



Figure 4.17 Relationship between foam wetness and NaCl concentration of nonequilibrium system



Figure 4.18 Relationship between foam flow rate and NaCl concentration of non-equilibrium system.



Figure 4.19 Relationship between enrichment ratio and air flow rate of non-equilibrium system.

4.2.4 Effect of air flow rate on froth flotation performance

Air flowrate is one of the potentially important parameters in froth flotation process. The system with 0.3 wt % AMA and 3 wt % NaCl was selected to determine the relationship between the air flow rate and froth flotation performance in terms of oil removal. As can be seen in Figure 4.20, oil removal is not affected significantly by the air flowrate in the studied range. Figure 4.21 shows the oil removal at the final operational time. It was found that the oil removal increased with increasing the air flowrate until it reached the maximum value at the air flow rate 300 ml/min. When the air flow rate increased further, the decreasing oil removal occurred. A higher air flow rate resulted in more bubbles passing through the solution, resulting in more oil, surfactant, and water in foam. However, the circulating velocity, which is induced by excess bubble produced at a very high air flowrate simply swarm rising through the column, increases the turbulence at the froth-collection zone interface, and some oil and water are entrained back into the solution.



Figure 4.20 Dynamic removal efficiency of EB of non-equilibrium system at different air flow rates.



Figure 4.21 Comparison of total oil removal at different air flow rates.

Figure 4.22 illustrates the surfactant removal at different air flow rates. The result indicates that the air flow rate has a small effect on the surfactant removal. From Figure 4.23, the foam is dryer when the air flow rate is lower because of the higher residence time of bubbles in the rising foam. As a result, more water drainage occurs, leaving dry foam. In addition, the air flow rate also affects on the foam flow rate as shown in Figure 4.24. As the air flow rate increased, a higher production rate of foam was obtained.

The effect of air flow rate on the enrichment ratio is shown in Figure 4.25. The result shows that these is the optimum air flowrate for the maximum enrichment ratio of ethylbenzene in froth flotation operation. In the studied system, the optimum air flow rate was found to be 300 ml/min corresponding to the highest enrichment ratio. When the system operated at a high air flowrate of 350 ml/min, the enrichment ratio of EB became lower than that at the optimum air flowrate of 300 ml/min. The lower enrichment ratio at air flowrate greater than the optimum is due to the foam collapses by too high flow velocity of rising air bubble.



Figure 4.22 Dynamic surfactant removal of non-equilibrium system at different air flowrate.



Figure 4.23 Relationship between foam wetness and air flowrate of non-equilibrium system.



Figure 4.24 Relationship between foam production and air flowrate of non-equilibrium system.



Figure 4.25 Enrichment ratio as a function of air flowrate of non-equilibrium system.

4.2.5 Effect of equilibration time on froth flotation performance

The equilibration time of microemulsion is one of interesting factors in flotation operation. The system with 0.3 wt % AMA and 2 wt % NaCl was selected to study the effect of the equilibration time. Three sets of one liter of the well-mixed solution were prepared as equilibrium (3 weeks), induced equilibrium (40 minutes), and non-equilibrium (without incubation) to run flotation experiment. As shown in Figure 4.26, the oil removal of the non-equilibrium system was very much lower than those of both induced equilibrium and equilibrium systems. In addition, the non-equilibrium system took the longest operation time as compared to the other systems. It was because the foam production of the non-equilibrium system was lower than that of the induced equilibrium and equilibrium systems as shown in Figure 4.27. It is interesting to point out that to obtain a high oil removal efficiency, the system has to reach equilibrium. However, a well mixing with a short time may be sufficient to obtain a high oil removal efficiency as closed to that of the equilibrium system.



Figure 4.26 Effect of equilibration time on dynamic oil removal



Figure 4.27 Effect of equilibration time on foam flowrate