

CHAPTER IV RESULTS AND DISCUSSION

4.1 Steady-State Operation

The multi-stage foam fractionation unit used in this study was operated under steady state conditions. Steady state was insured when all measured parameters were invariant with time. From the concentration profiles shown in Figure 4.1, it takes about 6 hours for the system to reach steady state. Consequently, all experiments were carried out for a minimum of 6 hours before the samples were taken. All experimental data are given in Appendix A.



Figure 4.1 Concentration profiles with respect to time under operational condition of [CTAB] = 0.49 mM (0.5 CMC); feed tray number 5; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm.

4.2 **Operating Limits**

The operating limits of the multi-stage foam fractionator were determined by varying both air and feed flow rates. Two important operational constraints; foam formation and flooding, are considered as the limits of the operation of foam fractionation. For the foam production, a sufficient air flow rate is needed to produce foam which can reach the foam outlet at the top stage when the very air flow but the liquid flow rate is not high enough to maintain sufficient liquid retention, the tray is completely filled with vapor leads to the foam production can not occurs. On the other hand, flooding is occurred when the liquid flow rate is too high the trays fill up completely with liquid. Figure 4.2 shows the boundary of the operational region of the foam fractionator used in this experiment. The maximum and minimum values of both air flow rate and liquid flow rate were used to run all experiments in order to avoid both flooding and no foam formation.



Figure 4.2 Operational zone under operational condition [surfactant] = 0.5 CMC of each surfactant; foam height = 60 cm and feed tray number 5.

4.3 Foam characteristics of Each Surfactant

Foam characteristics in terms of stability and foamability of each surfactant are shown in Figures 4.3 to 4.4. In comparison CPB, CTAB, TTAB and DTAB, the foam stability of CPB is higher than that of CTAB, which have the same number of the tail length, as shown in Figure 4.4. It can be explained that the repulsive force between the layers of lamellae of the foam produced from CPB system is greater than that produced from CTAB because the repulsive force between the head groups of CPB is greater than those of CTAB. Foam stability of CTAB is higher than that TTAB and DTAB, which have the same head group but difference in the number of the tail length, because increasing in length of hydrophobic group of the surfactant lower the CMC that more efficient the surfactant as a foamer (Rosen, 2004). Due to increase the tail length of surfactant it can get more surfactant adsorbed at the lamellae of the foam and not only reduce surface tension but also increase the viscosity resulted in the foam can occur easily and the liquid drainage from the foam lamella is decreased as can be seen from Figure 4.3 and 4.4.



Figure 4.3 Foamability of various surfactant systems under operating condition of air flow rate = 0.1 L/min, surfactant solution = 250 mL and [surfactant] = 0.5 CMC of each surfactant.



Figure 4.4 Foam stability of various types of surfactant solutions under operating condition of air flow rate = 0.1 L/min, surfactant solution = 250 ml and [surfactant] = 0.5 CMC of each surfactant.

 Table 4.1 The measured values of the foam stability and foam ability of each surfactant

Surfactant	Foam Stability(min)	Foamability (L/min)
СРВ	101.98	1.29
СТАВ	53.86	1.21
ТТАВ	26.62	1.17
DTAB	14.25	1.10

4.4 Critical Micelle Concentrations (CMC) of each surfactant

An increase in the tail length of the surfactant the CMC value decreased, as shown in Figures 4.5 CTAB (0.98mM), TTAB (3.6mM) and DTAB (20mM), because of an increase in the hydrophobic group the micelle can form easier and a general rule for ionic surfactants is that the CMC is halved by the addition of one methylene group to a straight-chain hydrophobic group attached to a single terminal hydrophilic group (Rosen, 2004). In comparison between CPB and CTAB, CPB (0.6mM) have lower CMC because of pyridine group of the CPB. A pyridine group that is part of a hydrophobic group with a terminal hydrophilic group is equivalent to about three and one- half methylene groups (Rosen, 2004).



Figure 4.5 Surface tension as a function of surfactant concentration.

Table 4.2 The measured values of the CMC of each surfactant

Type of surfactants	CMC(mM)
CPB C ₁₆	0.6
CTAB C ₁₆	0.98
TTAB C ₁₄	3.6
DTAB C ₁₂	20

4.5 Multi-stage Foam Fractionator Efficiencies of Single-surfactant Systems

The experimental data taken after the steady state established were analyzed to determine the effects of process parameters affecting the recovery of CPB, CTAB, TTAB and DTAB. Efficiencies of the surfactant separation were evaluated in terms of the %surfactant recovery and the enrichment ratio was as defined in the previous chapter.

4.5.1 <u>Hexadecyltrimethylammonium Bromide (CTAB)</u>

4.5.1.1 Effect of Surfactant Feed Flow Rate

The effects of the surfactant feed flow rate on the separation efficiencies of CTAB are shown in Figure 4.6. An increase in the surfactant feed flow rate result in a decrease in both enrichment ratio and %surfactant recovery because the residence time shorter at a higher surfactant feed flow rate, thus a higher amount of surfactant still remains in the liquid phase that agree with the pervious work. For this studied, the enrichment ratio and %surfactant recovery of CTAB as high as 14.26 and 91.26, respectively, were achieved at lowest surfactant feed flow rate of 40 mL/min. However the feed flow rate has a little bit effect on both % surfactant recovery and enrichment ratio at air flow rate 60 L/min as shown in Figure 4.7 that because of it reach the maximum point.



Figure 4.6 %Surfactant recovery and enrichment ratio of CTAB in the effect of surfactant feed flow rate under operational conditions of [CTAB] = 0.5 CMC; air flow rate = 40 L/min and foam height = 60 cm.



Figure 4.7 %Surfactant recovery and enrichment ratio of CTAB in the effect of surfactant feed flow rate under operational conditions of [CTAB] = 0.5 CMC; air flow rate = 60 L/min and foam height = 60 cm.

4.5.1.2 Effect of Air Flow Rate

Figures 4.8 and 4.9, Figure 4.8 for operating at constant surfactant feed flow rate at 40 ml/min and 60 ml/min for Figure 4.9 are shown the effect of air flow rate on the separation efficiencies of CTAB. For this studied, the lowest air flow rate that can operate is 40 L/min. Thus, the air flow rate lowers than this result in such a low production of foam that did collapse before reaching the overflow pipe. As can be seen from Figures 4.8 and 4.9, an increasing in air flow rate results in reduces in the enrichment ratio but increase in the %surfactant recovery. An increase in the air flow rate tends to produce wetter foam because of more bubble generated and lower the liquid drainage rate, result in lower the enrichment ratio. And for the %surfactant recovery increase in order to increasing in air flow rate because a higher volumetric rate of foam is occurred. In this studied the % surfactant recovery and enrichment of CTAB as high as 14.26 and 95.035, respectively, for highest % surfactant recovery was achieved at highest air flow rate of 100 L/min and for highest enrichment ratio was achieved at lowest air flow rate of 40 L/min that for the optimum condition of air flow rate is around 80L/min. However, from the effect of surfactant feed flow rate shows that the maximum both of %surfactant recovery and enrichment ratio at 40 ml/min surfactant feed flow rate. Therefore the optimum condition of CTAB are 40 ml/min of surfactant feed flow rate and 80 L/min of air flow rate.



Figure 4.8 %Surfactant recovery and enrichment ratio of CTAB in the effect of surfactant air flow rate under operational conditions of [CTAB] = 0.5 CMC; surfactant feed flow rate = 40 mL/min and foam height = 60 cm



Figure 4.9 % Surfactant recovery and enrichment ratio of CTAB in the effect of air flow rate under operational conditions of [CTAB] = 0.5 CMC; surfactant feed flow rate = 60 mL/min and foam height = 60 cm

4.5.2 <u>Tetradecyltrimethylammonium Bromide (TTAB)</u> 4.5.2.1 <u>Effect of Surfactant Feed Flow rate</u>

The % surfactant recovery and enrichment ratio of Tetradecyltrimethylammonium Bromide (TTAB) in the effect of surfactant feed flow rate are shown in Figure 4.10. An increase in the surfactant feed flow rate result in a decrease in %surfactant recovery because the residence time shorter at a higher surfactant feed flow rate, thus a higher amount of surfactant still remains in the liquid phase but a little bit effect on enrichment ratio because of short of hydrophobic group or tail length. For this studied, the enrichment ratio and %surfactant recovery of TTAB as high as 3.7and 73.32, respectively, were achieved at lowest surfactant feed flow rate has a little bit effect on %surfactant recovery and have a lot of effect on enrichment ratio at low flow rate.



Figure 4.10 %Surfactant recovery and enrichment ratio of TTAB in the effect of surfactant feed flow rate under operational conditions of [TTAB] = 0.5 CMC; air flow rate = 40 L/min and foam height = 60 cm



Figure 4.11 %Surfactant recovery and enrichment ratio of TTAB in the effect of surfactant feed flow rate under operational conditions of [TTAB] = 0.5 CMC; air flow rate = 60 L/min and foam height = 60 cm

4.5.2.2 Effect of Air Flow rate

The Figure 4.12 and 4.13 are shown the effect of air flow rate on %surfactant recovery and enrichment ratio of TTAB that have the similar tend of recovery of CTAB. An increasing in air flow rate resulted in a reduction in the enrichment ratio but it led to increased in %surfactant recovery the same as Chuyingsakultip N. (2004) work. In this studied the % surfactant recovery and enrichment of TTAB as high as 3.7and 87.21, respectively, for highest % surfactant recovery was achieved at highest air flow rate of 100 L/min and for highest enrichment ratio was achieved at lowest air flow rate of 40 L/min that for the optimum condition of air flow rate is around 80L/min for 40 ml/min surfactant feed flow rate and around 60L/min for 60 ml/min surfactant feed flow rate. Moreover, from the surfactant feed flow rate shows that the maximum both of %surfactant recovery and enrichment ratio at 40 ml/min surfactant feed flow rate. Therefore the optimum condition of TTAB are 40 ml/min of surfactant feed flow rate and 80 L/min of air flow rate.



Figure 4.12 % Surfactant recovery and enrichment ratio of TTAB in the effect of air flow rate under operational conditions of [TTAB] = 0.5 CMC; surfactant feed flow rate = 40 mL/min and foam height = 60 cm



Figure 4.13 % Surfactant recovery and enrichment ratio of TTAB in the effect of air flow rate under operational conditions of [TTAB] = 0.5 CMC; surfactant feed flow rate = 60 mL/min and foam height = 60 cm

4.5.3 <u>Dodecyltrimethylammonium bromide (DTAB)</u>4.5.3.1 <u>Effect of Surfactant Feed Flow Rate</u>

The Figure 4.14and 4.15 show the effects of the surfactant feed flow rate on the separation efficiencies of DTAB. An increase in the surfactant feed flow rate result in a decrease in both enrichment ratio and %surfactant recovery because of the shorter residence time at higher surfactant feed flow rate that agree with the pervious work. For this studied, the feed flow rate has a little bit effect on both % surfactant recovery and enrichment ratio at 40 L/min air flow rate as shown in Figure 4.16. However the enrichment ratio and %surfactant recovery of DTAB as high as 0.955 and 55.9, respectively, were achieved at lowest surfactant feed flow rate of 40 mL/min.



Figure 4.14 %Surfactant recovery and enrichment ratio of DTAB in the effect of surfactant feed flow rate under operational conditions of [DTAB] = 0.5 CMC; air flow rate = 40 L/min and foam height = 60 cm



Figure 4.15 %Surfactant recovery and enrichment ratio of DTAB in the effect of surfactant feed flow rate under operational conditions of [DTAB] = 0.5 CMC; air flow rate = 60 L/min and foam height = 60 cm

4.5.3.2 Effect of Air Flow Rate

The Figure 4.16 and 4.17 show the effect of air flow rate on both %surfactant recovery and enrichment ratio of TTAB. An increasing in air flow rate resulted in a decreased in the enrichment ratio but it led to increased in %surfactant recovery the same as Chuyingsakultip N. (2004) work. In this studied the % surfactant recovery and enrichment of DTAB as high as 1.766and 75.35, respectively, for highest % surfactant recovery was achieved at highest air flow rate of 100 L/min and for highest enrichment ratio was achieved at lowest air flow rate of 40 L/min that for the optimum condition of air flow rate is around 80L/min for both of 40and 60 ml/min surfactant feed flow rate. However, from the surfactant feed flow rate shows that the maximum both of %surfactant recovery and enrichment ratio at 40 ml/min surfactant feed flow rate. Therefore the optimum condition of DTAB are 40 ml/min of surfactant feed flow rate and 80 L/min for both



Figure 4.16 % Surfactant recovery and enrichment ratio of DTAB in the effect of air flow rate under operational conditions of [DTAB] = 0.5 CMC; surfactant feed flow rate = 40 mL/min and foam height = 60 cm



Figure 4.17 % Surfactant recovery and enrichment ratio of DTAB in the effect of air flow rate under operational conditions of [DTAB] = 0.5 CMC; surfactant feed flow rate = 60 mL/min and foam height = 60 cm

4.5.4 <u>Hexadecylpyridinium bromide (CPB)</u>4.5.4.1 <u>Effect of Feed Flow Rate</u>

The Figure 4.18 and 4.19 show the effects of the surfactant feed flow rate on the separation efficiencies of CPB. An increase in the surfactant feed flow rate result in a decrease in both enrichment ratio and %surfactant recovery. For this studied, the feed flow rate has a little bit effect on % surfactant recovery but has a lot of effect on enrichment ratio as shown in Figure 4.18 and 4.19. However the enrichment ratio and %surfactant recovery of CPB as high as 64.33 and 88.95, respectively, were achieved at lowest surfactant feed flow rate of 40 mL/min and 40 L/min of air flow rate.



Figure 4.18 %Surfactant recovery and enrichment ratio of CPB in the effect of surfactant feed flow rate under operational conditions of [CPB] = 0.5 CMC; air flow rate = 40 L/min and foam height = 60 cm



Figure 4.19 %Surfactant recovery and enrichment ratio of CPB in the effect of surfactant feed flow rate under operational conditions of [CPB] = 0.5 CMC; air flow rate = 60 L/min and foam height = 60 cm

4.5.4.2 Effect of Air Flow Rate

From Figure 4.20 and 4.21, the effect of air flow rate on both %surfactant recovery and enrichment ratio of CPB that increasing in air flow rate resulted in a decreased in the enrichment ratio but increased in %surfactant recovery. In this studied the % surfactant recovery and enrichment of CPB as high as 94.67 and 87.55 respectively, were achieved at highest air flow rate of 100 L/min that for the optimum condition of air flow rate is around 80L/min for both of 40and 60 ml/min surfactant feed flow rate. However, from the surfactant feed flow rate shows that the maximum both of %surfactant recovery and enrichment ratio at 40 ml/min surfactant feed flow rate. Therefore the optimum condition of CPB are 40 ml/min of surfactant feed flow rate and 80 L/min of air flow rate.



Figure 4.20 %Surfactant recovery and enrichment ratio of CPB in the effect of surfactant feed flow rate under operational conditions of [CPB] = 0.5 CMC; feed flow rate = 40 ml/min and foam height = 60 cm



Figure 4.21 %Surfactant recovery and enrichment ratio of CPB in the effect of surfactant feed flow rate under operational conditions of [CPB] = 0.5 CMC; feed flow rate = 60 ml/min and foam height = 60 cm.

Surfactant	Feed Flow rate (ml/min)	Air Flow rate (L/min)
СТАВ	40	80
TTAB	40	80
DTAB	40	80
СРВ	40	80

Table 4.3 The optimum condition of each surfactant

4.6 Multi-Stage Foam Fractionator in the Effect of Tail Length of Surfactants

The effects of the tail length of surfactants on the separation efficiencies of CTAB, TTAB and DTAB both of the same operating condition and optimum condition of each surfactant are shown in Figures 4.22 - 4.26. An increase in the tail length of the surfactant resulted in increased %surfactant recovery. %Surfactant recovery of CTAB, in the range of 90-97% was higher than TTAB and DTAB in the range of 70-85% and 10-70%, respectively. Because of foam stability of CTAB is higher than that TTAB and DTAB as show in Table 4.1. The result agree with Caskey in 1972 that is closer packing of the surfactant molecules in the film would therefore be expected to decrease the rate of diffusion of the gas between the bubbles. Consistent with this, interfacial resistance to gas diffusion has been shown to increase with increase in the number of carbon atoms in the hydrophobic group of the surfactant. Since inter chain cohesion increases with increase in the hydrophobic group, this may account for the observation that foam height often goes through a maximum with increase in the length of chain (Rosen, 2004). An increasing in the hydrophobic tail decreases its CMC and CMC is halved by adding one more methylene group (-CH₂-) as shown in the Figure 4.5 and Table 4.2. CTAB has the lowest CMC so the surfactant can adsorb at the lamella of foam easier than TTAB and DTAB that can higher %surfactant recovery. The higher of foam ability of CTAB system results in having much higher enrichment ratio as compared to TTAB and DTAB system. Generally, foaming ability increases with increasing alkyl chain length in the hydrophobic group (Schramm, 2005).



Figure 4.22 %Surfactant recovery and enrichment ratio in the effect of tail length under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate = 40 mL/min, air flow rate = 40 L/min and foam height = 60 cm



Figure 4.23 % Surfactant recovery and enrichment ratio in the effect of tail length under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 40 mL/min, air flow rate = 60 L/min and foam height = 60 cm



Figure 4.24 % Surfactant recovery and enrichment ratio in the effect of tail length under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 60 mL/min, air flow rate = 60 L/min and foam height = 60 cm



Figure 4.25 % Surfactant recovery and enrichment ratio in the effect of tail length under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 60 mL/min, air flow rate = 80 L/min and foam height = 60 cm



Figure 4.26 % Surfactant recovery and enrichment ratio in the effect of tail length under operating at optimum conditions of each surfactant.

4.7 Multi-Stage Foam Fractionator in Effect of Pyridine Group at the Head Group of Surfactant

The effect of the pyridine group at the head group of surfactant on the separation efficiencies of CPB and CTAB both of the same operating condition and optimum condition of each surfactant that are surfactant feed flow rate and air flow rate are shown in Figures 4.27 - 4.31. An increase in the pyridine group at the head group of surfactant has a little bit effect on %surfactant recovery. %Surfactant recovery of CPB, in the range of 85 - 95 was a little bit lower than CTAB, nonpyridine at the head group of surfactant in the range of 90 - 97 % surfactant recovery. However, it has a lot of effect on enrichment ratio. The enrichment ratio of CPB is in the range of 35 - 85 compare with CTAB in the range of 6-14. The increase in the enrichment ratio on the effect of pyridine group at the head group of surfactant can be attributed by the higher of foam stability and foam ability as shown in table 4.1. The pyridine group at the head group of surfactant can increase in the surface viscosity that higher foam stability and more enrichment ratio. Since branched-chain surfactant and those with centrally located hydrophilic group can depress the surface tension of water to lower values than isomeric straight-chain compounds or those with terminally located hydrophilic groups (Rosen, 2004) that more foam ability.



Figure 4.27 %Surfactant recovery and enrichment ratio in the effect of pyridine group at the head group of surfactant under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate = 40 mL/min, air flow rate = 40 L/min and foam height = 60 cm



Figure 4.28 % Surfactant recovery and enrichment ratio in the effect of pyridine group at the head group of surfactant under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 40 mL/min, air flow rate = 60 L/min and foam height = 60 cm.



Figure 4.29 % Surfactant recovery and enrichment ratio in the effect of pyridine group at the head group of surfactant under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 60 mL/min, air flow rate = 60 L/min and foam height = 60 cm



Figure 4.30 % Surfactant recovery and enrichment ratio in the effect of pyridine group at the head group of surfactant under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 60 mL/min, air flow rate = 80 L/min and foam height = 60 cm



Figure 4.31 % Surfactant recovery and enrichment ratio in the effect of pyridine group at the head group of surfactant under operating at optimum conditions of each surfactant.

4.8 Multi-Stage Foam Fractionator in the Effect of Salinity

The effects of salinity on the separation efficiencies of CTAB by varying NaCl concentrations are shown in Figure 4.34 - 4.37. The surfactant recovery increased with increasing salt concentration. Beyond the optimum salinity, the surfactant recovery decreased with increasing NaCl concentration. The Figure 4.34 shown the optimum at 0.02 M salt (NaCl) concentration, operating at 40 ml/min of surfactant feed flow rate and 40 L/min of air flow rate, for lower or higher salt concentration than this point the %surfactant recovery and enrichment ratio will be decreased. For Figure 4.35 - 4.37 that are operated at different condition shown the same optimum point of salt concentration. The effect of neutral electrolyte addition on the ionic surfactant head group, thereby decreasing the CMC (Rosen, 2004). The CMC of CTAB decreased with increasing salt concentration as shown in Figure 4.33. It can suggest that the reducing in the repulsive force at the head group of ionic

surfactant, the surfactant can adsorb more at the lamellae of the foam and can get more %surfactant recovery and enrichment ratio. The cause of increasing in the both %surfactant recovery and enrichment ratio can be explained by the foam stability as shown in the Figure 4.32. Electrolytes that increase the bulk viscosity of the foaming solution decrease the rate of drainage of the liquid in the lamellae (Rosen, 2004) that increase in foam stability. The Figure 4.38 and 4.39 shown the effect of surfactant feed flow rate under the operation condition of constant air flow rate at 60L/min and 0.1 and 0.02 M salt concentration, respectively. The surfactant feed flow rate was not significantly on the %surfactant recovery in the both of salt concentration but has a little bit effect on enrichment ratio. Figure 4.40 and 4.41 are shown the effect of air flow rate at 40 ml/min and 0.1 and 0.02 M salt concentration, respectively. The air flow rate at 40 ml/min and 0.1 and 0.02 M salt concentration and enrichment ratio that is the similar trend of the pure CTAB system.



Figure 4.32 Foam stability and foam ability of CTAB in the effect of salinity under operational conditions of [surfactant] = 0.5 CMC; air flow rate = 0.1 L/min and surfactant solution = 250 ml.



Figure 4.33 Surface tension as a function of surfactant concentration by vary salt (NaCl) concentration.



Figure 4.34 % Surfactant recovery and enrichment ratio in the effect of salinity under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 40 mL/min, air flow rate = 40 L/min and foam height = 60 cm



Figure 4.35 % Surfactant recovery and enrichment ratio in the effect of salinity under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 40 mL/min, air flow rate = 60 L/min and foam height = 60 cm



Figure 4.36 % Surfactant recovery and enrichment ratio in the effect of salinity under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 40 mL/min, air flow rate = 80 L/min and foam height = 60 cm



Figure 4.37 % Surfactant recovery and enrichment ratio in the effect of salinity under operational conditions of [surfactant] = 0.5 CMC; surfactant feed flow rate of 60 ml/min, air flow rate = 60 L/min and foam height = 60 cm



Figure 4.38 % Surfactant recovery and enrichment ratio in the effect of surfactant feed flow rate under operational conditions of [surfactant] = 0.5 CMC; air flow rate = 60 L/min, 0.1 M salt (NaCl) concentration and foam height = 60 cm



Figure 4.39 % Surfactant recovery and enrichment ratio in the effect of feed flow rate under operational conditions of [surfactant] = 0.5 CMC; air flow rate = 60 L/min, 0.02 M salt (NaCl) concentration and foam height = 60 cm



Figure 4.40 %Surfactant recovery and enrichment ratio in the effect of air flow rate under operational conditions of [surfactant] = 0.5 CMC; feed flow rate = 40 ml/min, 0.1 M salt (NaCl) concentration and foam height = 60 cm



Figure 4.41 %Surfactant recovery and enrichment ratio in the effect of air flow rate under operational conditions of [surfactant] = 0.5 CMC; feed flow rate = 40 ml/min, 0.02 M salt (NaCl) concentration and foam height = 60 cm