CHAPTER VI

DIESEL REMOVAL BY FROTH FLOTATION UNDER LOW INTERFACIAL TENSION CONDITIONS I: FOAM CHARACTERISTICS, COALESCENCE TIME AND EQUILIBRATION TIME

6.1 Abstract

Froth flotation is one of the surfactant based separation processes which is suitable for treating diluted wastewaters. In this technique, there are several advantages such as low space requirement, high removal efficiency, flexibility for various pollutants at different scales, and low cost. To achieve high performance for froth flotation operation, the combination of ultra-low interfacial tensions between excess oil and excess water and high foam production rates as well as high stability of foam produced must be achieved. To get the ultra-low interfacial tensions, a Winsor type III microemulsion or middle phase has to be formed. In this study, branched alcohol propoxylate sulfate sodium salt with 14 – 15 carbon number and 4 PO groups (Alfoterra 145 – 4PO) was used to form microemulsions with diesel. From the results in this work, an increase in surfactant concentration decreases interfacial tension (IFT), and increases foam stability. To promote Winsor type III microemulsion formation, NaCl was added and the minimum IFT was achieved at 5 wt% NaCl. However, this optimum salinity cannot be operated in froth flotation experiment due to poor foam characteristics. The results indicate that both IFT and foam characteristics should be optimized to achieve high efficiency of oil removal in froth flotation operation. Unlike the ethylbenzene work, agitated solution before operated in the flotation column yields the lowest diesel removal efficiency because of the poor foam characteristics.

Key words: Microemulsion, Froth flotation, Foam formation, Foam stability, Diesel removal

6.2 Introduction

In the presence, a number of vehicles have been increasing rapidly affecting the increasing amount of fuel usage. Diesel consumption is much higher than gasoline consumption. This may be because diesel provides more energy per unit volume than gasoline does (1). In the United State and Latin America, diesel is used primarily for the transportation of goods. However, In Europe, Japan, and elsewhere, diesel is a significant source of energy for personal transportation (2). The demand for diesel is forecasted to grow faster than the demand for other fuels in general. Therefore, diesel has high possibility to contaminate in water by leakage from gas station or underground storage tank.

To remove diesel from water, froth flotation was focused in this work. Firstly, froth flotation was first utilized to separate a desired ore from unwanted substrates in the mineral processing process (3). However, nowadays, froth flotation technique is widely employed in wastewater treatment application (4 – 5), and also in paper deinking processes (6 – 7). There are 2 main types of froth flotation which are dissolved and induced air flotation. The induced air flotation was focused in this work. In the latter type of froth flotation, filtered air is introduced into the solution through a sintered glass disk. Air bubbles generated in the solution are keys for successful separation. Droplets of emulsified oil which have hydrophobic surfaces can co-adsorb at the bubble surfaces, which are also hydrophobic, and then rise to the top of the column to form foam called froth. However, the stability of these bubble-droplet aggregates is generally low leading to lower separation efficiency. To achieve a higher separation efficiency, a proper type of surfactant with an optimum concentration is added into the solution to stabilize foam (8). Chang et al. (9) reported that the surfactant added should be adjusted at an appropriate concentration to maintain the foam stability.

To achieve high oil separation efficiency in froth flotation operation, a proper amount of surfactant added into the solution is a crucial issue. In our previous work (10), it has been found that the maximum oil removal corresponds to the formation of Winsor type III microemulsion. This seems to be a starting point of our group to further investigate the relationship between the froth flotation efficiency and a Winsor type III microemulsion. Later, Chavadej *et al.* (11) investigated what was the main source of oil removed from flotation column. They found that the most oil removed from the column during flotation operation came from the excess oil phase rather than the middle phase in the Winsor type III microemulsion system. After that, Yanatatsaneejit *et al.* (12) hypothesized that the maximum oil removal was achieved because of the ultra-low interfacial tension characteristic in Winsor type III microemulsion. Interestingly, they found that ultra-low interfacial tension is not only a factor affecting the performance of froth flotation but also foam characteristics are also important on flotation efficiency. In this work, the performance of froth flotation to remove diesel from water was correlated with interfacial tension and foam characteristics. In addition, the amount of oil covering at bubble surface is also important for high oil removal. To achieve high oil removal, the coalescence between oil droplets should be as fast as possible to obtain a very high thickness of oil film at bubble surfaces. Therefore, the coalescence time between oil droplets was also focused in this work.

6.3 Experimental Section

6.3.1 Materials

A model oil used in this study is a commercial grade of diesel obtained from the Petroleum Authority of Thailand (PTT). A branched alcohol propoxylate sulfate sodium salt (Alfoterra 145-4PO), an anionic surfactant which is an experimental (not yet commercially available) surfactant specially synthesized by Sasol Company (formerly Condea Vista Company), Rosebank, South Africa was used in this study. Analytical purity grade Sodium chloride (NaCl) from Aldrich Chemical Company Inc. was used as electrolyte in this work. All Chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

6.3.2 Methodology

This work can be divided into four parts. The first part was to study microemulsion phase behavior of aqueous solutions containing different Alfoterra concentrations with diesel. The second part was to investigate the foam characteristics which are foamability and foam stability. The coalescence between oil droplets was studied in the third part. The fourth part was the investigation of the efficiency of froth flotation. In all experiments, the surfactant and electrolyte concentrations are expressed in weight percentage (wt%) per volume of the aqueous solution consisting of water, surfactant, and electrolyte.

To investigate the phase behavior of microemulsions, 5 mL of homogeneous aqueous solution, prepared at various surfactant and NaCl concentrations, was mixed with 5 mL of diesel in a vial sealed with a screw cap. These vials were shaken every day for 3 days, and then allowed to equilibrate at a constant temperature of 30°C in a water bath for 1 month to reach equilibrium, which was verified by the invariant height of each phase. The interfacial tensions between equilibrated excess oil and excess water phases were measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

A schematic diagram of the froth flotation unit used in this work is shown in Figure 6.1. A glass cylindrical column with 5 cm internal diameter and 120 cm height was used as the froth flotation column. A 750 mL sample with different initial oil:water ratios and various surfactant and NaCl concentrations which had been equilibrated at 30°C for 1 month in the incubator, was transferred to the froth flotation column. Filtered air at a flow rate of 300 mL/min was introduced at the bottom of the column through a sintered glass disk having pore size diameters about 16 – 40 μm. The generated air bubbles rose through the solution to the top of the column. The foam collected in the receiver over a period of time was broken by freezing for diesel concentration analysis. Moreover, the solution in the column was sampled at the same time interval as the foam collected for analysis of untreated diesel and remained surfactant concentrations. All experiments were stopped when no more foam came overhead from the column as a result of too low surfactant concentrations in the solution.

In order to obtain a better understanding about the phenomena in the froth flotation process, foamability and foam stability experiments were conducted in the same flotation column. A 250 mL sample containing a given surfactant and NaCl concentrations and an oil to water ratio of 1:1 was transferred to the column. Filtered air was introduced at the bottom of the column through the solution at a constant flowrate of 100 mL/min until the maximum foam height in the column was achieved. The maximum foam height was then measured. After that the filtered air was stopped introducing to the column, and the time required for the foam volume to collapse to half of the maximum height was recorded to quantify foam stability. All experiments of froth flotation operation, foamability, and foam stability were conducted at room temperature of about 25 – 27° C. The ratio of maximum foam height to initial solution height is considered as foamability while foam stability ($t_{1/2}$) is defined as the time required for the foam to collapse to the half of the maximum foam height.

To investigate the coalescence between oil droplets, an aqueous solution having different surfactant, and NaCl concentrations was mixed with diesel in a vial at various oil to water ratios. After that, this mixture was gently shaken for 1 minute. The light generated from Light Emitting Diode (LED) having wavelength of 568 nm passing through the solution in the vial was measured by a photo sensitive detector. The light intensity obtained from photo sensitive detector was recorded with time until reaching a constant value. In this research, the time that the light intensity begins to reach plateau is defined as coalescence time between oil droplets. The measurement of the coalescence time was conducted at room temperature of about 25 – 27 °C.

6.4 Results and Discussion

To achieve a very high oil removal efficiency in froth flotation operation, the mechanism in froth flotation operation should be well understood. From the observation during the operation, we propose that there are 4 sequential steps in froth flotation operation as shown in Figure 6.2. Firstly, air bubbles are generated within liquid solution by introducing air into the bottom of the flotation column. At this step, oil droplets adhere on the surfaces of the air bubbles by the interaction with the hydrophobic portion of surfactant. During the air bubbles rising up called the second step, the formation of the oil film coverage on the air bubble surfaces appears. The thickness of oil film should be high enough to achieve a high oil removal; thus the coalescence between oil droplets has to be maximized. The next step is the rising of bubble-droplet to the top of the column. High stability of the air bubbles covered by oil film is required in this step. The fourth step is the air bubbles coming out from the liquid phase to form froth. To operate froth flotation successfully, high stability of froth is needed to obtain dry foam with a high oil content. Parameters affecting in each step of the proposed mechanism were systematically investigated in this research. These parameters which are interfacial tensions obtained from phase behavior study, foam stability and foamability obtained from the foam characteristic study, and coalescence time obtained from the coalescence experiment are simultaneously analyzed to correlate to the efficiency of froth flotation.

6.4.1 Phase Behavior

Interfacial tension (IFT) is one of the major factors affecting the performance of froth flotation operation (12, 14). In the proposed mechanism of froth flotation operation, a lower IFT is required in the first step of air bubbles covered by oil droplets. Figure 6.3 shows the effect of surfactant concentration on IFT value. At 3 wt% NaCl concentration, increasing Alfoterra 145 – 4PO concentration decreases IFT between excess oil and excess water phases because a number of surfactant at the interface increases corresponding to the decrease of IFT (13). However, Alfoterra 145 – 4PO concentration cannot be increased to more than 0.15 wt% because macroemulsion is formed rather than microemulsion. As a result, the optimum surfactant concentration was not achieved in this study. The result indicates that Alfoterra 145 – 4PO alone cannot promote the formation of Winsor type III microemulsion. This is because Alfoterra 145 – 4PO is an anionic surfactant having a high value of HLB (hydrophilic – lipophilic balance). To enhance the formation of a Winsor type III microemulsion, another surfactant having a low HLB is needed to act as a likner. However, from the previous work (11), it was found that most of oil removed from flotation column came from the excess oil phase instead of middle phase. Therefore, in this study, the ultra-low IFT (i.e. 10^{-2} mN/m) was focused rather than the presence of the middle phase.

For the observation of the effect of NaCl concentration on IFT, at a fixed Alfoterra concentration of 0.10 wt%, the minimum IFT was found at 5 wt% NaCl (Figure 6.4). The explanation of the effect of NaCl concentration on IFT was already discussed in our previous work of ethylbenzene (12).

The system having 0.1 wt% Alfoterra 145 – 4PO concentration and 3 wt% NaCl concentration was selected to study the effect of oil to water ratio on IFT. The IFT of different oil to water ratio systems is in the same order of magnitude as shown in Figure 6.5. This result is consistent with the ethylbenzene results from our previous work (14). Hence, an oil to water ratio is insignificant effect on IFT may be because the surfactant concentration and salinity are the same resulting in almost constant excess interface free energy.

6.4.2 Foam Characteristic

As described in our previous works (12, 14), removal efficiency of oil in froth flotation operation is also influenced by foam characteristics (foamability and foam stability). Foam formation or foamability affects the bubbles generation step (step 1) whereas foam stability influences on the rising of bubble-droplet step (step 3) as well as that of froth (step 4) in the proposed mechanism. Therefore, the higher the foamability and the foam stability, the higher the oil removal should be obtained.

The effects of Alfoterra 145 – 4PO concentration on both foam stability and foamability are illustrated in Figure 6.3. The foam stability tends to increase with increasing Alfoterra 145 – 4PO concentration because more surfactant molecules adsorb at the surface of air bubbles. Therefore, the repulsive force between surfactants increases with increasing concentration as a result that the foam stability increases. In addition, when the Alfoterra concentration increases from 0.005 to 0.10 wt%, the foamability increases. However, the foamability decreases when the surfactant concentration further increases to 0.15 wt%. At low Alfoterra concentrations, the formability increases with increasing Alfoterra concentration because the foam stability increases. When the Alfoterra concentration further increases, however, the thicker foam lamellae causes more water content, resulting in a decline of foamability.

For the effect of NaCl concentration on foam characteristics, the descent of foam stability appears when NaCl concentration increases as shown in Figure 6.4. Perhaps because the negative charge of surfactant is neutralized by the positive charge of NaCl, and also the repulsive force between the head groups of surfactant in the lamellae decreases. The thickness of the lamellae between two air bubbles become thinner until the critical thickness is reached resulting in coalescence of these bubbles. In case of foamability as a function of NaCl concentration, the foamability increases when NaCl concentration increases from 2 to 3 wt%. However, further increasing NaCl concentration to 4 wt% substantially decreases the foamability as shown in Figure 6.4. Increasing NaCl concentration from 2 to 4 wt% causes lower interfacial tensions. Therefore, the system with 3 wt% NaCl needs a lower energy to form air bubbles within the liquid solution comparing to that with 2 wt% NaCl; so foams in 3 wt% NaCl system are easily formed. However, the foamability of 4 wt% NaCl system is lower than that of 2 and 3 wt% NaCl systems because the foam stability of 4 wt% NaCl is lower even though IFT of 4 wt% NaCl is much lower than that of 2 and 3 wt% NaCl. Consequently, to achieve high foamability, both of the interfacial tensions and foam stability have to be optimized.

The effects of oil to water ratio on both foam stability and foamability are shown in Figure 6.5. Both foamability and foam stability tend to increase slightly with increasing oil to water ratio. These results are consistent with the results of ethylbenzene system (14). The explanations of the effect of oil to water ratio on foam stability and foamability are available elsewhere (14).

Figure 6.6 shows the effect of air superficial velocity (u_G) on foam characteristics of the system, having an Alfoterra concentration of 0.10 wt%, a NaCl concentration of 3 wt%, and an oil to water ratio of 1 to 1. As shown in Figure 6.6, the foam stability is strongly affected by u_G; the foam stability decreases substantially with increasing u_G. This is because at a higher u_G, the velocity of bubble swarm rising through the column is higher, leading to increasing coalescence between air bubbles. However, in case of foamability, the foam formation is proportional to u_G because a number of bubbles increases when u_G increases. In this work, u_G above 15 cm/min cannot be operated because foam can overflow from the flotation column. However, extrapolation u_G above 15 cm, the foamability should decrease while the foam stability should decrease.

6.4.3 Coalescence of Oil Droplets

According to the proposed mechanism of froth flotation, coalescence between oil droplets is one of the major parameters affecting the performance of froth flotation. To maximize the coalescence between oil droplets, the coalescence time should be minimized. The effects of three parameters which are surfactant concentration, NaCl concentration, and oil to water ratio on coalescence time between oil droplets were investigated in this research. Figure 6.3 depicts the effect of Alfoterra concentration on coalescence time. The coalescence time is proportional to the Alfoterra concentration. Since hydrodynamic interactions that arise from the viscosity of the continuous fluid are one of the effects determining the possibility of coalescence (15), coalescence of oil droplets with a lower surfactant concentration (a lower viscosity of continuous fluid) occurs easily. The effect of NaCl concentration on coalescence time is shown in Figure 6.4. Increasing NaCl concentration from 2 to 3 wt% substantially increases the coalescence time whereas the coalescence time tends to decrease again when the NaCl concentration further increases to 4 wt%. Basically, it is assumed that the presence of NaCl will suppress the electric double layer of oil droplets, and thus promote the coalescence phenomena. However, at very low NaCl concentrations, the coalescence time increases when the NaCl concentration increases from 2 to 3 wt% due to the increase of the interfacial tension gradients (16). The deformation of the aqueous layer between two oil droplets appears during coalesce process as shown in Figure 6.7. The increase in the interfacial area in region 1 causes the difference between the interfacial tension at region 1 and 2 causing flow of liquid from region 2 toward region 1, which, in tern, prevents further thinning of the film (8). Since the interfacial tension of 3 wt% NaCl system is lower than that of 2 wt% system, 3 wt% NaCl can reduce interfacial tension gradients more than 2 wt% NaCl can. Therefore, coalescence of oil droplets of 3 wt% NaCl systems occurs difficultly, comparing to that of 2 wt% NaCl system. This result is consistent with the previous work (16). However, the tendency of coalescence time is vise versa when NaCl concentration increases to 4 wt%. This is because the suppression of the electric double layer caused by adding more NaCl becomes dominant. For the observation of the effect of oil to water ratio on coalescence time, increasing oil to water ratio increases coalescence time as shown in Figure 6.4. Since, viscosity of a higher oil to water ratio system is high (more oil content in solution), similar to effect of surfactant concentration, the coalescence between oil droplets of a higher oil to water ratio solution occurs slowly.

6.4.4 Froth Flotation

To verify the proposed mechanism of froth flotation, the data of IFT, foam characteristics, coalescence time between oil droplets, and performance of froth flotation were simultaneously correlated. As shown in the previous work (12), three parameters which are oil removal, surfactant removal, and enrichment ratio of oil are defined as the performance parameters of froth flotation operation. In this work, enrichment ratio of diesel is defined as the diesel concentration in the collapsed froth to the diesel concentration in the initial feed. Therefore, to achieve the separation, the enrichment ratio of diesel has to be higher than unity.

6.4.4.1 Removal of diesel and Alfoterra

Figure 6.3 shows the effect of Alfoterra concentration on IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability and foam stability, and coalescence time between oil droplets. Similar to ethylbenzene system (12), the total cumulative diesel removal is the highest at the Alfoterra concentration corresponding to the maximum foamability and the maximum foam stability but not the minimum IFT. The same trend of the Alfoterra removal was found. This result implies that IFT is not the sole factor affecting the performance of froth flotation. Basically, IFT should be reduced to a critical value to enhance the amount of oil attached with foam. However, for system having IFT lower than the critical value, the effect of foam characteristics on the performance of flotation is dominant. For the process performance of froth flotation comparing to the coalescence data, both diesel and Alfoterra removal do not correspond to the minimum coalescence time between oil droplets as shown in Figures 6.3 to 6.5. This unexpected result indicates that the thickness of oil film on the air bubble surface depending upon the hydrophobic region at bubble surface is not the primary importance in froth flotation operation.

IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability, foam stability, and coalescence time between oil droplets as a function of NaCl concentration are depicted in Figure 6.4. The maximum diesel and Alfoterra removal corresponds to the highest foam stability but the lowest coalescence time. Similar to the effect of Alfoterra concentration, the lowest IFT does not yield the maximum removal of both diesel and Alfoterra. From Figure 6.4, the removal of diesel and Alfoterra is not significantly affected by NaCl concentration in the range of 2 to 3 wt% due to the trade-off between foamability and foam stability. However, at a NaCl concentration above 3 wt%, the NaCl concentration substantially affects the removal efficiency since both foamability and foam stability are extremely low. From the results of the effects of both Alfoterra and NaCl concentrations, it indicates that even though either coalescence time between oil droplets or IFT is low, the separation efficiency can be low if the foam characteristics are poor. Again, the lowest coalescence time between oil droplets is not a main factor to obtain a maximum separation efficiency.

Figure 6.5 depicts IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability, foam stability, and coalescence time as a function of oil to water ratio. Similar to the previous work (14), the removal efficiency of oil is not significantly affected by the oil to water ratio whereas the surfactant removal is reached the minimum value at 1 to 9 ratio for diesel system but at 1 to 4 ratio for ethylbenzene system (14). From this result, it indicates that even though the coalescence time of the system having 1 to 9 of oil to water ratio is the lowest, the removal efficiency of both oil and surfactant is not the highest because both foamability and IFT are not significantly altered within the studied range of oil to water ratio.

The effects of superficial velocity (u_G) on total cumulative diesel removal, total cumulative Alfoterra removal, foamability, and foam stability are shown in Figure 6.6. The highest removal efficiency of diesel corresponds to the u_G which has the highest foamability but the foam stability is relatively low. This is because a number of bubbles passing through the solution increases rapidly with increasing u_G. From the results, it indicates that under the studied condition, the effect of the foamability is more significant than that of foam stability on the diesel removal. In contrast, the total cumulative Alfoterra removal is not significantly affected by u_G even though the volume of foam generated increases. This may be due to some of surfactants is entrained back into the solution since circulation velocity of bubble swarm is higher at a higher u_G.

Table 6.1 shows the effects of equilibrium condition on total cumulative diesel removal, total cumulative Alfoterra removal, foamability, and foam stability. The total cumulative diesel removal from the equilibrium system is the highest as espected, with the same trends for the foamability and the foam stability. It is interesting to note that the total cumulative diesel removal from the non-equilibrium system is very close to that of the equilibrium system. Unlike the ethylbenzene system (14), the diesel removal of the induced-equilibrium system has the lowest oil removal because both foamability and foam stability are extremely low. In contrast with the results of the diesel removal, the maximum Alfoterra removal was found in the non-equilibrium system. The induced-equilibrium system also gives the lowest Alfoterra removal. These results are not consistent with our previous work on ethylbenzene (14). Further investigation will be carried out to determine why induced equilibrium by well mixing with a short period of time (e.g. 40 min) cannot enhance diesel removal. However, it can be summarized that solution agitated before being transferred to the flotation column is not necessary to yield satisfactory performance of both oil and surfactant removal but the maximum oil removal is always obtained from the equilibrium system.

6.4.4.2 Enrichment ratio of diesel

The enrichment ratio of diesel as a function of Alfoterra concentration is shown in Figure 6.3. As the Alfoterra concentration increases, the enrichment ratio of diesel reaches the maximum at 0.10 wt% Alfoterra. This result is similar to the result from our previous work (12). Actually, increasing surfactant concentration should decrease the enrichment ratio of oil because of several aspects such as thicker foam lamellae causing higher water content in foam lamellae, and higher viscosity of solution leading to lower drainage rate of water from foam lamellae. However, the amount of oil content in the froth increases with increasing surfactant concentration due to the more hydrophobic region in the froth.

For the observation of the effect of NaCl concentration on the diesel enrichment ratio, at low surfactant concentrations, increasing NaCl concentration from 2 to 3 wt% increases the enrichment ratio of diesel because repulsive force between the head groups of anionic surfactant at the opposite site of the foam lamellae decreases, resulting in a thinner foam lamellae. Therefore, at 3 wt% NaCl, a lower amount of water can be carried over with foam to the top of the column, leading to a higher enrichment ratio of diesel.

Figure 6.5 shows the enrichment ratio of diesel at different oil to water ratios. The separation occurs in all oil to water ratios because all enrichment ratios of oil are higher than unity. The highest diesel enrichment ratio is located at the moderate oil to water ratio. Increasing oil to water ratio increases almost linearly the enrichment ratio of diesel until 1:4 oil to water ratio is reached. The diesel enrichment ratio declines substantially when the oil to water ratio increases to 1:1. This may be due to foam lamellae become thinner as the oil to water ratio increases. Therefore, less water is attached to the foam with increasing lower oil to water ratios. However, increasing oil to water to 1:1 does not yield the highest enrichment ratio because viscosity of solution is higher resulting in lower water drainage rate from the foam lamellae. For the effect of u_G, the diesel enrichment ratio is not significantly affected by u_G because some water entrains back to the solution at high u_G (Figure 6.6). It is interesting to note that, as shown in Table 1, the diesel enrichment ratio of the non-equilibrium system is the same as that of the equilibrium system while the induced equilibrium system yields a slightly higher enrichment ratio of diesel than both non-equilibrium and equilibrium systems.

6.5 Conclusions

In this study, the process performance of froth flotation was correlated with IFT, foam characteristics, and coalescence time between oil droplets. From the results in this work, the foam characteristics have profound effect on oil removal apart from the system IFT. However, the coalescence time between oil droplets does not significantly affect the efficiency of froth flotation. This may be because the limitation of the hydrophobic space at the bubble surfaces governs the oil removal efficiency. Even though the coalescence between oil droplets occurs easily but there is no enough space for those coalesced oil droplets to sustain in the froth. The effects of operating variables in flotation cell were also elucidated. Similar to our previous work (14), the air superficial velocity has to be optimized to get the maximum efficiency of diesel removal. However, unlike the ethylbenzene study (14), agitation of solution before being transferred to the column was found to yield the lowest diesel removal. Therefore, a short period of time of agitation is not necessary to move solution towards to its equilibrium state.

6.6 Acknowledgements

The Thailand Research Fund is acknowledged for providing a Royal Golden Jubilee Ph.D. Fellowship to Ms. Ummarawadee Yanatatsaneejit as well as providing a research grant under TRF Advanced Research Scholar. The Research Unit of Applied Surfactants for Separation and Pollution Control supported by the Ratchadapiseksompoch Fund from Chulalongkorn University and the Petroleum and Petrochemical Technology Consortium under the Minister of Education are also acknowledged for providing financial support and facilities, respectively. Financial support for this research was also received from the industrial sponsors of the Institute for Applied Surfactant Research, University of Oklahoma including Akzo Nobel, Clorox, Conoco/Phillips, Church and Dwight, Dial, Ecolab, Halliburton, Kerr-McGee, Huntsman, Procter & Gamble, Shell, and Unilever.

6.7 References

1. State Home Page. http://www.state.co.us/gov_dir/leg_dir/olls/sl1993/sl.79.htm (accessed April 2004).
2. UOP Home Page. http://www.uop.com/solutions and innovation/ Issues%20&%20 Solutions/UOPDieselFuel.pdf (accessed April 2004).

3. Yarar, B. Flotation, In *Encyclopedia of separation technology Vol.2*; Ruthven, D.M., Ed.; John Wiley & Sons: New York, 1997; 913 – 939.

4. Nabih, H.I.; Omar, A.M.A.; Kenawi, F.I. Development of a Froth Flotation Process for Recovery of Used Emulsified Oil. Pet. Sci. Technol. **2003**, *21*, 211 – 219.

5. Walcarius, A.; Lamdaouar, A.M.; Kacemi, K.E.; Marouf, B.; Bessiere, J. Recovery of Lead-Loaded Zeolite Particles by Flotation. Langmuir. **2001**, *17*, 2258 – 2264.

6. Zhu, J.Y.; Wu, G.H.; Deng, Y. Flotation Deinking of Toner-Printed Papers Using Frother Spray. J. Pulp Pap. Sci. **1998**, *24*, 295 – 299.

7. Moon, T.; Nagarajan, R. Deinking Xerographic and Laser-Printed Paper Using Block Copolymers. Coll. Surf. A. **1998**, *132*, 275 – 288.

8. Rosen, M.J. *Surfactant and Interfacial Phenomena*; 2nd Ed.; Wiley: New York, 1989; 276 – 303.

9. Chang, Z.D.; Liu, H.Z.; Chen, J.Y. Foam Separation of Tributyl Phosphate from Aqueous Solutions: Part I Exteriment. Sep. Purif. Technol. **2000**, *19*, 131 – 136.

10. Pondstabodee, S.; Scamehorn, J.F.; Chavadej, S.; Harwell, J.H. Cleanup of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation. Sep. Sci. Technol. **1998**, *33*, 591 – 609.

11. Chavadej, S.; Phoochinda, W.; Yanatatsaneejit, U.; Scamehorn, J.F. Clean-up of Oily Wastewater by Froth Flotation: Effect of Microemulsion Formation III: Use of Anionic/Nonionic Surfactant Mixtures and Effect of Relative Volumes of Dissimilar Phases. Sep. Sci. Technol. **2004**, *39*, 3021 – 3036.

12. Yanatatsaneejit, U.; Witthayapanyanon, A.; Rangsunvigit, P.; Acosta, E.J.; Sabatini, D.A.; Scamehorn, J.F.; Chavadej, S. Ethylbenzene Removal by Froth Flotation Under Conditions of Middle-Phase Microemulsion Formation I: Interfacial Tension, Foamability, and Foam Stability. Submitted to Sep. Sci. Technol.

13. Huh, C. Equilibrium of a Microemulsion that Coexists with Oil or Brine. Soc. Pet. Eng. J. **1983**, *23*, 829 – 847.

14. Yanatatsaneejit, U.; Chavadej, S.; Rangsunvigit, P.; Scamehorn, J.F. Ethylbenzene Removal by Froth Flotation Under Conditions of Middle-Phase Microemulsion Formation II: Effects of Air Flow Rate, Oil to Water Ratio, and Equilibration time. Submitted to Sep. Sci. Technol.

15. Hudson, S.D.; Jamieson, A.M.; Burkhart, B.E. The Effect of Surfactant on The Efficiency of Shear-Induced Drop Coalescence. J. Coll. Int. Sci. **2003**, *265*, 409 – 421.

16. Nandi, A.; Agterof, W.G.M.; Van Den Ende, D.; Mellema, J. Investigation of the effect of a simple salt on the kinetics of gravity induced coalescence for a viscosity matched emulsion system. Coll. Suf. A **2003,** *213*, 199 – 208.

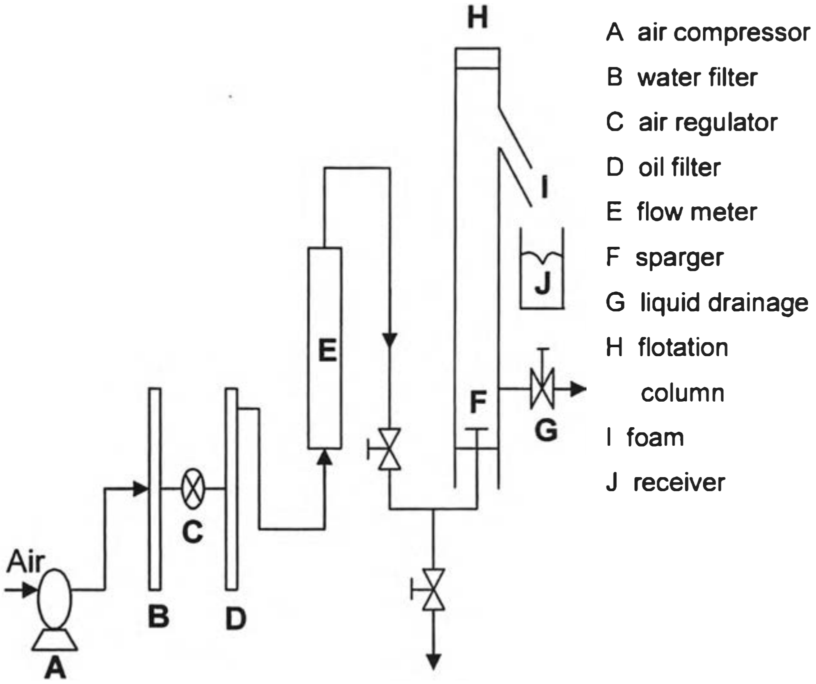

Figure 6.1 Schematic diagram of the froth flotation apparatus

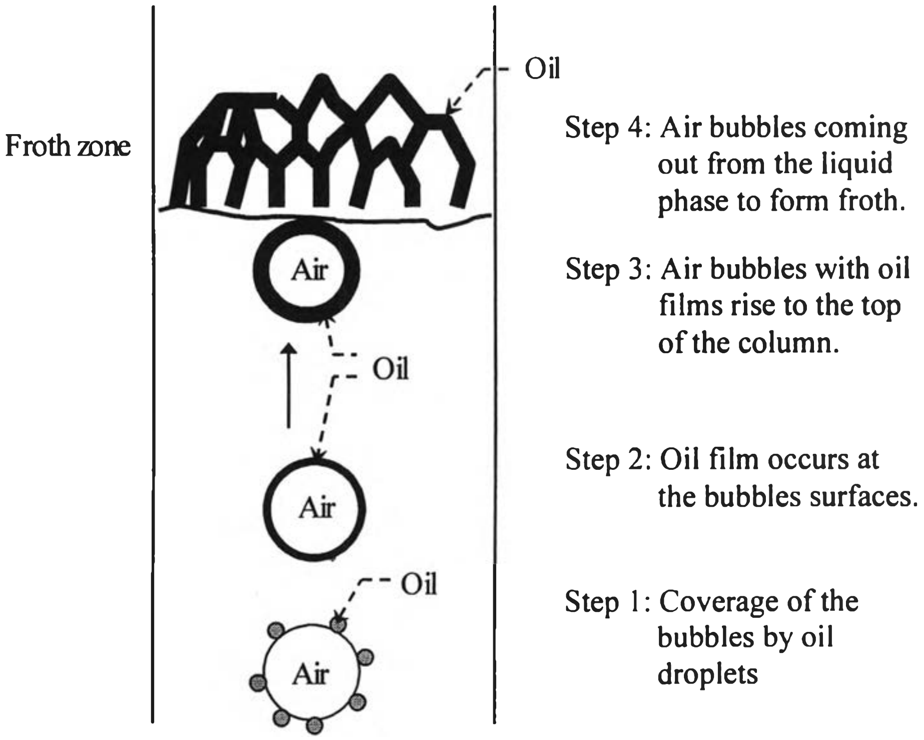

Figure 6.2 Proposed mechanism in froth flotation operation

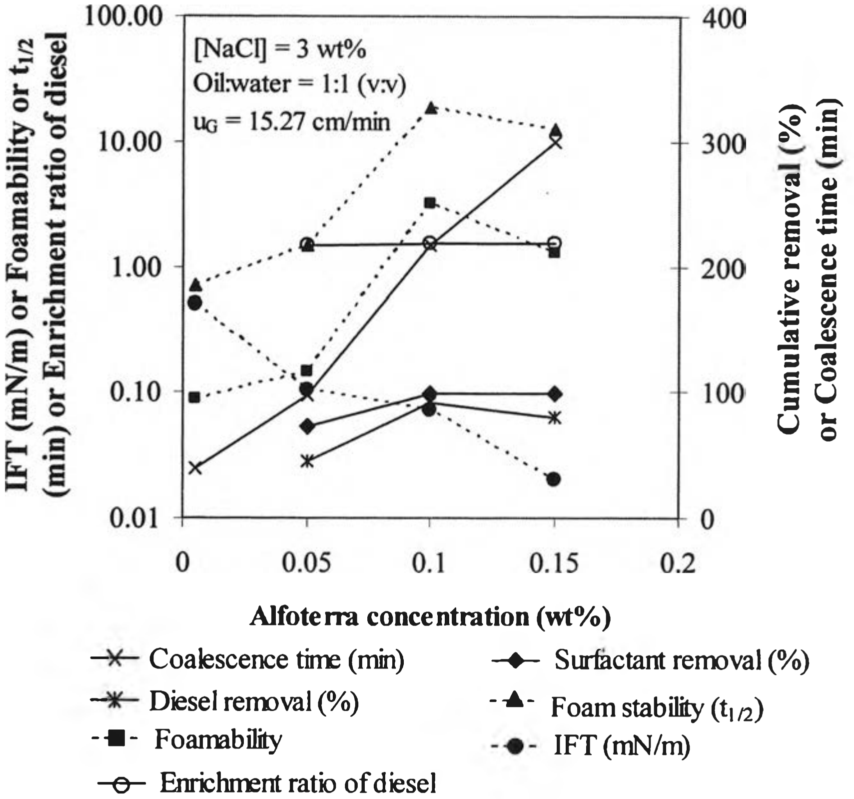

Figure 6.3 Effect of surfactant concentration on process parameters

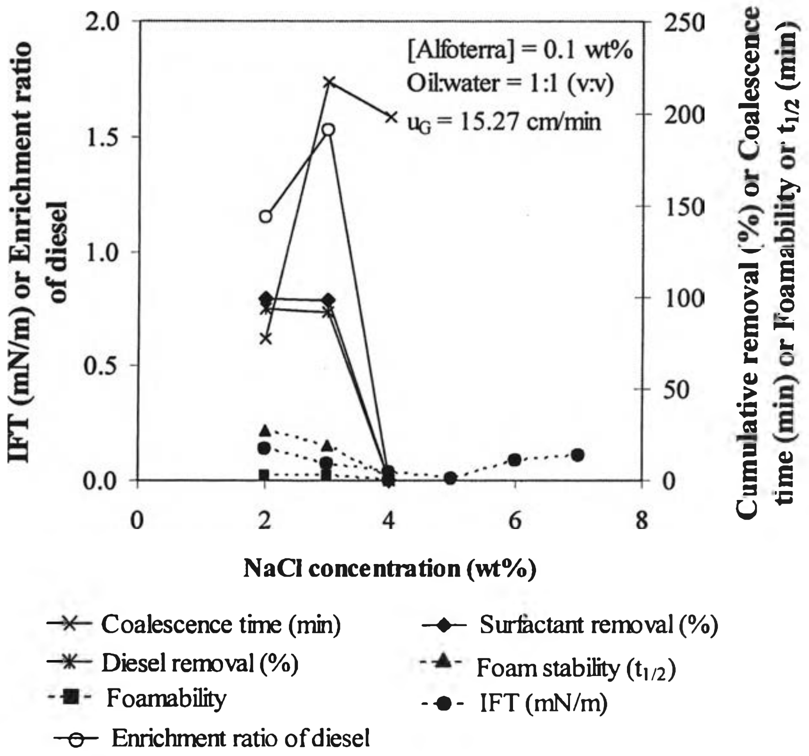

Figure 6.4 Effect of NaCl concentration on process parameters

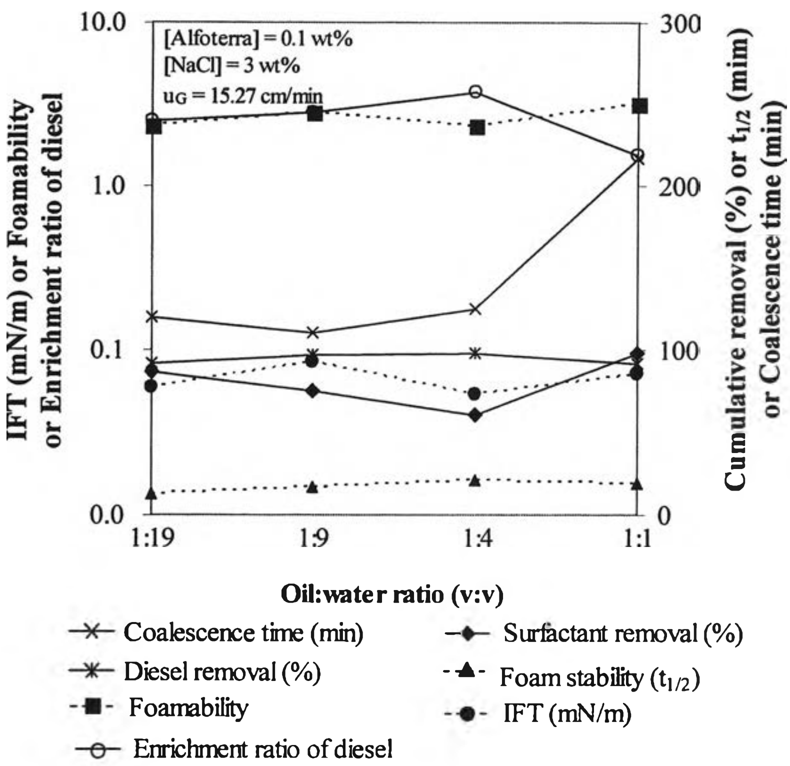

Figure 6.5 Effect of oil to water ratio on process parameters

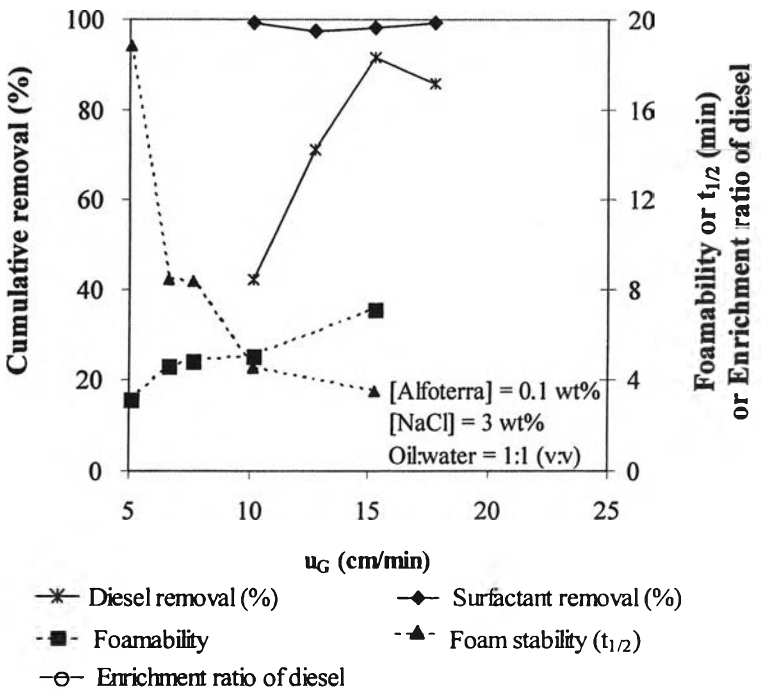

Figure 6.6 Effect of air superficial velocity on process parameters

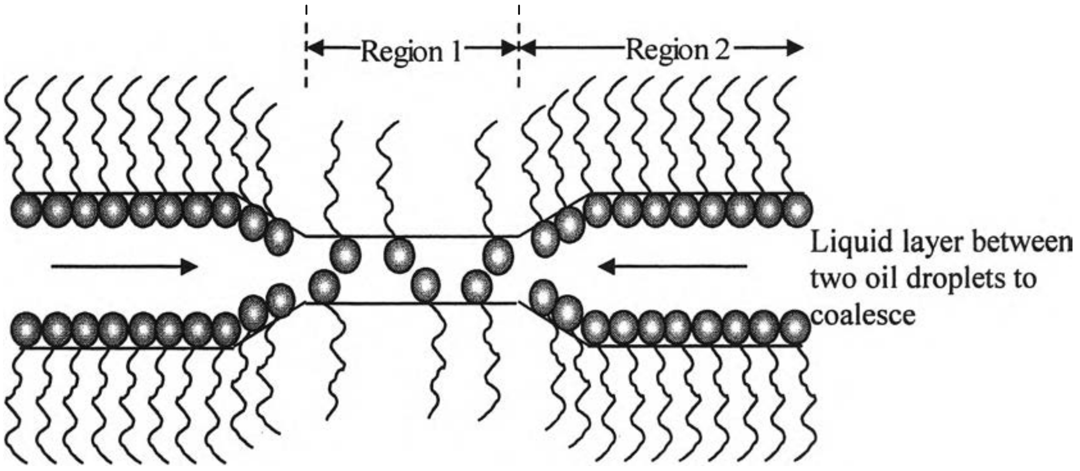

Figure 6.7 Mechanism for film elasticity (8)

Table 6.1 Effect of equilibration condition on process parameters at fixed Alfoterra concentration of 0.10 wt%, NaCl concentration of 3 wt%, and oil to water ratio of 1:1

System	IFT (mN/m)	Total cumulative removal (%)		Enrichment ratio of diesel	Foamability	$t_{1/2}$ (min)
		Diesel removal	Alfoterra removal			
Non-equilibrium	0.109	91.54	98.30	1.53	3.13	18.82
Induced-equilibrium	0.159	54.46	46.89	1.62	0.11	0.87
Equilibrium	0.036	96.86	74.06	1.53	3.21	20.03