



CHAPTER IV

DIESEL OIL REMOVAL FROM WATER BY FROTH FLOTATION UNDER LOW INTERFACIAL TENSION AND COLLOIDAL GAS APHRON CONDITIONS

4.1 Abstract

The objective of this work was to investigate the relationship between the froth characteristics, the system interfacial tension (IFT), and the efficiency of diesel oil removal by froth flotation under colloidal gas aphon (CGA) conditions. Branched alcohol propoxylate sulfate sodium salt ($C_{14-15}(PO)_5SO_4Na$) as an extended surfactant, was used to form CGA and microemulsions with diesel oil. For the CGA studies, the effects of salinity, surfactant concentration, stirring speed, and stirring time were investigated in order to determine the optimum conditions of the CGA formation which were further used for the froth flotation experiments. The air bubble size measurement was carried out in order to correlate the air bubble size to the froth flotation performance. The results showed that the use of CGA enhanced the process performance of froth flotation in terms of both the removal and the enrichment ratio of diesel oil since CGA increased both froth formation and stability. The froth flotation column which was operated at an air flow rate of 0.30 l/min with the feed solution prepared under non-equilibrium and the CGA conditions at 0.1 wt.% $C_{14-15}(PO)_5SO_4Na$, 3 wt.% NaCl, with a stirring speed of 5,000 rpm and a stirring time of 5 min, gave the highest oil removal of 97%.

Keywords: Froth flotation, Colloidal gas aphon, Microemulsion, Bubble size

4.2 Introduction

In most countries around the world, including Thailand, the demand for diesel oil is much higher than that for gasoline. This is because diesel oil provides more energy per unit volume than gasoline does (1). Apart from being used mainly for transportation, diesel oil is widely used in industry. In the US and Latin America, diesel oil is used primarily for the transportation of goods. Interestingly, in Europe, Japan, and elsewhere, diesel oil is a significant source of energy for personal transportation (2). Hence, the demand for diesel oil is forecasted to grow faster than those for other fuels, in general. Consequently, the contamination of groundwater by diesel oil from leakage from gas stations and underground storage tanks is of concern. Diesel oil is often found to be present as free oil and as an oil-in-water emulsion in polluted water because many components in diesel oil have low water solubilities.

Froth flotation is a surfactant-based separation process in which a surfactant is added to help the separation (3). It was first used in ore processing, and it has been pointed out to be a promising technique for oily wastewater treatment (4-6). The froth flotation process is suitable for treating wastewater containing suspended solids as well as oils in both emulsified and undissolved forms since it offers several advantages, including rapid operation, low space requirements for equipment set-up, high removal efficiency, flexibility for application to various pollutants at various scales, and its low cost in operation (7). In a froth flotation operation, a surfactant is added to an oily wastewater and air is introduced into the bottom of a flotation cell in order to generate fine bubbles. The surfactant tends to adsorb preferentially at the air/water interface with the hydrophilic, or head groups, in the water and the hydrophobic, or tail groups, in the air. As a result, oil will concentrate at the bubble surfaces while they rise through the solution to form froth, at the top of the flotation cell, which is continuously skimmed off. Basically, the formation of stable bubble particle aggregates, or froth, is required in the froth flotation operation to achieve a high separation efficiency (8).

From previous work (9), the maximum oil removal was found to correspond to a Winsor Type III microemulsion condition, and this was the starting point of our research group to continue studying the relationship between the Winsor Type III microemulsion and the froth flotation efficiency with different types of oils. A Winsor Type III microemulsion has superior characteristics, such as relatively large interfacial area, high solubilization capacity, and ultralow interfacial tension (IFT) (10). The last one is the most interesting characteristic and has been focused on in our series of published papers. Recently, Yanatatsaneejit *et al.* (11) studied ethylbenzene removal from water by froth flotation under Winsor Type III microemulsion conditions. An important finding of this work is that both low IFT and good frothing are necessary for a high efficiency separation of ethylbenzene. This finding of the importance of froth stability was also observed by Carre *et al.* (12). In addition, Yanatatsaneejit *et al.* (13) reported that a high froth stability was needed in order to obtain a dry froth with high oil content. They determined that there were two important parameters used to indicate froth characteristics — froth formation and froth stability. Froth formation is the foam-generating power at the initial stage of foaming, whereas froth stability is the persistence of froth collapse. Therefore, the higher the froth formation and froth stability, the higher the percentage of oil removal. Yanatatsaneejit *et al.* (14) further correlated the performance of batch froth flotation to remove diesel oil from water with IFT, froth characteristics, and coalescence time between oil droplets. From the results in their work, the froth characteristics were revealed to have a profound effect on oil removal, apart from the system IFT. However, the coalescence time between oil droplets did not significantly affect the efficiency of the froth flotation. Based on their work, to maximize the performance of the froth flotation operation, the combination of an ultralow IFT between the oil and the water and good stability of the produced froth must be achieved. Recently, Watcharasing *et al.* (15) studied the relationship between IFT and froth characteristics with the diesel oil removal efficiency of continuous froth flotation by using the mixed surfactants of branched alcohol propoxylate sulfate, sodium salt ($C_{14-15}(PO)_5SO_4Na$), and sodium dodecyl sulfate (SDS). Because the use of $C_{14-15}(PO)_5SO_4Na$ alone was found to produce froth with very poor stability, SDS was added in order to obtain a highly stable froth

for the success of the continuous froth flotation operation with a high diesel oil removal. Both froth formation and stability were found to be more important than the system IFT to achieve a high oil removal in the continuous froth flotation operation. Moreover, the air flow rate was suggested to be optimized to get maximum diesel oil removal efficiency.

In order to solve the low froth stability of diesel oil systems mentioned in the previous work, colloidal gas aphron (CGA) was introduced in the present study, instead of adding SDS. The use of CGA was hypothesized to enhance the efficiency of froth flotation by increasing froth stability. CGA was first described by Sebba (16) as microfoams with colloidal properties. The term "colloidal" is used because of the small sizes of the bubbles generated (10-100 μm in diameter). CGA can be created by intense stirring (5,000-10,000 rpm) of a surfactant solution (16, 17). The intense stirring of a surfactant solution causes air entrainment in the microbubbles, leading to increasing froth stability. The structure of CGA proposed by Sebba (17) is composed of a gaseous inner core surrounded by a thin aqueous surfactant film or shell composed of two surfactant layers; moreover, there is a third surfactant layer that stabilizes this structure (see Figure 4.1). The attractive features of CGA have been reported to be: 1) CGA has a large interfacial area per unit volume, as a result of its small size and high gas hold-up; 2) CGA exhibits relatively high stability; 3) the flow properties of CGA are similar to those of pure water (e.g. can be pumped easily, without collapse, from one location to another); and, 4) the CGA phase can be separated easily from the bulk liquid phase due to its buoyancy. As a result of these unique properties, CGA was reported to be employed in several studies: in the removal of biological and non-biological products (18-19), in protein recovery (20-22), in bioremediation (23), and in the enhancement of oxygen mass transfer (24).

Therefore, in this study, CGA was applied for the enhancement of froth stability in the froth flotation operation, which was hypothesized for the improvement of oil removal efficiency. The effects of stirring speed, stirring

time, surfactant concentration, and salinity on the CGA formation were studied in order to find the optimum conditions for the froth flotation experiment. The froth flotation performance and froth characteristics were correlated to the stability of CGA.

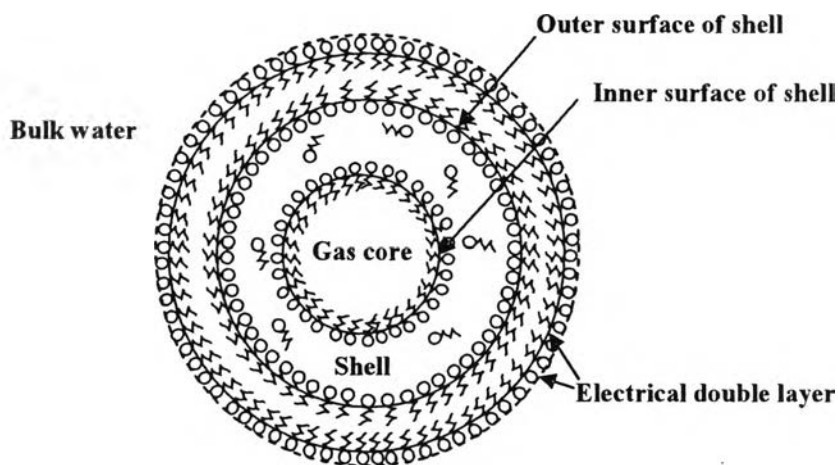


Figure 4.1 Structure of CGA proposed by Sebba (1987).

4.3 Experimental Section

4.3.1 Materials

In this work, branched alcohol propoxylate sulfate, sodium salt ($C_{14-15}(PO)_5SO_4Na$), with a purity of 28.7% in liquid form, was supplied by Sasol North America Inc., Texas, USA. $C_{14-15}(PO)_5SO_4Na$ is an anionic extended surfactant having 14-15 carbon atoms and 5 groups of propylene oxide (PO) in the tail group which provides high hydrophobicity. Diesel oil is selected as a model contaminant oil in this research work was purchased from PTT Public Co., Ltd (Thailand). Analytical grade sodium chloride (NaCl) with 99% purity was obtained from Labscan Asia Co., Ltd. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

4.3.2 Methods

This experimental work was divided into five main parts. The first part was a phase study of microemulsions with diesel oil. The second was a study of colloidal gas aphon (CGA). The third was froth flotation experiments conducted at various air flow rates for three different feed solution conditions: 1) non-equilibrium without CGA; 2) equilibrium without CGA; and 3) non-equilibrium with CGA. For the fourth part, froth formation and stability experiments were conducted. In the last part, the air bubble size measurement was done in order to correlate the air bubble size to the froth flotation performance. For all experiments, the surfactant concentration and salinity were expressed as percentage by weight based on aqueous solution volume.

4.3.2.1 Microemulsion Phase Studies

A 5 ml quantity of diesel oil was added to a series of vials, each containing 5 ml of a surfactant solution having different surfactant concentrations and salinities. After that, each vial was shaken gently by hand for 1 min and then equilibrated in a temperature-controlled incubator (Binder, KB400/E2) at 30°C until the system reached equilibrium. The equilibrium state was considered to be attained when the volume of each phase of the microemulsion system was invariant. The measurement of phase height was conducted by using a cathetometer, model TC-II from Titan Tool Supply, Inc., attached to a digimatic height gauge, model 192-631, from Mituyo, with ± 0.002 mm accuracy. The interfacial tension (IFT) between the diesel oil and the various surfactant solutions was measured using a spinning drop tensiometer (Krüss, SITE 04).

4.3.2.2 Studies of Colloidal Gas Aphrons

A 5 ml quantity of diesel oil was added to 95 ml of a surfactant solution which contained different concentrations of $C_{14-15}(PO)_5SO_4Na$ and NaCl. CGA was generated at different speeds in the range of 4,000 to 8,000 rpm, and different stirring times, by using a homogenizer (Kinematica, PT 3100). After that, the system was allowed to separate to obtain a milky CGA (top) phase, or froth, and a clear solution (bottom) phase. Both phases were analyzed for oil content and

volume in order to calculate the separation ratio and gas hold-up. The separation ratio is defined as the ratio of the oil concentration in the collapsed CGA phase to that in the retaining liquid phase:

$$\text{Separation ratio} = \frac{C_g}{C_l} \quad [1]$$

where C_g is the concentration of oil in the collapsed CGA, C_l is the concentration of oil in the clear liquid phase below the CGA phase (retaining liquid phase). Gas hold-up is another factor affecting the stability of the CGA phase since the higher the gas hold-up in the CGA phase is, the lower the water content in the CGA phase is, leading to a lower density. The gas hold-up was determined immediately after stopping the stirring. The term “gas hold-up” is calculated by the following equation:

$$\text{Gas hold-up (\%)} = \frac{(V_g)}{V_i}(100) = \frac{(V_i - V_l)}{V_i}(100) = \frac{(h_i - h_l)}{h_i}(100) \quad [2]$$

where V_g is the gas volume in the CGA phase, V_l is the liquid volume of the collapsed CGA, V_i is the initial CGA volume, h_l is the height of the initial liquid volume, and h_i is the height of the dispersion. The stability of the CGA is defined as the time required for the volume of CGA to reduce by half the initial value after mixing is stopped. The enrichment ratio of diesel oil is defined as the diesel oil concentration in the collapsed CGA to that in the initial feed:

$$\text{Enrichment ratio} = \frac{C_g}{C_i} \quad [3]$$

where C_g is the concentration of oil in the collapsed CGA, C_i is the concentration of oil in initial solution. The oil removal is calculated by the following equation:

$$\text{Oil removal (\%)} = \frac{(C_i V_i - C_l V_l)}{C_i V_i}(100) \quad [4]$$

where C_1 is the concentration of oil in the clear liquid phase below the CGA phase, C_i is the concentration of oil in the initial solution, V_1 is the volume of the clear liquid phase, and V_i is the volume of the initial solution. To achieve a high enrichment ratio and high removal of diesel oil, it is desirable to have a stable CGA system, since the separated oil simply concentrates in the CGA phase. The CGA experiments were conducted at room temperature ($26 \pm 1^\circ\text{C}$).

4.3.2.3 Froth Flotation Experiments

Figure 4.2 is a schematic of the batch froth flotation unit used in this study. The froth flotation apparatus consisted of a glass cylindrical column with a 5-cm inside diameter and a 120-cm height. A 100 ml quantity of fresh CGA slurry produced at the optimum conditions was transferred to the froth flotation column. Compressed air was first filtered to remove all solid particles and oil and was then passed through a water filter before sparging through a sinter glass disk (16-40 μm pore size) at the bottom of the froth flotation column. The flow rate of the filtered air was regulated by a mass flow controller (GFC171S, Aalborg). The air bubbles ascended through the CGA slurry generated foam. The froth overflowing from the column was collected over different time intervals. The experiment was conducted until no froth came out from the column due to the surfactant depletion. After that, the collected froth was allowed to collapse and was analyzed for its diesel oil and surfactant concentrations by using the extraction method with methylene chloride and titration method with methylene blue chloride, respectively. The details of the analytical methods for determining the concentrations of diesel oil and surfactant are reported elsewhere (25, 26). Table 4.1 shows design and froth flotation operating conditions used in this study.

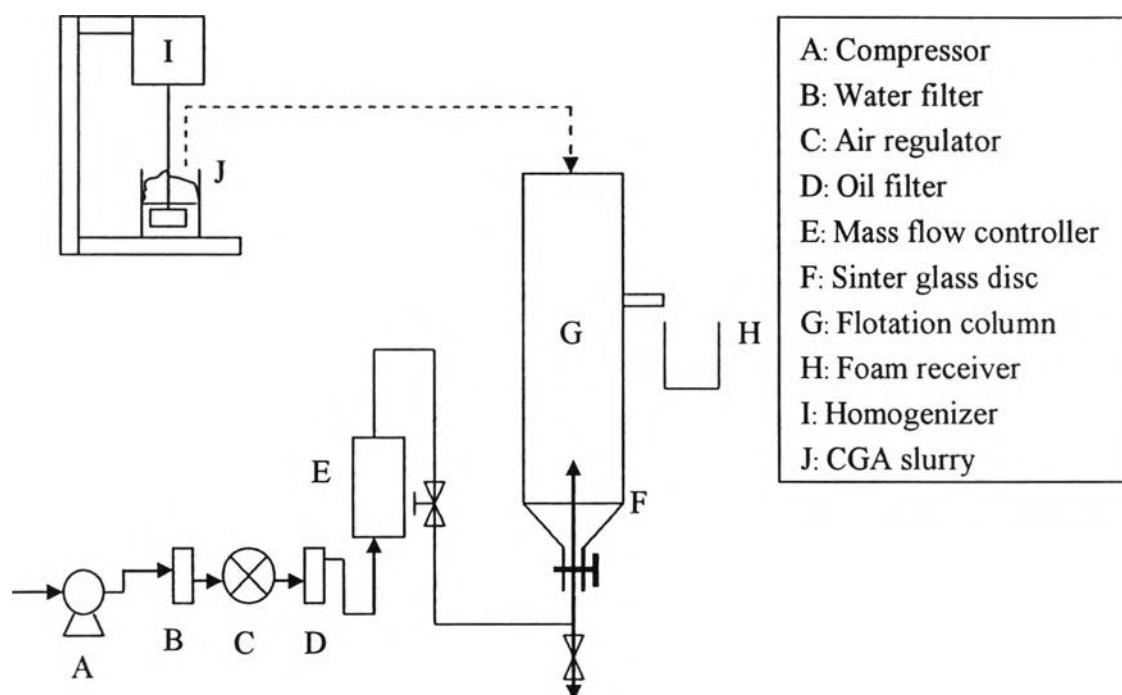


Figure 4.2 Schematic of the froth flotation apparatus applied with CGA.

Table 4.1 Design and operating specifications of froth flotation column

Column variable	Value
Inside diameter (cm)	5
Height (cm)	120
Sinter glass disk (μm)	16-40
Air flow rate (l/min)	0.2, 0.25, 0.3, 0.35
$[\text{C}_{14-15}(\text{PO})_5\text{SO}_4\text{Na}]$ (wt.%)	0.1
$[\text{NaCl}]$ (wt.%)	3
Oil:water ratio	1:19

The diesel oil removal can be calculated by the following (5):

$$\text{Oil removal (\%)} = \frac{(C_i V_i - C_f V_f)}{C_i V_i} (100) \quad [5]$$

where C_f is the concentration of oil in the collapsed froth, C_i is the concentration of oil in a feed solution, V_f is the volume of the collapsed froth, and V_i is the initial volume of the feed solution. The enrichment ratio of diesel oil is defined as the ratio of the oil concentration in the overhead froth to that in the feed:

$$\text{Enrichment ratio} = \frac{C_f}{C_i} \quad [6]$$

where C_f is the concentration of oil in the overhead collapsed froth, C_i is the concentration of oil in a feed solution. In order to determine the effects of CGA and equilibration time on the performance of froth flotation, the studied froth flotation column was operated with three different feed conditions: 1) non-equilibrium without CGA; 2) equilibrium without CGA; and, 3) non-equilibrium with CGA. All froth flotation experiments were conducted at room temperature ($26 \pm 1^\circ\text{C}$). For any particular studied conditions, the experiment was run at least a few times to ensure reproducibility, and the experimental data with a standard deviation were averaged to assess the process performance. The percent relative standard deviation is less than 5%.

4.3.2.4 Froth Formation and Froth Stability Experiments

For the froth formation and froth stability experiments, 100 ml of a sample having different conditions from those used in the froth flotation experiments was transferred to the same froth flotation column. The solution in the column was sparked at different air flow rates until the froth height in the column reached a maximum. The maximum froth height is used to indicate the ability to form froth or froth formation. After that, the introduction of filtered air into the column was stopped. The time required for the froth volume to collapse by half was recorded to express froth stability.

4.3.2.5 Measurement of Size of CGA Froth and Air Bubbles in Froth Flotation Column

The measurement of froth sizes of the CGA sample was performed immediately after finishing stirring the surfactant solution at different conditions used to form CGA. In addition, the measurement of air bubble sizes was conducted in the same column that was used in the froth flotation experiments. Images of the air bubbles were taken by using a color video camera (Sony, SSC-DC58AP/1) connected to the optical lens (OPTEM). A light generation unit (Photonic, PL 3000) was used as a light source to obtain clear-cut images. In order to minimize the effect of the curvature of the column on the images taken by the camera, the point on the centerline of the column was used for taking the photographs at the position 1 cm above the sinter glass disc. One hundred images were taken at a time interval of 1 s. In addition to the measurement of the froth size of CGA, at least 500 pictures of air bubbles were fitted to evaluate the diameter of individual bubbles, and then the average bubble diameter was calculated using Image-Pro Plus software (version 5.1). Figure 4.3 shows images of the CGA froth and air bubbles in the froth flotation column.

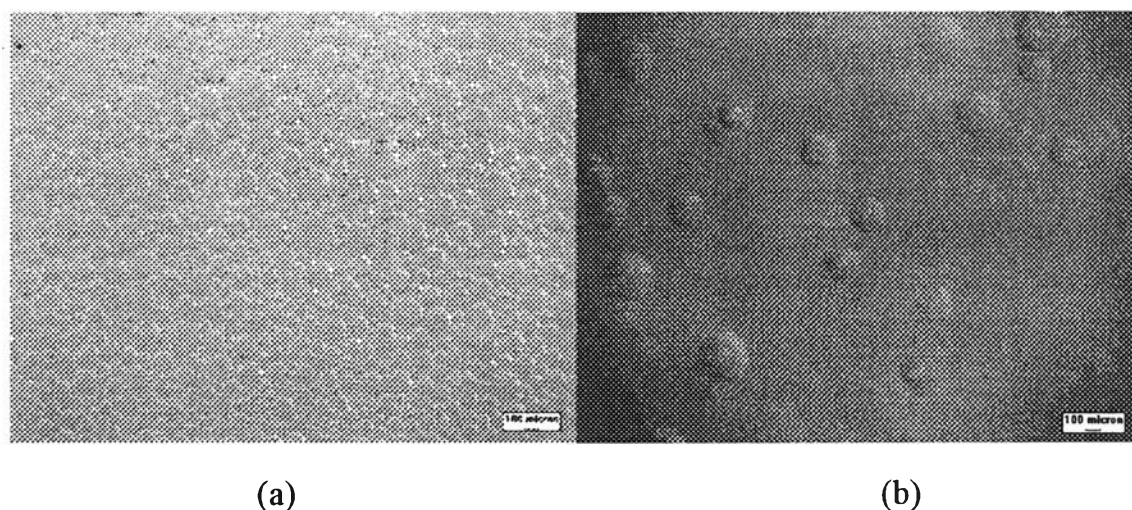


Figure 4.3 Images of air bubbles: (a) CGA froth (at a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, a $[NaCl]$ of 3 wt.%, an oil:water ratio of 1:19, a stirring time of 5 min, and a stirring speed of 5,000 rpm) and (b) air bubbles in the froth flotation column (non-equilibrium with CGA).

4.4 Results and Discussion

4.4.1 Interfacial Tension (IFT) and Microemulsion Types

From our series of previous studies (9, 11, 13, 14, 15), to maximize oil removal in the froth flotation operation, the system IFT, which is the surface free energy across the interface of diesel oil and surfactant solution phases, primarily needed to be minimized. In this study, $C_{14-15}(PO)_5SO_4Na$ was selected to form microemulsions with diesel oil, which was found to exhibit low or ultralow IFT. However, this studied system exhibited only two obvious phases, the water and oil excess phases, suggesting that $C_{14-15}(PO)_5SO_4Na$ alone cannot promote the formation of a Winsor Type III microemulsion with a large volume fraction of the middle phase. Hence, a minimum IFT was used to indicate the optimum conditions for the preparation of feed solutions to run froth flotation experiments, instead of using the point having the largest volume of the middle phase, as described in our previous works. Figure 4.4 shows the equilibrium IFT between the diesel oil and aqueous phases as a function of salinity and $C_{14-15}(PO)_5SO_4Na$ concentration. For any given salinity, an increase in surfactant concentration decreased the system IFT. Interestingly, the results showed that there was an optimum range of surfactant concentration for a minimum IFT. Beyond the optimum surfactant concentration, the IFT system reaches the minimum IFT. For any given surfactant concentration, the system IFT decreased with increasing salinity and reached a minimum. A further increase in salinity beyond the optimum salinity (at the minimum IFT) increased the system IFT. An increase in salinity caused the phase transformation from Winsor Type I (oil-in-water) to Type III (middle phase) and Type II (water-in-oil) microemulsions. This result of the Winsor Type boundary also corresponds with a microemulsion phase diagram (fish diagram) of diesel oil, which is reported elsewhere (15). The explanation of the effects of surfactant and NaCl concentrations on the IFT has been given in previous work (15). Regarding minimizing the cost of surfactant, a lowest surfactant concentration of 0.1 wt.% was selected for further investigation.

4.4.2 Performance of Colloidal Gas Aphron (CGA)

The CGA experiments were carried out to investigate the effects of salinity, surfactant concentration, stirring speed, and stirring time at a constant diesel oil-to-surfactant solution ratio of 1:19. In this part, diesel oil removal and enrichment ratio were considered to be significant parameters to evaluate the performance of CGA. In addition, CGA stability, gas hold-up, and separation ratio were also used to determine the CGA performance.

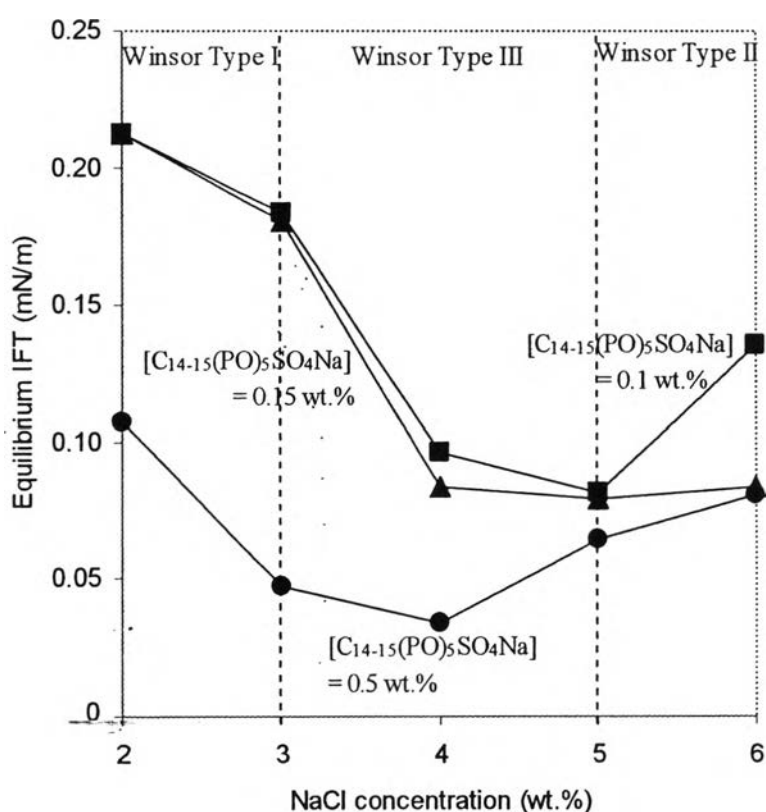
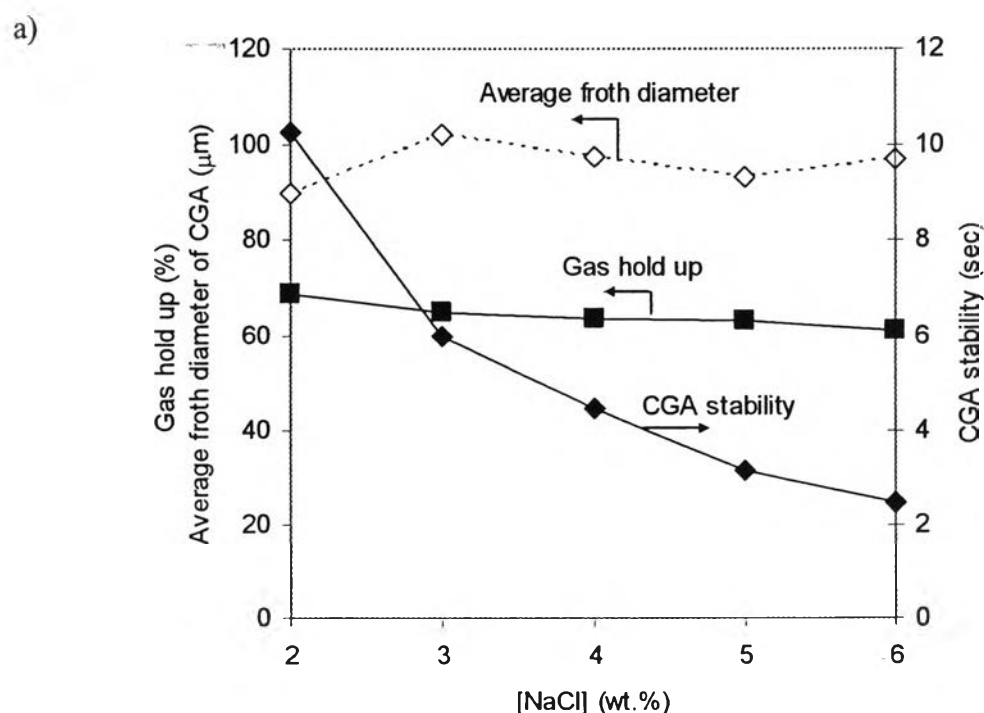


Figure 4.4 Equilibrium IFT and microemulsion type with diesel oil as a function of salinity at various $C_{14-15}(PO)_5SO_4Na$ concentrations, an oil-to-water ratio of 1:1, and at 30°C.

4.4.2.1 Effect of NaCl Concentration on the CGA Performance

Salinity (ionic strength) has an important effect on CGA stability when CGA is generated using an ionic surfactant. As shown in Figure 4.5(a), when the NaCl concentration increases from 2 to 6 wt.%, the CGA

stability decreases, confirming that the electrostatic interactions between the head group of the surfactant and the counterion play an important role in the stability of this type of dispersion. The addition of NaCl simply reduces the electrostatic interactions between the inner and outer shells of CGA, leading to lowering the stability of CGA. Interestingly, the separation ratio of the CGA system had the same trend as the CGA stability as shown in Figure 4.5(b). The gas hold-up appeared to be independent of the change of salinity. This is because the gas hold-up was determined immediately after stopping the stirring. As the NaCl concentration increased, the diesel oil removal decreased, but the enrichment ratio increased. The explanation for this is that the stability of CGA decreased with increasing NaCl concentration. The results suggest that the lower the IFT is, the higher the enrichment ratio is. Moreover, the average diameter of the froth in the CGA phase does not change significantly with salinity in the studied range. For the effect of NaCl concentration on the CGA performance, the CGA stability is an important parameter, strongly affecting the CGA performance more than the diameter of froth. From the results, 3 wt.% NaCl, which corresponded to the highest diesel oil removal and separation ratio, was selected for investigating the effect of surfactant concentration.



b)

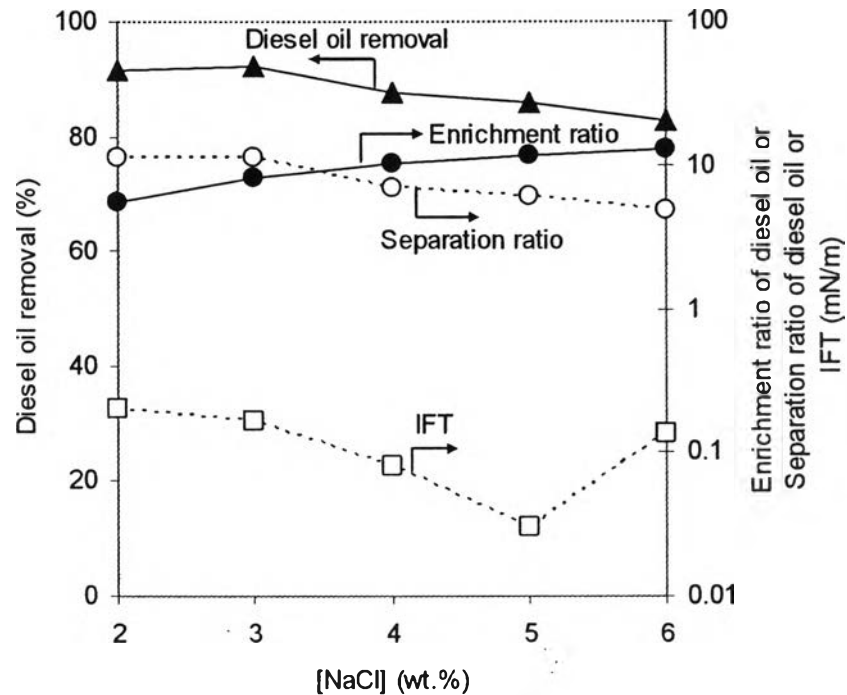


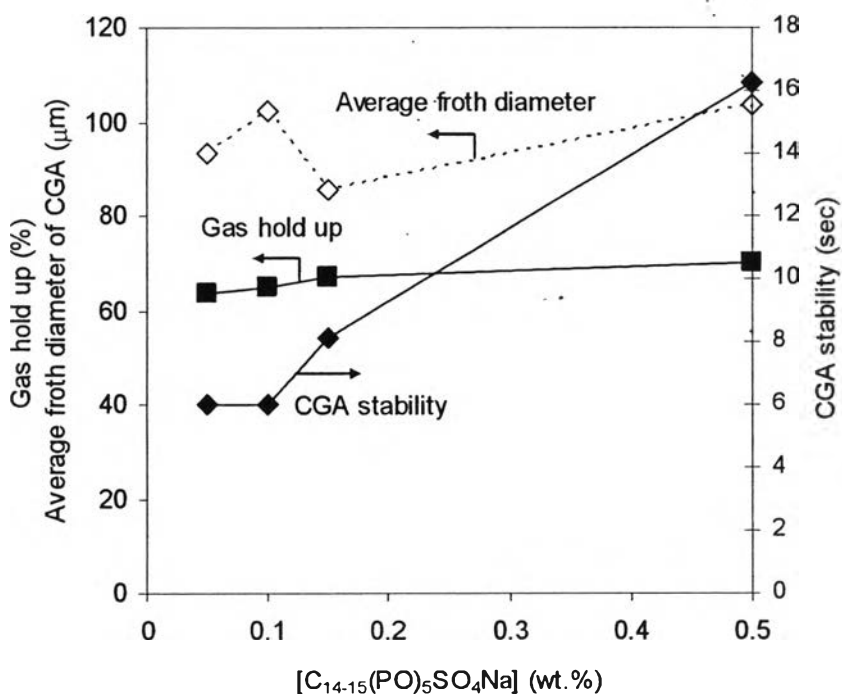
Figure 4.5 Effect of NaCl concentration on the performance of CGA: (a) CGA properties, and (b) separation efficiency of CGA and IFT (operated at a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, an oil:water ratio of 1:19, a stirring speed of 5,000 rpm, and a stirring time of 5 min).

4.4.2.2 Effect of Surfactant Concentration on the CGA Performance

Figure 4.6(a) shows that the CGA stability and gas hold-up increase slightly with increasing surfactant concentration; these results are consistent with previous work (27, 28). As the surfactant concentration increases, the repulsive and stabilizing forces between the air bubbles in the CGA phase and in the bulk liquid phase are likely to increase. Consequently, it will delay the coalescence rate of aephrons. Moreover, a larger amount of aephrons should be formed at a higher surfactant concentration. As shown in Figure 4.6 (b), The enrichment ratio of diesel oil decreases slightly with increasing surfactant concentration and reaches a minimum at a surfactant concentration of 0.1 wt.%. Beyond a 0.1 wt.% surfactant concentration, the enrichment ratio slightly increased with increasing surfactant

concentration. The diesel oil removal showed an opposite trend as the enrichment ratio of diesel oil. Interestingly, the trend of the average froth diameter in the CGA phase was found to be similar to that of the diesel oil removal, except at the highest surfactant concentration of 0.5 wt.%. The highest percentage of oil removal was found at a $C_{14-15}(PO)_5SO_4Na$ concentration of 0.1 wt.%; and the separation ratio also had a similar trend. It is very interesting to point out that the maximum diesel oil removal corresponds to the lowest system IFT, as shown in Figure 4.6(b). The results suggest that the lower the IFT is, the higher the diesel oil removal is. However, at a very high surfactant concentration of 0.5 wt.%, the average froth diameter of CGA further increased. From the results, 0.1 wt.% $C_{14-15}(PO)_5SO_4Na$, which gave the highest for both diesel oil removal and separation ratio corresponding to the largest froth size, was chosen as the optimum concentration for the next experiments.

a)



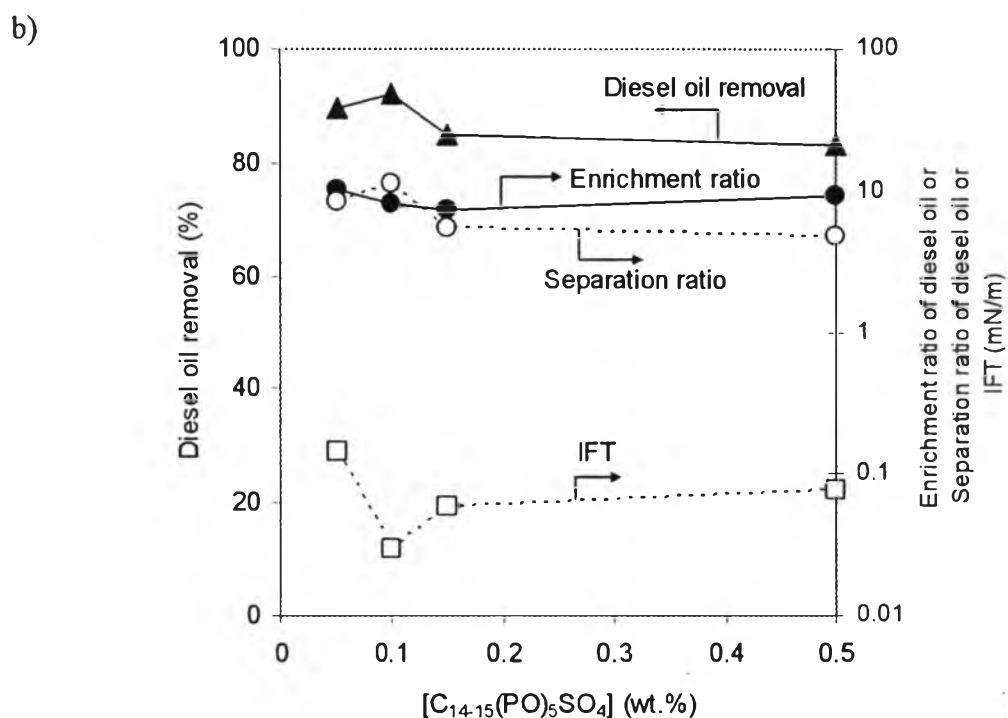
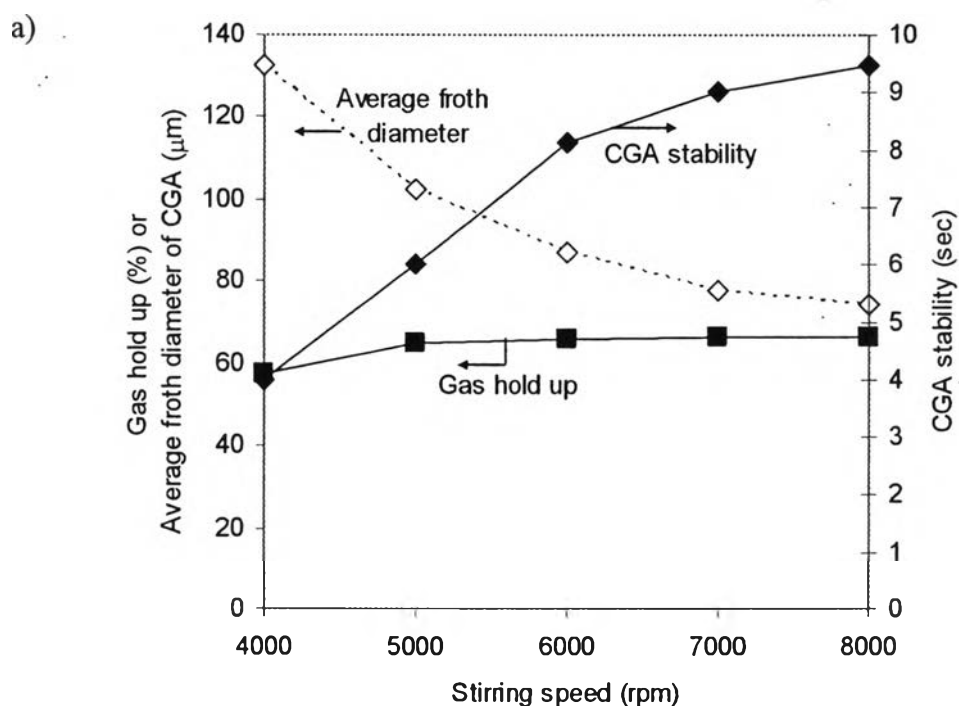


Figure 4.6 Effect of $C_{14-15}(PO)_5SO_4Na$ concentration on the performance of CGA: (a) CGA properties, and (b) separation efficiency of CGA and IFT (operated at a $[NaCl]$ of 3 wt.%, an oil:water ratio of 1:19, a stirring speed of 5,000 rpm, and a stirring time of 5 min).

4.4.2.3 Effect of Stirring Speed on the CGA Performance

Figure 4.7(a) shows the effect of stirring speed on the characteristics of CGA. An increase in stirring speed increased substantially the CGA stability because of the increasing rate of CGA generation. As shown in Figure 4.7(b), all the removal, enrichment ratio, and separation ratio of diesel oil show a similar trend as they increase with increasing stirring speed in the range of 4,000 to 5,000 rpm, and then decrease with an increasing stirring speed over 5,000 rpm. These results can be explained in that a very high stirring speed can partially damage the CGA, as indicated by the decrease in the slope of CGA stability, as shown in Figure 4.7(a). Moreover, an increase in stirring speed decreases substantially the average froth diameter of CGA, as shown in Figure 4.7(a). The average froth diameter decreased rapidly when the stirring speed increased from 4,000 to 6,000 rpm, but the average froth diameter did not dramatically change when the stirring speed

continuously increased from 6,000 to 8,000 rpm. It can be concluded that there is no need to stir the surfactant solution with an extremely high speed for obtaining fine bubbles. These results can be explained in that an increase in stirring speed clearly reduces the froth size of the CGA, which simply increases the mass transfer surface area, affecting directly the oil removal efficiency. However, the diesel oil removal did not increase with a further decreasing of the froth size of the CGA. Since the increase in stirring speed increases the collapsing rate of the CGA, it is necessary to compromise the stirring speed for obtaining the best CGA performance. From the results, an optimum stirring speed of 5,000 rpm, which provided the highest diesel oil removal as well as the highest separation and enrichment ratios, was selected as a base condition for further investigation.



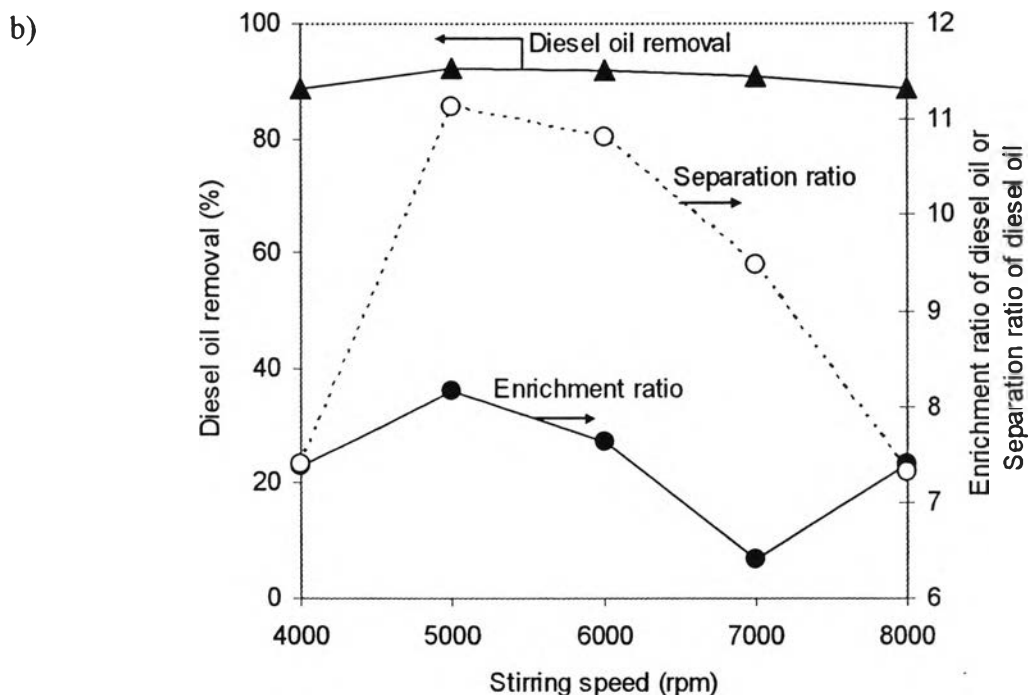


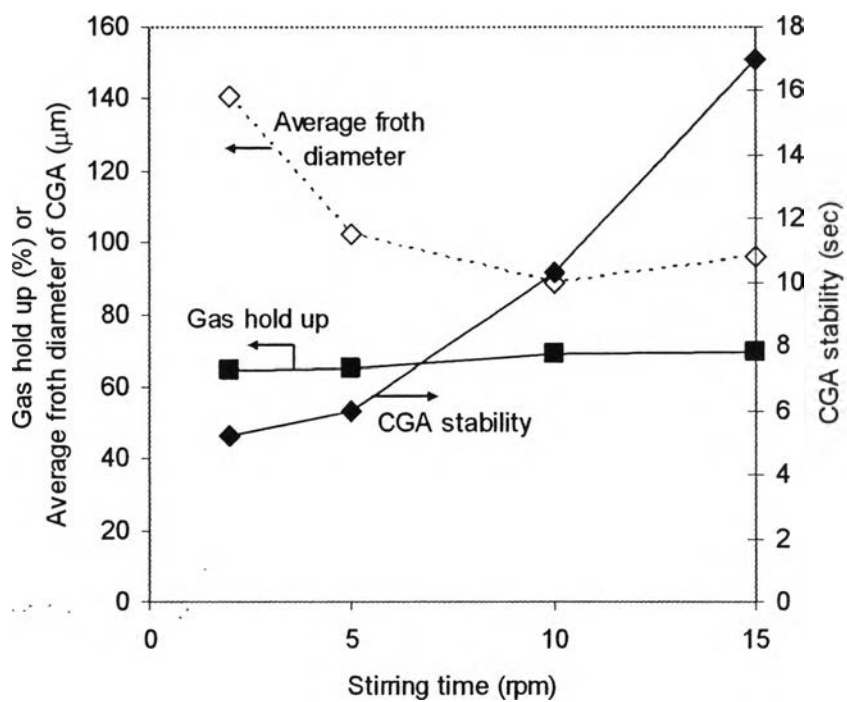
Figure 4.7 Effect of stirring speed on the performance of CGA: (a) CGA properties, and (b) separation efficiency of CGA (operated at a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, a $[NaCl]$ of 3 wt.%, an oil:water ratio of 1:19, and a stirring time of 5 min).

4.4.2.4 Effect of Stirring Time on the CGA Performance

Figure 4.8(a) shows the effect of stirring time on the CGA characteristics. As the stirring time increased, the CGA stability increased substantially. With the increasing time of stirring, the rate of dispersion increases much higher than the rate of coalescence; thus resulting in a higher CGA stability (29). As shown in Figure 4.8(b), both the removal and separation ratios of diesel oil show similar trends, as they increase and then decrease with increasing stirring time. The average froth diameter of CGA decreased with increasing stirring time and reached a minimum at a high stirring time, suggesting that a decrease in air bubble size increases the CGA stability. The results suggest that the stirring time has to be optimized to obtain the maximum CGA performance in terms of both separation ratio and removal of diesel oil. From the results, an optimum stirring time of 5 min, which

gave the highest oil removal, was selected as a base condition for further investigation.

a)



b)

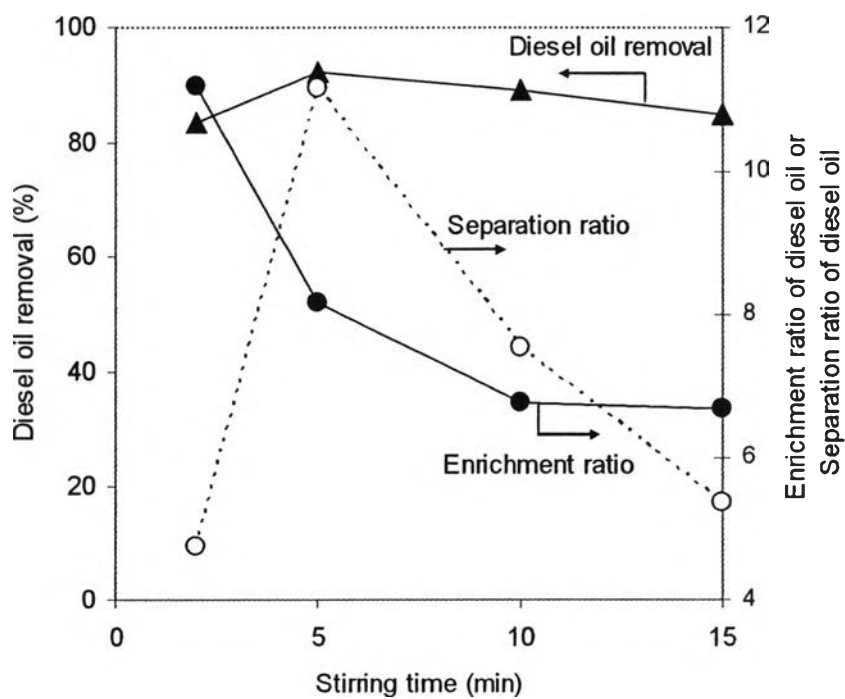


Figure 4.8 Effect of stirring time on the performance of CGA: (a) CGA properties, and (b) separation efficiency of CGA (operated at a $[\text{C}_{14-15}(\text{PO})_5\text{SO}_4\text{Na}]$ of 0.1 wt.%, a $[\text{NaCl}]$ of 3 wt.%, an oil:water ratio of 1:19, and a stirring speed of 5,000 rpm).

4.4.3 Process Performance of Froth Flotation

For the froth flotation experiments, both the effects of CGA and equilibrium time were investigated by preparing three different feed conditions; non-equilibrium without CGA, equilibrium without CGA, and non-equilibrium with CGA. The feed solution used in this study contained 0.1 wt.% $C_{14-15}(PO)_5SO_4Na$, 3 wt.% NaCl, and an oil-to-water ratio of 1:19. For the non-equilibrium feed, the prepared solution was immediately transferred into the froth flotation column; whereas, in the case of the equilibrium feed, it was incubated for a month before being fed into the froth flotation column. For the CGA condition, the feed solution was homogenized at 5,000 rpm for 5 min. To assess the performance of the batch froth flotation operation, the removal and enrichment ratios of both diesel oil and surfactant were correlated to the froth characteristics.

Figures 4.9, 4.10, and 4.11 show the effect of air flow rate on the performance of the batch froth flotation system using the three different feed conditions. For any given feed condition, the removal of both diesel oil and surfactant changed slightly with air flow rate. The highest diesel oil removal was found to be at an air flow rate of 0.3 l/min for all three feed conditions. To gain a better understanding of froth flotation, both froth formation and froth stability were also investigated. For any given feed condition, an increase in air flow rate simply increased the generation rate of froth or froth formation, but at a very high air flow rate greater than 0.3 l/min; increasing air flow rate resulted in lowering both the froth stability and froth formation because of the turbulence effect as in a good agreement with our previous work (13). For all the studied feed conditions, the highest removal of diesel oil and surfactant was found to correspond to the highest froth formation and froth stability at an air flow rate of 0.3 l/min which is in good agreement with our previous results (11, 13, 14). Conversely, the enrichment ratio of diesel oil decreased slightly with increasing air flow rate and it seemed to reach a minimum when the air flow rate was beyond 0.3 l/min, for all feed conditions. The result can be explained in that increasing the air flow rate causes a decrease in the drainage rate, leading to a higher water content in the froth and at a very high air flow rate, the collapse rate of froth increases with increasing air flow rate.

Figure 4.12 is a comparison of the froth flotation performance of three different feed conditions at the optimum air flow rate of 0.3 l/min. In a comparison between the non-equilibrium without CGA and the equilibrium without CGA, the use of the equilibrium feed condition resulted in the deterioration of the separation performance of froth flotation, which is in agreement with previous work [14]. The results can be explained in that the higher the froth formation and stability, the higher the removal efficiency. The use of CGA was found to enhance both the diesel oil and surfactant separation in the froth flotation operation. The finding that the non-equilibrium feed yields better removal than the equilibrium feed, as well as the enhancement of CGA, is beneficial for real applications of froth flotation. Figure 4.12 also gives a comparison of the average air bubble diameters of three different feed conditions in the froth flotation column. The non-equilibrium with CGA system gives an average air bubble diameter around two times smaller than that of the non-equilibrium without CGA system and the equilibrium without CGA system. The use of CGA was found to provide a smaller average air bubble diameter, resulting in a higher mass-transfer surface area of the air bubbles, which subsequently leads to a greater possibility for the diesel oil to be carried out with the air bubbles. For any given feed condition, froth formation and froth stability play an important role in the removal of diesel oil and surfactant, more than the effect of the air bubble diameter in the froth flotation column. However, the enrichment ratio of diesel oil did not alter with changing feed condition.

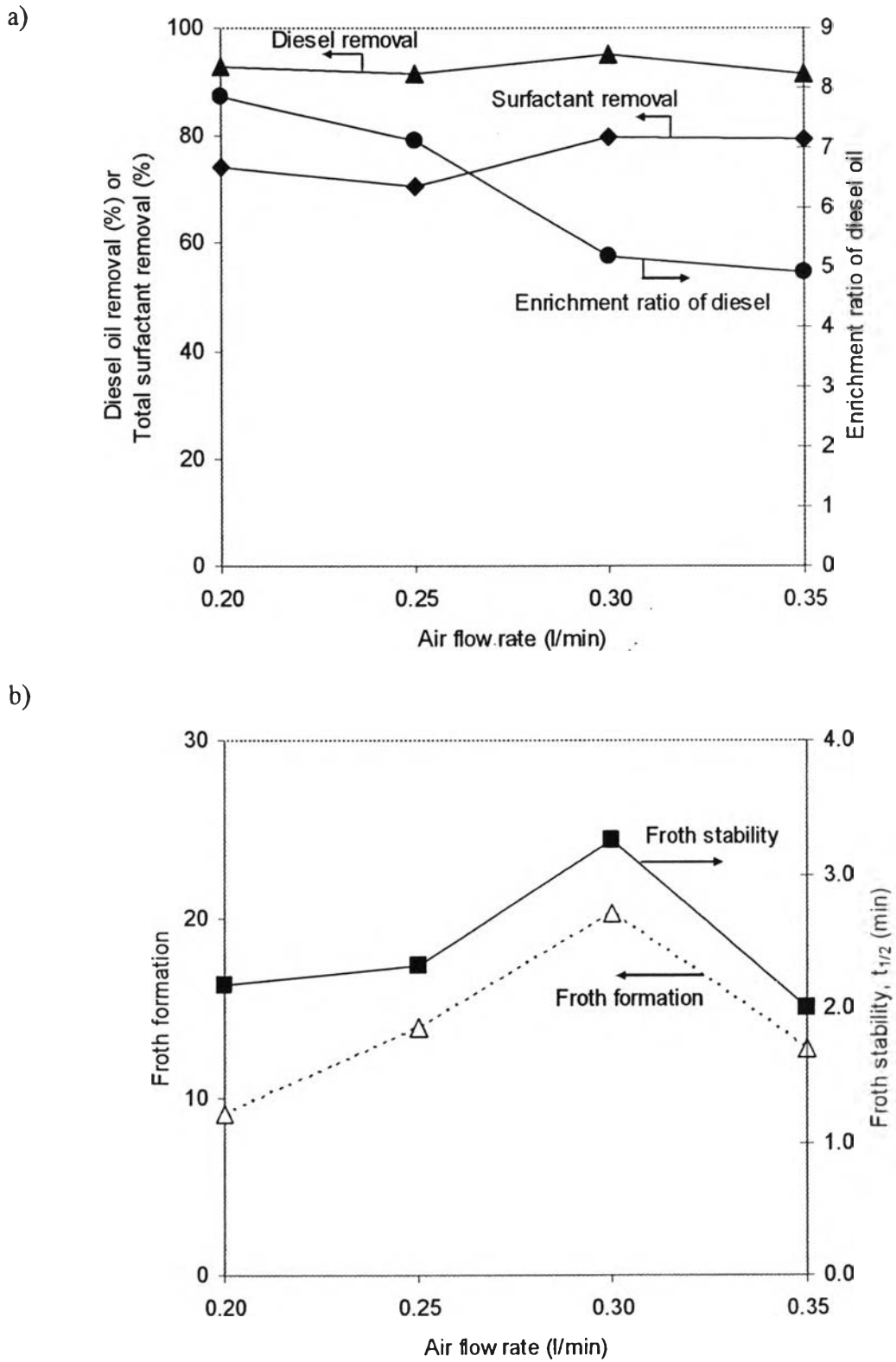


Figure 4.9 Froth flotation performance using a non-equilibrium feed without CGA: (a) separation efficiency, and (b) foam characteristics (operated at a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, a $[NaCl]$ of 3 wt.%, an oil:water ratio of 1:19).

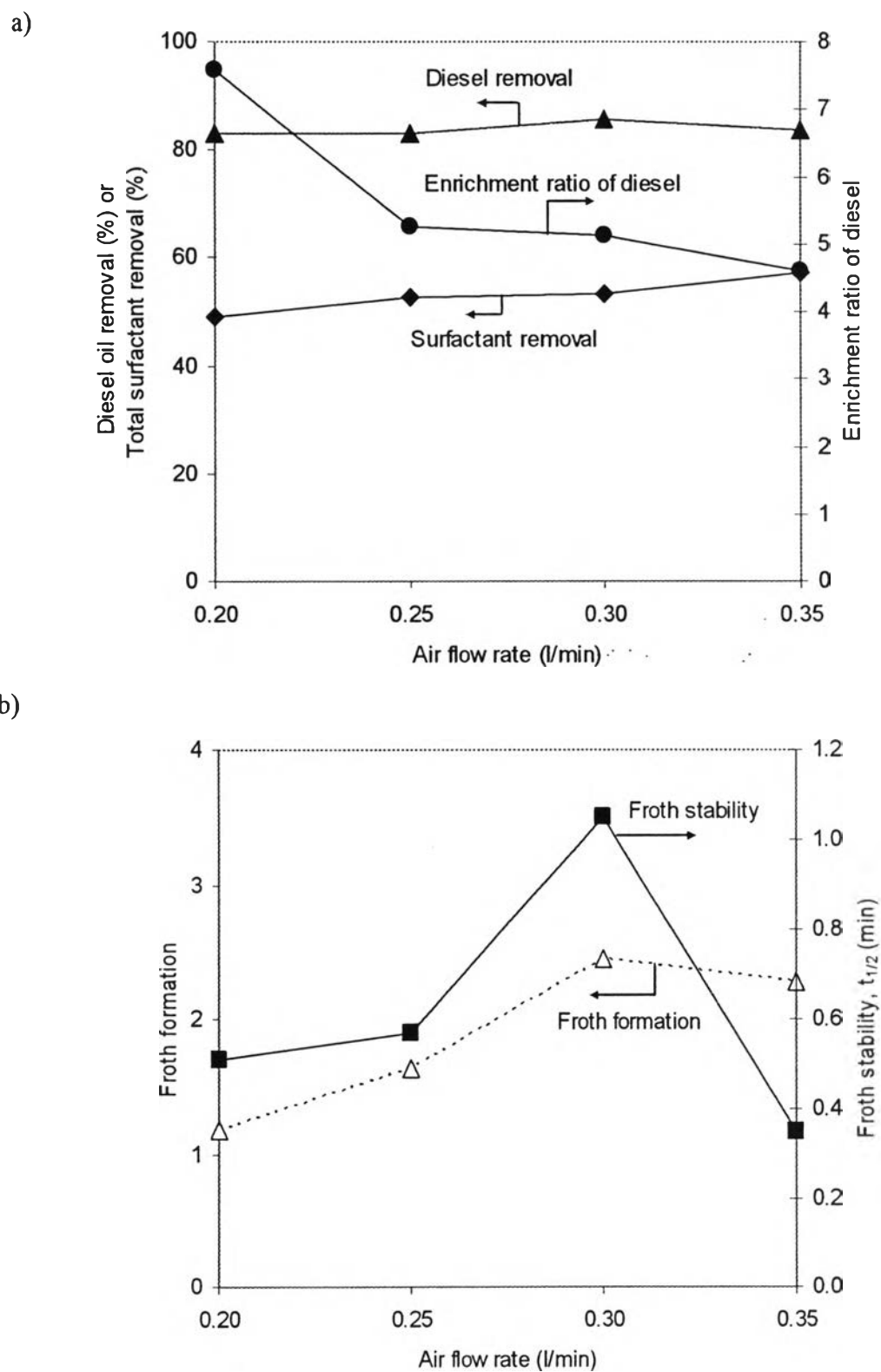


Figure 4.10 Froth flotation performance using an equilibrium feed without CGA: (a) separation efficiency, and (b) foam characteristics (operated at a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, a $[NaCl]$ of 3 wt.%, and an oil:water ratio of 1:19).

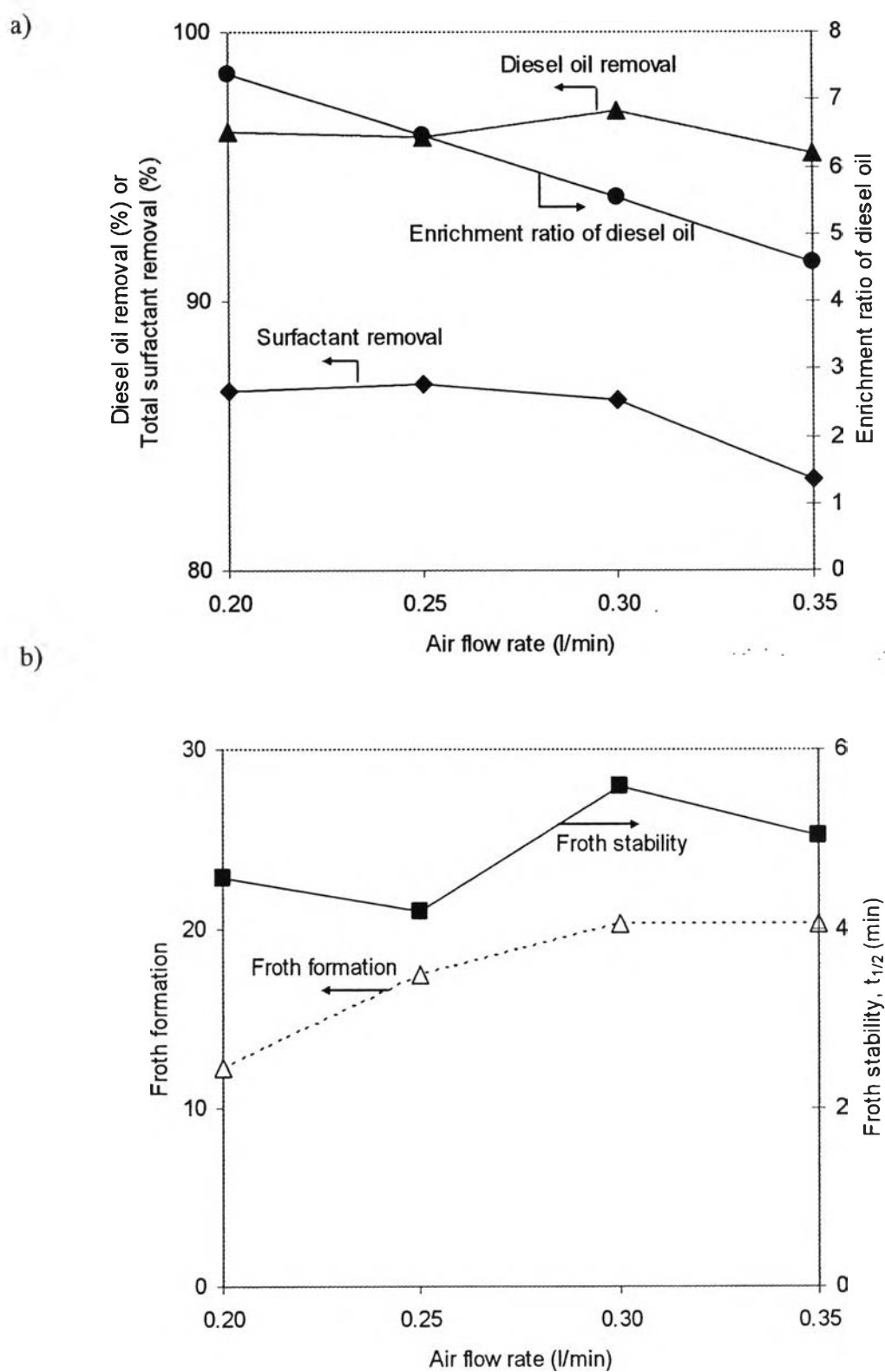


Figure 4.11 Froth flotation performance using a non-equilibrium feed with CGA: (a) separation efficiency, and (b) foam characteristics (operated at a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, a $[NaCl]$ of 3 wt.%, an oil:water ratio of 1:19).

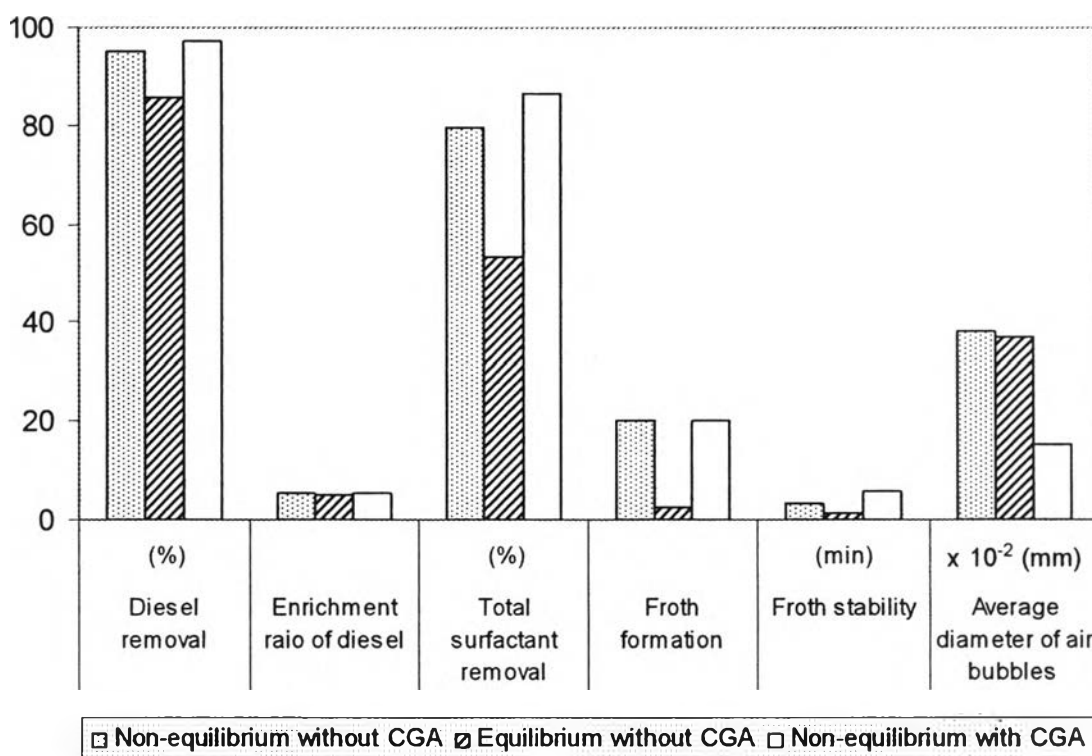


Figure 4.12 Comparison of the froth flotation performance of three feed conditions at optimum air flow rate of 0.3 l/min, a $[C_{14-15}(PO)_5SO_4Na]$ of 0.1 wt.%, a $[NaCl]$ of 3 wt.%, and an oil:water ratio of 1:19.

4.5 Conclusions

Phase studies of microemulsion with diesel oil using $C_{14-15}(PO)_5SO_4Na$ were carried out by varying concentrations of $C_{14-15}(PO)_5SO_4$ and NaCl, and studies of colloidal gas aphrons (CGA) with diesel oil were done by varying surfactant concentration, NaCl concentration, stirring speed, and stirring time. Both stirring speed and stirring time were found to play an important role of CGA stability more than the concentration of surfactant and NaCl. To form the CGA with diesel oil, the optimum conditions for the maximum diesel oil removal were found to be 0.1 wt.% $C_{14-15}(PO)_5SO_4Na$, 3 wt.% NaCl, 5,000 rpm stirring speed, and 5 min stirring time. For the froth flotation experiments, three feed conditions — non-equilibrium without CGA, equilibrium without CGA and non-equilibrium with CGA — were investigated for the effects of equilibrium and CGA

formation. From the results, the equilibrium feed condition had a negative effect on the froth flotation performance as compared to the non-equilibrium feed condition. The use of CGA enhanced the separation performance of froth flotation. Froth formation and froth stability play an important role in the removal of diesel oil and surfactant; more than the air bubble diameter effect.

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