CHAPTER VI

SEPARATION OF CARBON BLACK FROM SILICA BY FROTH FLOTATION*

6.1 Abstract

Froth flotation can be applied to separate hydrophobic particles from hydrophilic ones in aqueous solution with the use of an appropriate surfactant. In this work, carbon black was separated from silica gel by mean of froth flotation. Since the point of zero charge or PZC of the carbon black (3.5) is close to that of the silica gel (4.1), a nonionic surfactant (ethoxylated alcohol) was selected as the separating agent. Based on experimental results using a surfactant concentration of 75% of its critical micelle concentration (CMC), up to 70% of carbon black recovery was achieved with a carbon black enrichment ratio around 3.5. Added electrolyte (NaCl) has negligible effect on the separation efficiency.

6.2 Introduction

Froth flotation is a surfactant-based separation process [1] which is widely used in various applications such as mineral processing [2] and paper deinking [3]. There are several advantages of flotation, such as its rapid operation, minimal space requirements, high removal efficiency, and low operation costs [4]. In a typical froth flotation operation, air is sparged into the surfactant solution at the bottom of the column through a sintered glass disk. With the aid of surfactant, hydrophobic particles such as carbon black attach to the air bubbles and are carried to the top of the column [5] where these particles accumulate in the froth which can be skimmed off. To obtain a highly selective separation in froth flotation, an appropriate surfactant is added to create the conditions where the silica gel particles do not tend to adhere to the air bubbles, while the carbon black is selectively carried over in the froth. The objective of this work was to demonstrate a relatively inexpensive method

of froth flotation in separating hydrophobic from hydrophilic particles having similar surface charge as indicated by the PZC.

Single-walled carbon nanotubes (SWNTs) [6,7] have illustrated their potential in many applications [8]. The required purity of SWNTs varies with the application [9]. Production of SWNTs via the supported catalyst is a method to produce SWNTs economically [10]. However, residual catalysts and catalyst support can contaminate the as produced SWNTs. The silica catalyst support as an impurity in SWNTs is of particular concern. To purify these products, the bond between the SWNTs and the silica gel support must be broken, followed by a physical separation step to separate the silica gel particles from the SWNTs.

The froth flotation technique proposed here has the potential to achieve a selective separation between SWNTs and silica. Since carbon black and SWNTs both have hydrophobic surfaces, there may be analogies between the separations of the two substrates from silica. At least, this study of carbon black can help define the role of hydrophobicity versus other factors when comparing these results to carbon nanotubes froth flotation in a later study. We do not want to overemphasize the analogy between carbon black and carbon nanotubes due to the substantial difference in particle size and the van der Waals interactions between carbon nanotubes that causes them to bundle [11]. Future work will involve the purification of as-produced SWNTs by froth flotation.

6.3 Experimental Section

6.3.1 Materials

Carbon black, type 400R, having an average particle size of 0.24 μm and density of 0.3 g/cm^3, was supplied by Cabot Company, USA. The as-received carbon black was rinsed with deionized water, centrifuged and dried overnight at 120°C to remove all impurities before use. Silica gel having an average particle size of 62-210 μm (70-230 mesh), an average pore diameter of 6 nm, and a density of 1.5 g/cm^3, was supplied by Aldrich Chemical Company, USA. Surfonic L24-7, a nonionic surfactant with a high purity of 100%, composed of linear alcohol

polyethoxylate, with an average degree of polymerization of 7 and a linear alkyl chain of 12-14 carbons number, was obtained from Huntsman Company, USA, and used as received. Hydrochloric acid with a concentration of 37 %, sodium hydroxide with a purity of 99%, and sodium chloride with a purity of 99% were obtained from Labscan Asia Company, Thailand. Deionized water was used to prepare all solutions throughout this work.

6.3.2 Methodology

6.3.2.1 Measurement of Point of Zero Charge (PZC) and Contact Angle

To measure the PZC of either carbon black or silica gel, 10 mL of aqueous solutions having different pH values ranging from 1 to 11 were prepared in vials by adding hydrochloric acid or sodium hydroxide to deionized water with an initial pH of 6.2. The ionic strength of the solutions was kept constant to 0.1M by using sodium chloride to more quickly attain a state of equilibrium without affecting the final pH [12]. After that, 0.5 g of carbon black or silica gel was added to each vial, stirred and then left overnight to equilibrate at 25±1°C. The equilibrium pH was then measured and plotted against the initial pH for each substrate. The PZC can be readily obtained from the point at which the initial pH equals the equilibrium pH.

The contact angle of the solid was determined by grinding and then pressing the powder of the carbon black or the silica gel with a hydraulic press under a pressure of 15 N/m^2 to obtain flat surface pellets. The pellets were then used to measure the contact angle by a KRUSS drop shape analysis system (DSA10-Mk2) with the sessile drop method using a drop of 5 μL of deionized water.

6.3.2.2 Surfactant Adsorption Experiment and CMC Determination

The surfactant adsorption onto carbon black and silica gel was studied at 25 ±1°C. Carbon black or silica gel (0.1 g) was mixed with 20 mL of a surfactant solution having different initial concentrations. The mixture was well shaken and allowed to equilibrate for three days, which has been shown to be

sufficient for equilibrium to be attained. After that, it was centrifuged at 15,000 rpm for 30 min. The supernatant was decanted and the equilibrium surfactant concentration in the supernatant was analyzed by a total organic carbon analyzer (Shimadzu, TOC - V_{CSH}). The specific surface areas of both the carbon black and the silica gel were measured by using a surface area analyzer (Sorptomatic,Thermo Finnigan, 1990).

To measure the critical micelle concentration (CMC) of the surfactant, the surface tensions of aqueous solutions containing various surfactant concentrations were measured by using a DuNouy-Ring Tensiometer (Krüss, K10ST). The CMC of surfactant was determined from the concentration at which the surface tension reaches a plateau [13].

6.3.2.3 Froth Flotation Experiments

A schematic of the froth flotation apparatus used in this work is shown in Figure 6.1. The flotation column was a glass tube with a 3.8 cm inside diameter and 120 cm length. In this study, the composition of the solid mixture was fixed at 25 wt% carbon black and 75 wt% silica gel. A surfactant solution of 750 mL, having different surfactant concentrations, and the solid sample, having different total weights, were well mixed. The resultant mixture solution was then transferred to the flotation column. Air was introduced at the bottom of the column through a sintered glass disk having pore size diameters of about 16-40 μm. The air flow rate was varied from 150 to 300 mL/min by using a mass flow controller (AALBORG, GFC171S). The initial surfactant concentration was varied in the range of 0.25-1 times the CMC.

During the froth flotation experiments, the generated foam was collected at the top of the column until no further foam was generating out of the column due to surfactant depletion. Then the collected foam was allowed to collapse to analyze the weight of carbon black and silica gel in the overhead froth. All of the flotation experiments were performed at room temperature (25±1°C). To get rid of the remaining surfactant, deionized water was added to the foamate (collapsed foam), which was followed by centrifugation to obtain the solid residue. This step was repeated a few times. After that, the solid was dried in an oven at 110° C to obtain the

dried weight. The purity of carbon black in the dried solid samples was determined by mass balance after the carbon black was completely oxidized in air at $700^{\circ}C$ and the sample reweighted.
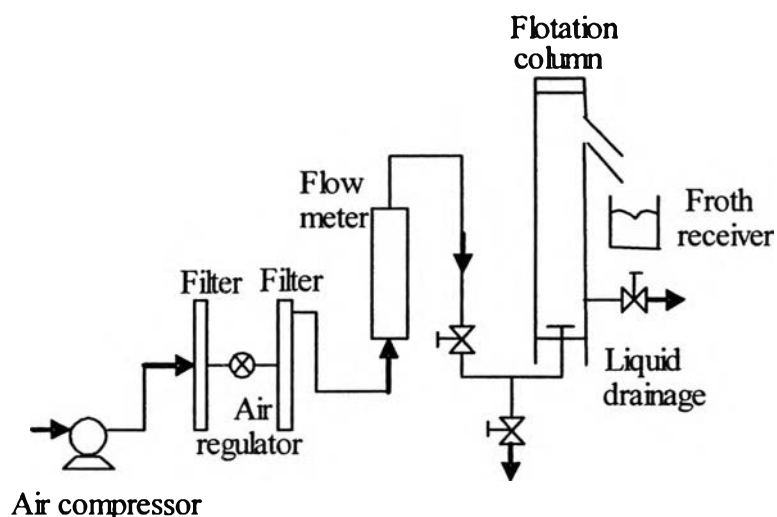

Figure 6.1 Schematic of the froth flotation apparatus.

6.3.2.4 Foam Characteristics

Foam characteristic experiments were also conducted independently in the same flotation column. After the solid mixture and surfactant solution, having different concentrations of solid mixture and surfactant, were transferred to the column and well mixed, filtered air was introduced at the bottom of the column at a desired flow rate until a maximum foam height was achieved. The maximum foam height divided by the initial solution height in the column is defined as foamability. The introduction of air to the column was then stopped and the time required for the foam volume to collapse to one half of the maximum height was used to quantify foam stability ($t_{1/2}$).

6.4 Results and Discussion

The separation efficiency of the froth flotation column is quantified by both the recovery and the enrichment ratio of carbon black. The recovery of carbon black

is defined as the weight of carbon black in the foamate as a percentage of the weight of the carbon black in the initial feed. The enrichment ratio of carbon black is the ratio of fraction of carbon black in the total solid recovered from the foamate to the fraction of carbon black in the total solid that is originally in the initial feed. An enrichment ratio greater than one indicates the selective separation of carbon black.

6.4.1 Point of Zero Charge (PZC) and Contact Angle

The equilibrium pH as a function of initial pH for carbon black and silica gel are shown in Figure 6.2. The crossing point of each curve with the y = x line corresponds to the PZC of the solid sample. From the figure, the PZC values of carbon black and silica gel are 3.5 and 4.1, respectively. Therefore, the surfaces of both solids become negatively charged when exposed to a solution pH above 4.1 and positively charged at a pH lower than 3.5. Moreover, as shown in Figure 6.3, the solution pH decreases with increasing weight of solid particles (with an initial pH of 6.2). Interestingly, the effect of the weight of carbon black was obviously more significant than that of silica gel. The pH of the solution changes from the initial pH toward the PZC. The final pH approaches the PZC at a high enough solid loading. The final pH values of these two solids as shown in Figure 6.3 at high solid loadings are consistent with the PZC values deduced from Figure 6.2. An ionic surfactant may not provide good selective separation of carbon black from silica gel because the PZC values of carbon black and silica gel are not significantly different. Consequently, a nonionic surfactant was selected for use in this study.

From the contact angle of deionized water, it was determined that carbon black has an average contact angle of 59.8°, whereas the silica gel has an average contact angle of 15.8°. Therefore, the results show that the carbon black has a higher hydrophobicity than the silica gel, as expected.
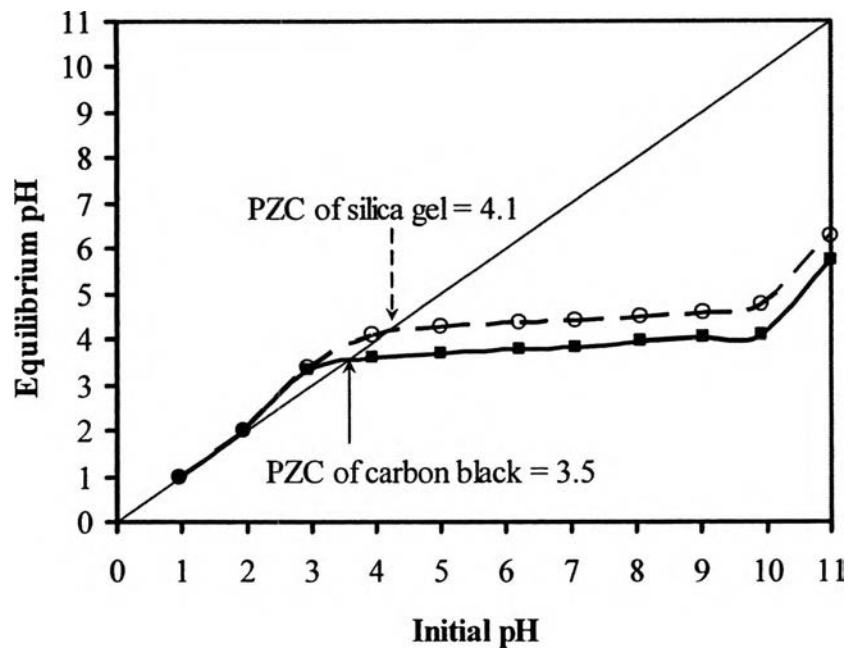
Figure 6.2 Determination of point of zero charge (PZC) for carbon black and silica gel at solid loading of 5 wt%.
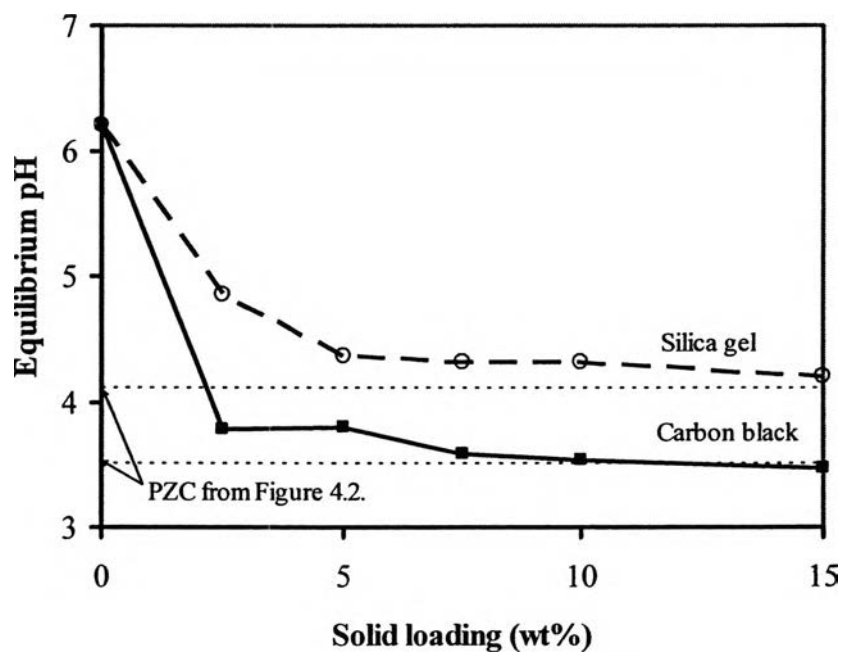

Figure 6.3 pH changes upon the addition of carbon black or silica gel into water with initial pH of 6.2.

6.4.2 Surfactant Adsorption Isotherms and CMC

The CMC of the studied surfactant is 82.1 μM, in agreement literature CMC values for this type of surfactant structure [14]. The adsorption isotherms of surfactant on carbon black and silica gel are depicted in Figure 6.4. The specific surface areas of carbon black and silica gel are 132.5 and 403.7 m^2/g respectively. The amount of adsorbed surfactant is then reported on the basis of unit surface area. As expected, the surfactant adsorption reaches a plateau at about the CMC. The reason the surfactant adsorption levels off above the CMC is that the chemical potential of the surfactant in solution becomes constant there, not because the surface of the solid is saturated [15]. In the froth flotation operation, the surfactant present in the system can adsorb on all surfaces including carbon black, silica gel, and air bubbles. The amount of surfactant at the air/water interface is generally negligible when compared to the total amount of surfactant. Moreover, under the studied conditions, based on the maximum adsorption of surfactant on solid/liquid interfaces, the majority of the surfactant (more than 90%) will remain in the bulk solution. Therefore, the bulk concentration of surfactant is approximately equal to the initial surfactant concentration. Since the surfactant concentration was varied in the range of 0.25 to 1 times the CMC in this froth flotation study, the adsorption isotherms also suggests more surfactant adsorption on carbon black than on silica gel, as indicated in Figure 6.4.
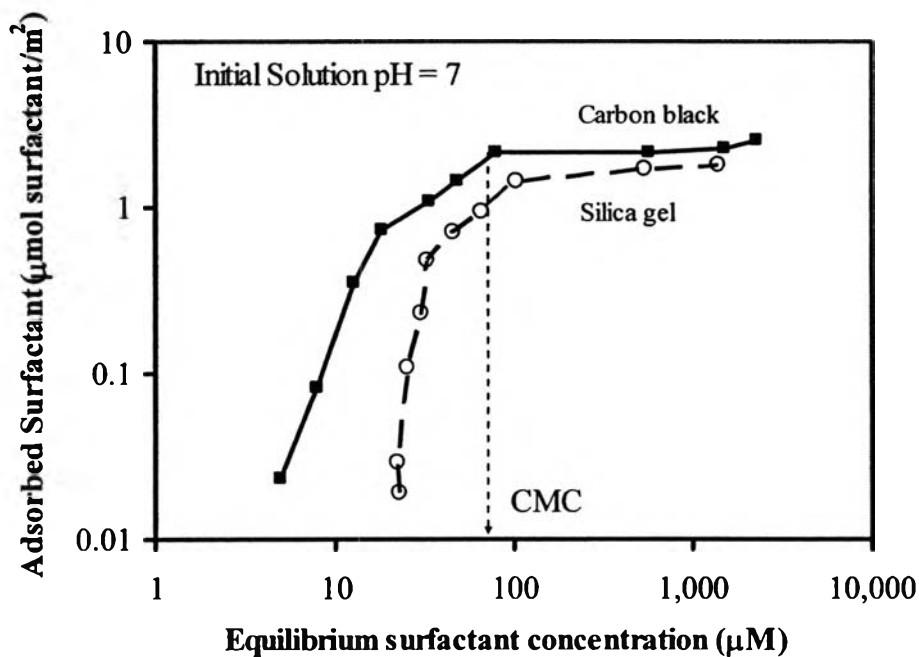
Figure 6.4 Adsorption isotherms of surfactant on carbon black and silica gel.

6.4.3 Effect of Surfactant Concentration

In a froth flotation operation, the presence of surfactant plays an important role in both promoting and stabilizing the foam [16]. From the previous studies of froth flotation to remove emulsified oil from water [17-20], the separation efficiency was found to be highest at the surfactant concentration which corresponds to the maximum values of both foam formation (foamability) and foam stability. Figure 6.5 shows the effect of surfactant concentration on foam characteristics. As surfactant concentration increased, foamability increased, whereas foam stability decreased. Maximum foamability or foam formation is around the CMC, which is generally observed in other surfactants system [15]. However, the relationship of foam stability to surfactant concentration is more complicated and system-dependent.

Figure 6.6 shows the recovery and the enrichment ratio of carbon black as a function of surfactant concentration. For the conditions studied here, the carbon black recovery as high as 70 % and the enrichment ratio of carbon black as high as 3.5 demonstrate the technical feasibility of froth flotation for the selective separation of carbon black from silica gel. At surfactant concentrations in the range of 0.25 to 0.75 times the CMC, the carbon black recovery increased with increasing

surfactant concentration. However, as observed in Figure 6.6, when the surfactant concentration approaches the CMC, both the recovery and enrichment ratio of carbon black decrease substantially. By comparing Figures 6.5 and 6.6, both high foamability and high foam stability are needed to achieve a high carbon black recovery and a high carbon black enrichment ratio. The offsetting trends of increasing foamability and decreasing foam stability with increasing surfactant concentration result in an optimum surfactant concentration of around 0.75 times the CMC, so this initial surfactant concentration was used for further investigation in this work. Since the surfactant adsorption isotherms on carbon black and silica gel are similar (Figure 6.4), and the interaction between particles and air bubbles and foam lamellae are complex, a fundamental interpretation of selectivity is difficult. However, since silica gel has a higher density than carbon black, the silica gel tends to settle faster due to gravity than the carbon black, augmenting the enrichment ratio of carbon black, which is always greater than one in this study, so carbon black is floated selectively compared to silica gel.
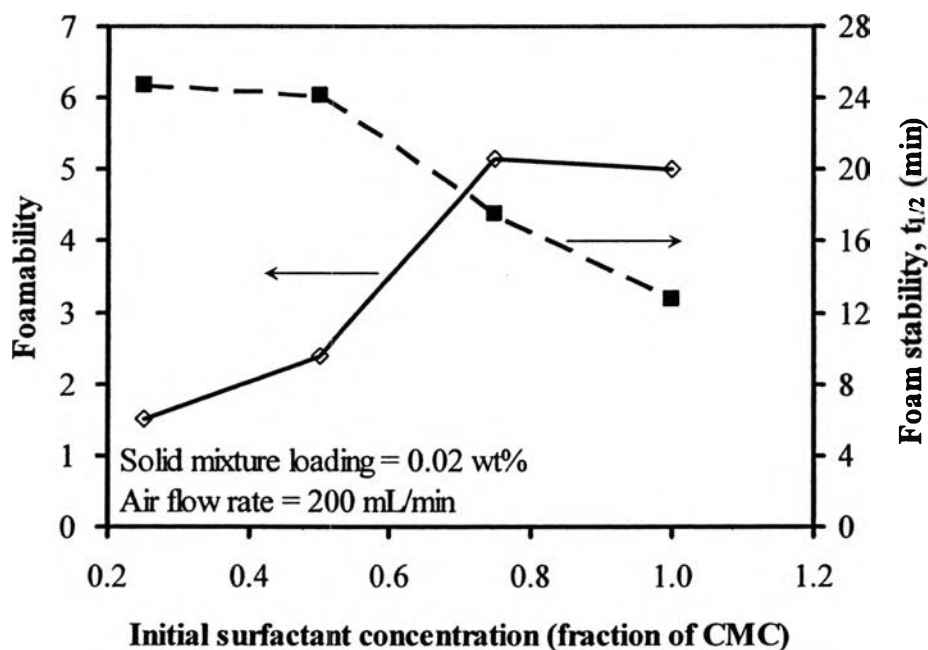

Figure 6.5 Effects of surfactant concentration on foamability and foam stability.
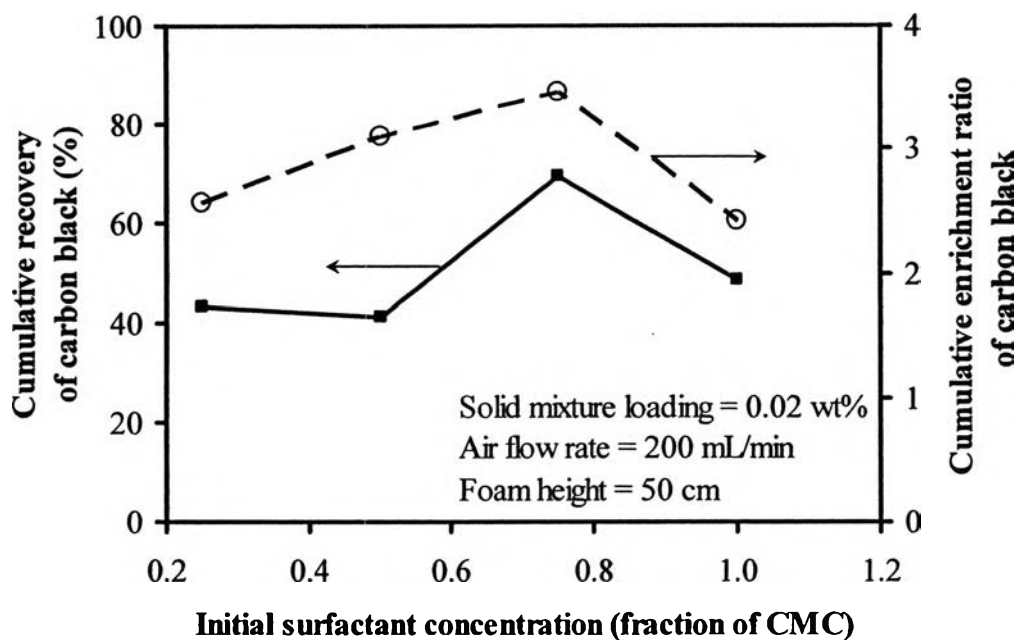
Figure 6.6 Effects of initial surfactant concentration on recovery and enrichment ratio of carbon black.

6.4.4 Effect of Solid Mixture Loading

Influences of the solid mixture loading (weight of total solids/volume of slurry) in the feed solution on the foam characteristics and the separation efficiency are shown in Figures 6.7 and 6.8, respectively. Up to 0.02 wt% solid loading, both foamability and foam stability remained constant, but at higher loadings, they declined dramatically with increasing solid loading. Hydrophobic particles, like carbon black, commonly act as antifoams or defoamers, while hydrophilic particles, like silica gel, can stabilize or destabilize foam [21], so the dramatic reduction in foamability and foam stability at high solid loadings is expected. The modest decrease in the recovery of carbon black with increased solid loading above 0.02 wt% solid loading is probably related to the decreases in both foamability and foam stability. Interestingly, in the solid loading range of 0.02-0.04%, the enrichment ratio remained almost constant. Since the recovery is on a percentage basis, the total weight of carbon black recovered actually increases as the solid loading increases above 0.02%. Increased solid loading does not cause the carbon black recovery to decrease as significantly as would be expected from the dramatic decrease in foamability and foam stability, but in fact causes carbon black

recovery to increase between solid loadings of 0.01 and 0.02 wt%. As a result, the enrichment ratio increases or remains unchanged with increasing solid loadings. Reasons for these effects are unclear. Since the highest carbon black recovery occurred at 0.02 wt% solid loading, this condition was used in subsequent experiments as a base condition.
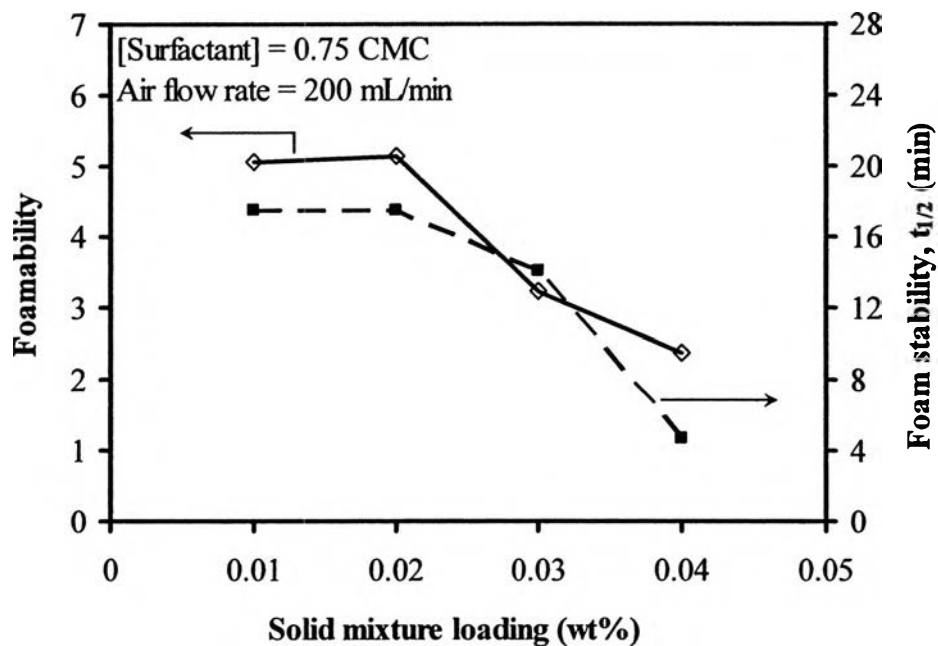

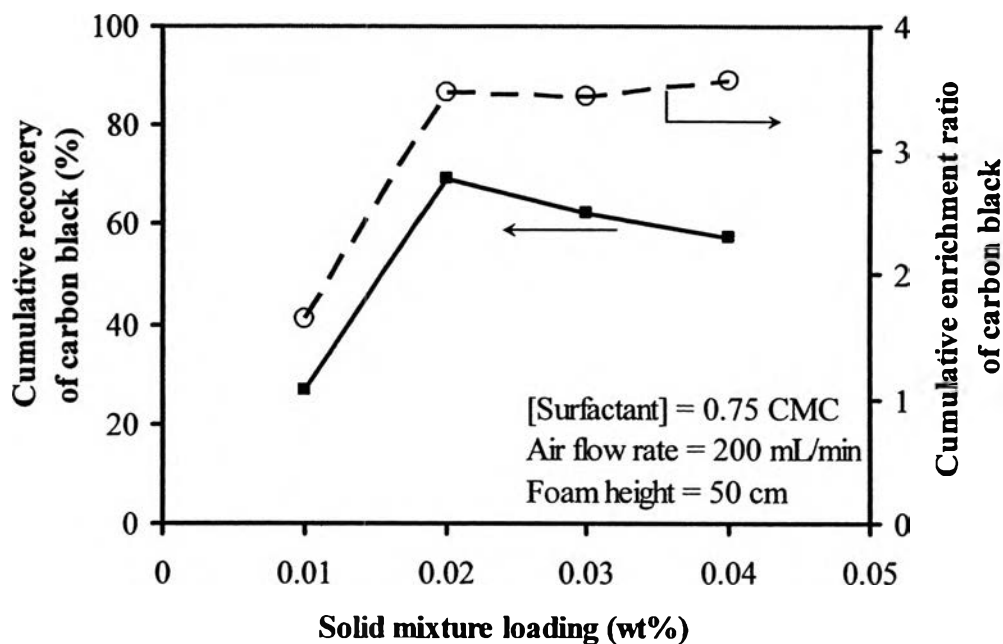**Figure 6.7** Effects of solid mixture loading on foamability and foam stability.

Figure 6.8 Effects of solid mixture loading on recovery and enrichment ratio of carbon black.

6.4.5 Effect of Air Flow Rate

Both bubbles size and volumetric flow rate of air influence the separation efficiency of froth flotation [22]; in this study, only the latter was investigated. The effects of air flow rate on the foam characteristics and on the separation efficiency of carbon black are shown in Figures 6.9 and 6.10, respectively. The foamability is nearly constant at an air flow rate below 250 mL/min, but it greatly increased at a flow rate above 250 mL/min. In contrast, the foam stability was almost invariant in the studied range of air flow rate. To obtain separation, a certain minimum air flow rate is required to cause any foam to flow from the top of the column. When air flow rate increases above the required flowrate, 150 mL/min to 200 mL/min, carbon black recovery increases with increasing air flow rate, as observed in Figure 6.10. However, if the air flow rates increased above 200 mL/min, the trend of the recovery of carbon black reversed. This may be due to the increased turbulence altering the flow pattern in the column to a severe circulation velocity in

the solution and some portion of carbon black attached to the bubble surface is carried back into the solution by this turbulence effect.
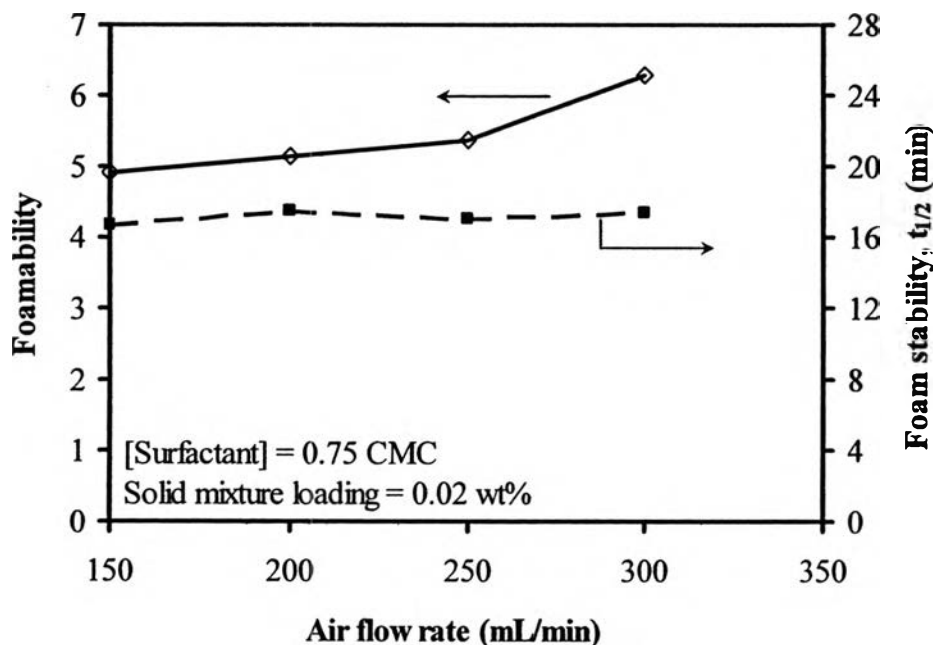

Figure 6.9 Effects of air flow rate on foamability and foam stability.

Consequently, carbon black recovery is reduced at high air flow rates between 200 and 250 mL/min. However, at a much higher air flow rate (300 mL/min), the carbon black recovery was found to increase moderately as compared to that at 250 mL/min because the foamability at this point increased. This can be explained by the fact that at this very high air flow rate, the effect of foamability or foam production rate is more significant than that of foam stability. From Figure 6.10, the enrichment ratio of carbon black decreases monotonically with increasing air flow rate. This implies that carbon black selectively attaches to air bubbles rising through the solution and/or to the air/water interface in the foam lamellae. However, at very high air flow rates, the violent turbulence in the solution causes the physical attachment to be relatively less important than the gross flow effects causing flotation; overcoming the particle density differences which cause silica gel to preferentially settle, for example. Since the maximum observed carbon black recovery occurred at 200 mL/min air flow rate, this condition was selected as the base case for further experiments.
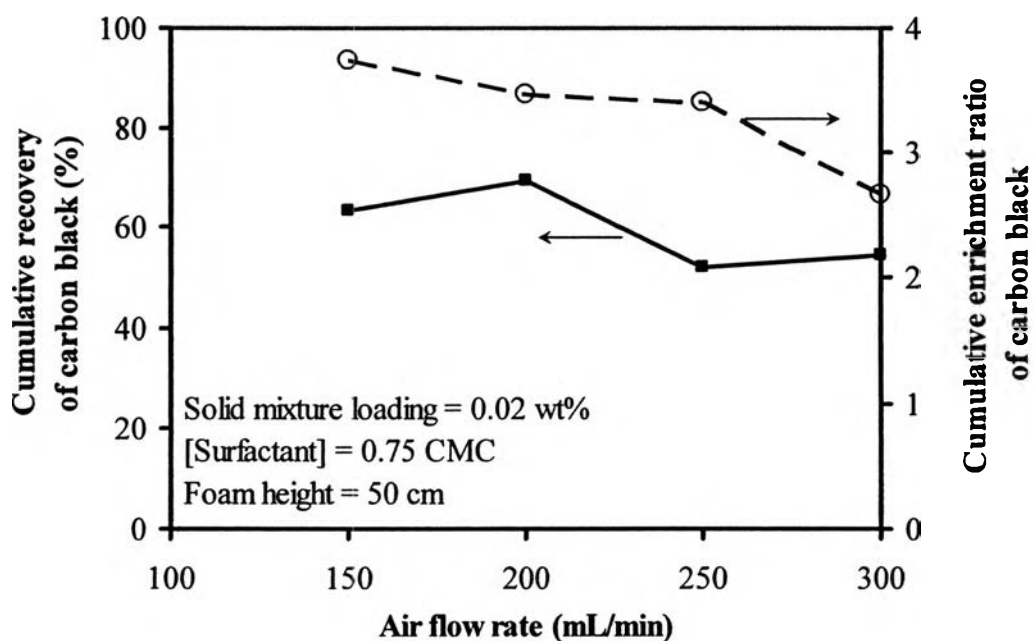
Figure 6.10 Effects of air flow rate on recovery and enrichment ratio of carbon black.

6.4.6 Effect of Initial Foam Height

A greater foam height results in a greater residence time, causing more foam drainage to occur before it overflows from the column, so foam height is one of the important operating parameters affecting the separation performance of a froth flotation unit. In this study, the froth flotation column was designed by fixing the height of the column, so the effect of initial foam height was investigated by changing the volume of the feed surfactant solution. The enrichment ratio and the recovery of carbon black as a function of initial foam height are shown in Figure 6.11. As initial foam height increases, the residence time of the particles in the foam lamellae increases, increasing settling time, reducing solid flow rate overheads, leading to reduction of carbon black recovery with increasing foam height, as seen in Figure 6.11, above a foam height of 50 cm. Also, due to foam drainage, foam flow rates also decrease with increasing foam height. However, at too low of a foam height, there is insufficient space for the foam to separate from the entrained liquid, so separation is poor, as seen by low carbon black recovery, at a height of 30 cm. In

addition, the enrichment ratio increased only modestly with increasing foam height above 50 cm. Based on the results in Figure 6.11, a foam height of 50 cm was selected as the base case for further experiments. In contrast to carbon black recovery, the enrichment ratio of carbon black increases with increasing foam height as shown in Figure 6.11. This is because of increasing foam drainage with increasing foam height.
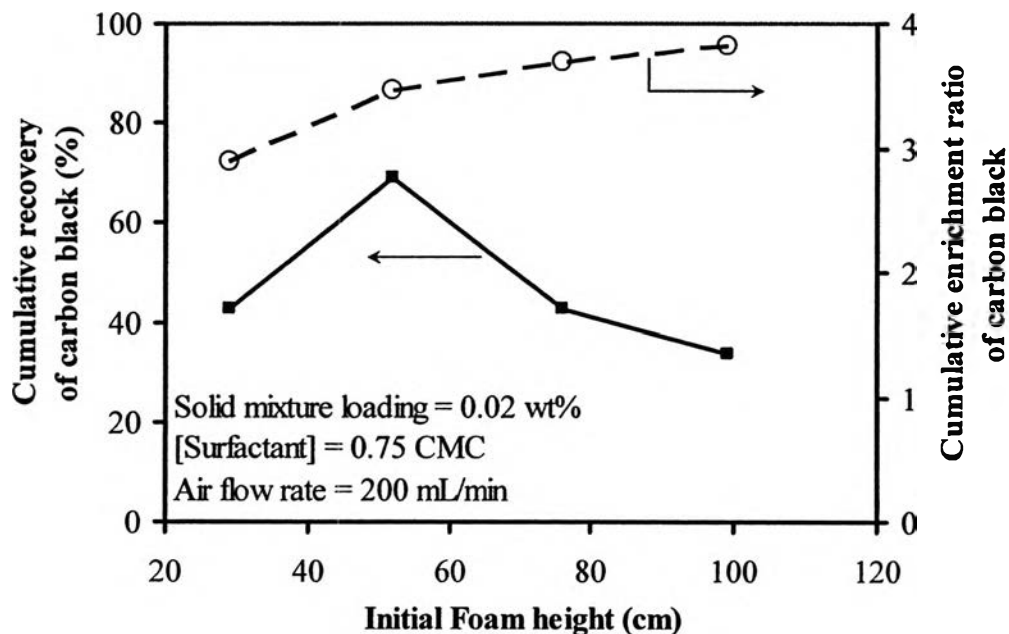

Figure 6.11 Effects of initial foam height on recovery and enrichment ratio of carbon black.

6.4.7 Effect of NaCl Concentration

Normally, NaCl influences the performance of froth flotation because it affects the foam characteristics within a flotation column using anionic surfactants [19,20]. Figure 6.12 shows that foamability and foam stability decrease when NaCl is initially added to the system. However, with increasing concentration of NaCl beyond 1 wt%, foamability increased, whereas foam stability further decreased. It was observed qualitatively that the foam bubbles became bigger, wetter, and more unstable when the NaCl content was increased.

The recovery and enrichment ratio of carbon black are depicted in Figure 6.13 as a function of NaCl concentration. The recovery of carbon black mirrored the foamability, as it decreased then increased with increasing NaCl concentration. The carbon black enrichment ratio also mirrored the foamability, except at NaCl concentrations above 4 wt% where low foam stability caused a reduction in enrichment ratio. The highest carbon black recovery and enrichment ratio corresponded to no added NaCl, so adding an electrolyte does not improve the separation.
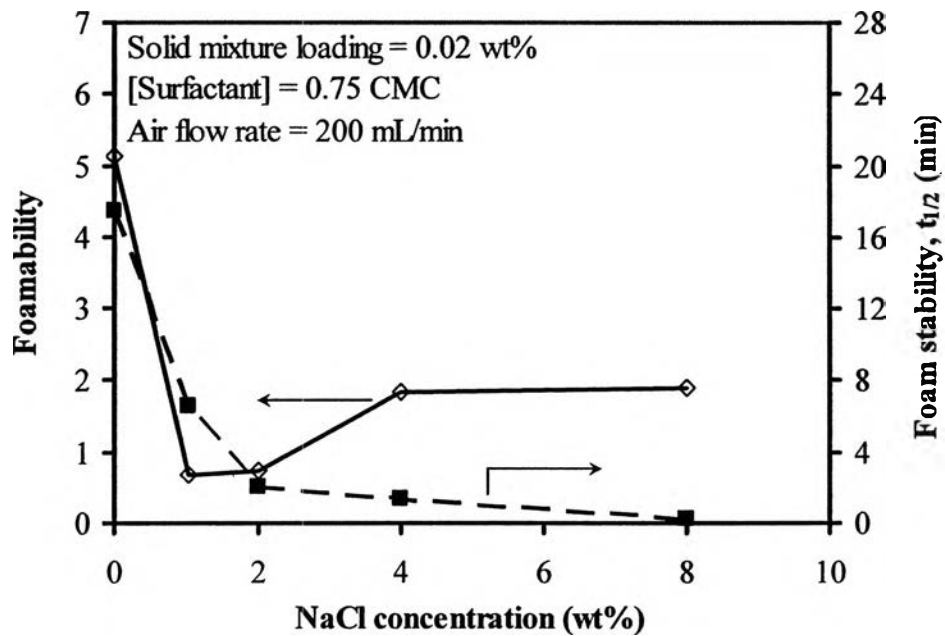

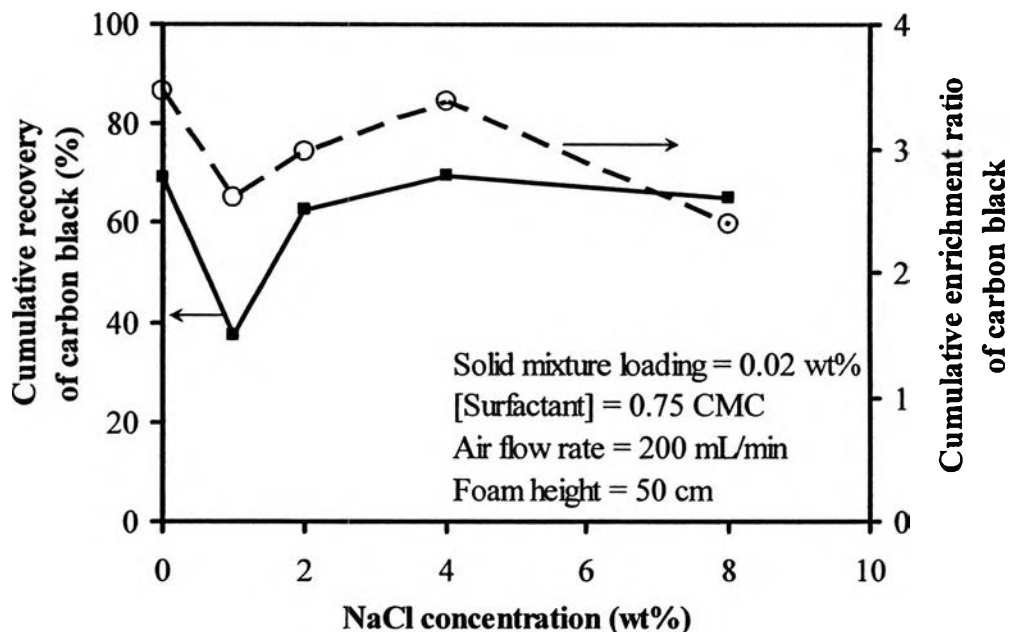**Figure 6.12** Effects of NaCl concentration on foamability and foam stability.

Figure 6.13 Effects of NaCl concentration on recovery and enrichment ratio of carbon black.

6.5 Conclusions

In this research, silica gel removal and recovery of carbon black by froth flotation were studied. It was found that, froth flotation can be used to separate hydrophobic particles from hydrophilic particles in aqueous solution. Since the point of zero charge (PZC) of the carbon black is close to that of the silica gel, a nonionic surfactant was used as the separating agent. To achieve a high recovery of carbon black, surfactant concentration should be optimized to generate voluminous, stable foams, but avoid silica gel entrainment to the top of the column. A surfactant concentration of 75% of the CMC, solid mixture loading of 0.02 wt%, air flow rate of 200 mL/min, foam height of 50 cm, and no added NaCl as electrolyte yield a carbon black recovery of 70% and a carbon black enrichment ratio of about 3.5.

6.6 Acknowledgements

6.7 REFERENCES

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