

CHAPTER IV RESULTS AND DISCUSSION

4.1 CMC of DTAB

The CMC of DTAB can be determined from the plot between surface tension and bulk concentrations of DTAB solution, as shown in Figure 4.1. At the concentrations of DTAB solution from 100 to 500 $\mu\text{mol/l}$, surface tension slightly decreased with an increase in the bulk concentration of DTAB.

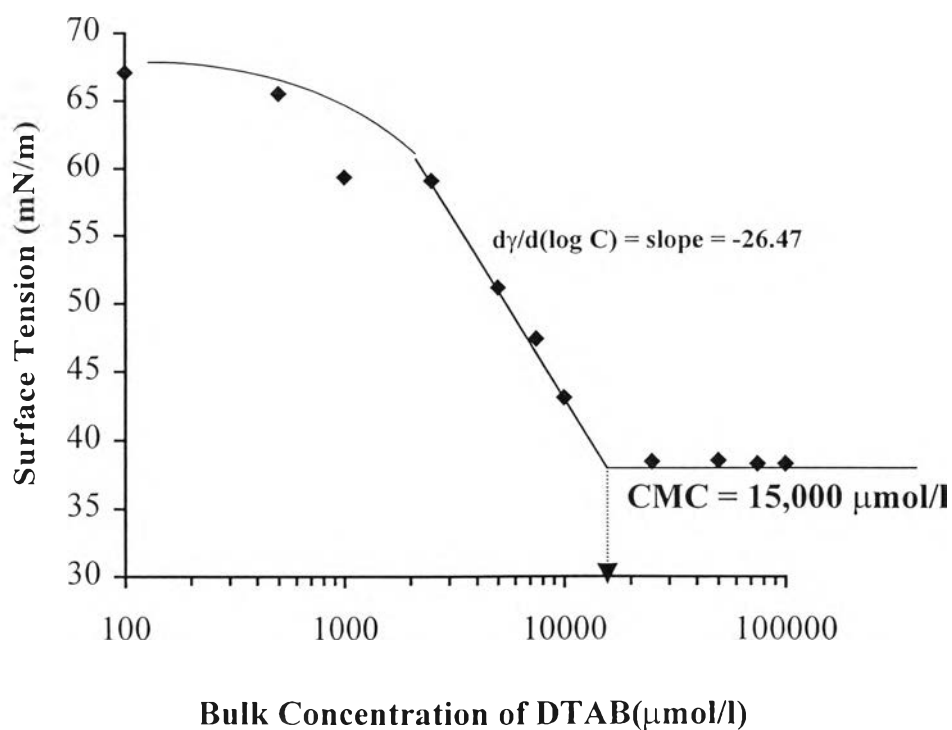


Figure 4.1 Relationship between surface tension and bulk concentration of DTAB solution at $\text{pH } 6.2 \pm 0.05$ and under room temperature (26°C).

As the concentration of DTAB solution increased from 500 to 15,000 $\mu\text{mol/l}$, the surface tension sharply decreased. This decrease is due mainly to the increased activity of surfactant in the bulk phase rather than at the interface. As the concentration of DTAB solution increased above 15,000 $\mu\text{mol/l}$, the surface tension tends to be constant or slightly to decrease. This phenomenon indicates that the concentration of surfactant monomers is almost constant. The meeting point between two straight lines, as shown in Figure 4.1, is commonly used to determine the CMC of such systems. The CMC of DTAB at $\text{pH } 6.2 \pm 0.05$ under room temperature (26°C) was 15,000 $\mu\text{mol/l}$ corresponding to 4,600 mg/l . This measured value of CMC of DTAB is found to be close to the value given in literature which is 16,000 $\mu\text{mol/l}$ (Rosen, 1988). The impurities in the studied DTAB and the presence of counterions from the pH adjustment probably caused the measured value of the CMC of DTAB to be different from the value given in the literature.

4.2 Adsorption Isotherm of DTAB on Quartz

It is necessary to determine the time to equilibrium for a study of adsorption isotherm experiment. Figure 4.2 shows the adsorption density of DTAB on quartz at different times. As can be seen from Figure 4.2, for both DTAB concentrations of 1.0 and 100 $\mu\text{mol/l}$, the adsorption density is constant after 5 minutes. This result is quite similar to the work conducted by Takeda and Usui (1987). They conducted a study of adsorption of dodecylammonium ion on quartz in relation to its flotation. In their study, dodecylammonium acetate (DAA, $\text{C}_{12}\text{H}_{25}\text{NH}_3\text{CO}_2\text{CH}_3$), also a cationic surfactant, was adsorbed on quartz. It was found that the adsorption density of DAA did not alter in the range of time 7-40 minutes. Thus, it can be concluded that the adsorption

process of DTAB on quartz is quiet fast. Therefore, 20 minutes time was used in this experimental study for adsorption equilibrium.

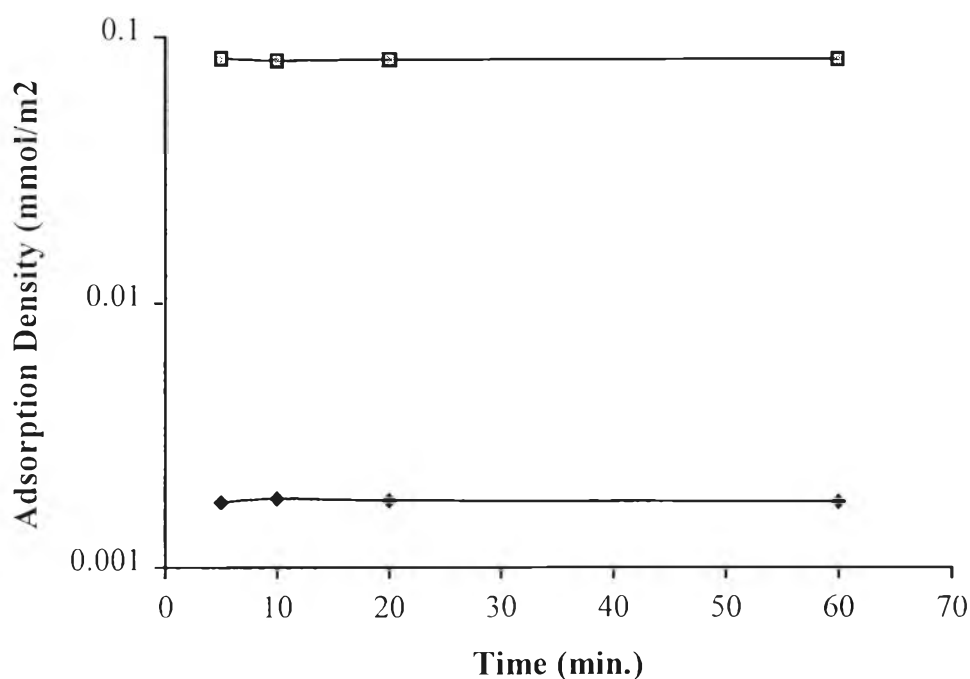


Figure 4.2 Relationship between adsorption density of DTAB and time at the initial concentration of DTAB for 1.0 and 100 $\mu\text{mol/l}$, pH 6.2 ± 0.05 and under room temperature (26 ± 1.0 °C).

Figure 4.3 shows the adsorption density of DTAB on quartz versus equilibrium concentration of DTAB on a log-log scale. By locating the CMC of DTAB on the adsorption isotherm into 3 main regions of I, II and IV. Region III is very difficult to be located in this system.

Region I. As the equilibrium concentration of DTAB increased in the range of 0.1 and 7.5 $\mu\text{mol/l}$, the adsorption density was increased slightly. This slightly increase is referred at Henry's law behavior. Hence, region I of the

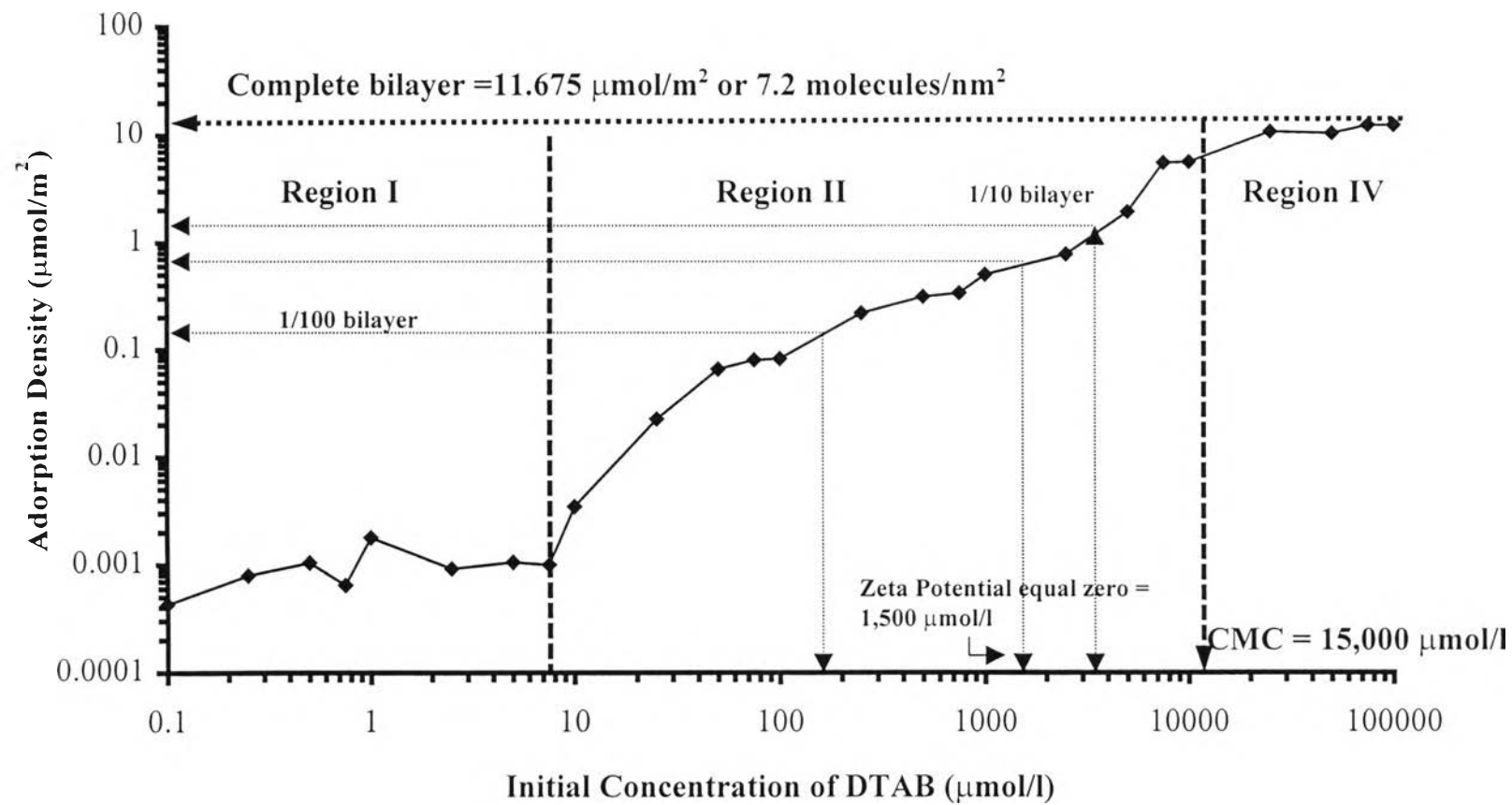


Figure 4.3 Adsorption isotherm of DTAB on quartz at $\text{pH } 6.2 \pm 0.05$ at room temperature ($26 \pm 1.0 \text{ }^\circ\text{C}$).

adsorption isotherm can be located at the concentration of DTAB solution less than 7.5 $\mu\text{mol/l}$. At equilibrium concentrations above 7.5 $\mu\text{mol/l}$, the adsorption density increased significantly. This point of change in the slope is commonly referred to the critical hemimicelle concentration.

Region II. For equilibrium concentrations of DTAB in the range 7.5 to 15,000 $\mu\text{mol/l}$, the adsorption density was sharply increased with increase in the concentration of DTAB. The increase of the slope in region II indicates surfactant aggregate formation on the solid surface, which are known as hemimicelles or admicelles. Region I and II can be simply distinguished by the change in the slope. The change in the slope is known as critical hemimicelle concentration. Region II and III cannot be divided clearly so that region III is include in region II in this analysis.

Region IV. As can be seen in Figure 4.3, the adsorption density becomes approximately constant with increasing of the DTAB equilibrium concentration when the DTAB concentration exceeds 15,000 $\mu\text{mol/l}$. The maximum adsorption density was approximately 11.7 $\mu\text{mol/m}^2$. This value is constant because of the adsorbed layer possesses a complete bilayer structure and became the excess surfactant molecules form micelles in the aqueous phase. This adsorption density corresponds to 7.2 molecules/ nm^2 , or an average area per headgroup of only 14 A^2 /molecule. Since the cross-sectional area of the tail group is 22 A^2 (Rosen, 1988), a bilayer adsorption density is implied.

4.3 Electrophoretic Mobility

In this study, electrophoretic mobility was expressed in terms of zeta potential. The zeta potential results from the charge on the solid's surface. When surfactant molecules are adsorbed on a solid surface, the zeta potential of the solid surface will be changed. This experiment was used to verify that

DTAB could be adsorbed on the quartz's surface. In this study, the quartz surface was negatively charged and surfactant (DTAB) was a cationic surfactant having positive charge. When DTAB molecules are adsorbed on the quartz's surface the zeta potential will become more positive. Figure 4.4 shows the plot between zeta potential and the DTAB equilibrium concentration. At a low concentration of DTAB solution between 0.1 and 7.5 $\mu\text{mol/l}$, the zeta potential was slightly increased with increasing of DTAB concentration. This corresponds to the result of the adsorption isotherm in region I. At DTAB concentrations between 7.5 and 15,000 $\mu\text{mol/l}$, the zeta potential increased sharply with increasing of DTAB concentration, which was corresponded to the result of the adsorption isotherm in region II/III. The zeta potential was equal to zero millivolt at the DTAB concentration of 1,500 $\mu\text{mol/l}$. A zero charge on the quartz's surface, does not implies that surfactant is adsorbed fully on the solid surface, only that the overall charge on the solid surface is balanced by the charge of the adsorbed surfactant. For DTAB concentration greater than 15,000 $\mu\text{mol/l}$ the zeta potential appeared constant at 22.0 millivolt, which was corresponded to region IV of the adsorption isotherm. This results indicate that the surfactant molecules are fully adsorbed to form a bilayer structure of surfactant on the quartz surface.

It is frequently, but not always, observed that the boundary between Region II and Region III corresponds to the point of zero zeta potential. This is not the case in this study. There is no obvious decrease in the slope of the isotherm above the zero of zeta potential. In this study the zero in zeta potential occurs at only about 6% of bilayer coverage or about 12 % of monolayer coverage.

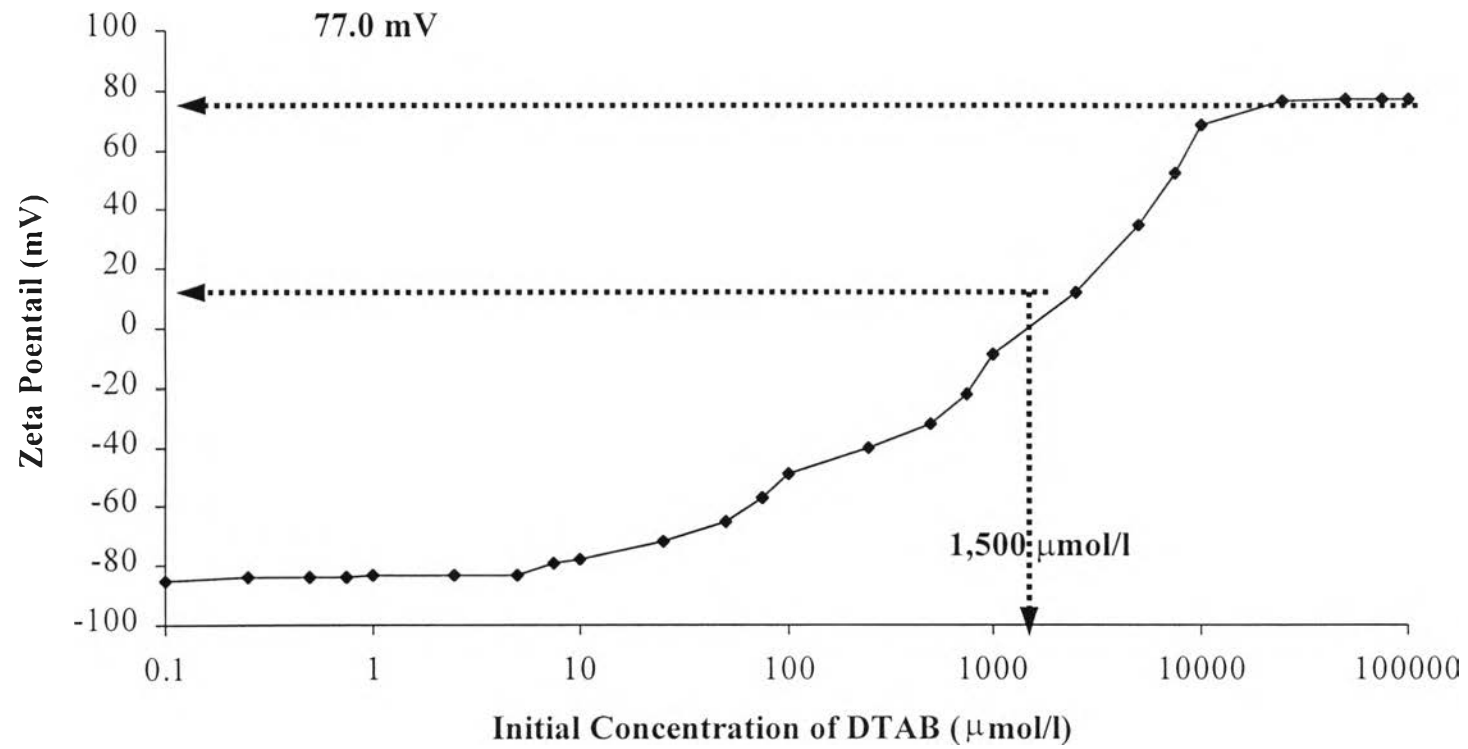


Figure 4.4 Relationship between quartz particle zeta potential and equilibrium concentration of DTAB.

4.4 Flotation

In this part of the study flotation was conducted to determine the effects of DTAB concentration and air flowrate on the flotation efficiency.

4.4.1 Effect of Surfactant Concentration

Figure 4.5 illustrates the comparison between the adsorption isotherm and the flotation efficiency isotherm at an air flowrate of 5.7 m./s. At equilibrium concentration of DTAB solution between 0.1 and 7.5 $\mu\text{mol/l}$, the percentage of quartz floated is slightly increased with increasing DTAB concentration. This concentration range corresponds to the adsorption isotherm in region I. Flotation is increased because some particles stick together even in this region (see below and in Appendix B) but the aggregates are still small. When air bubbles were added into the system the hydrophobic patches can be exposed to the air bubbles. The air bubble will be constant but the flotation efficiency is increased with increasing of DTAB concentration because of increasing quartz particles aggregation.

At equilibrium concentration of DTAB between 7.5 and 5000 $\mu\text{mol/l}$, the flotation efficiency is sharply increased, with increasing efficiency in the range of concentration between 7.5 and 500 $\mu\text{mol/l}$ and relatively constant efficiency between 500 to 5,000 $\mu\text{mol/l}$. This range of concentrations corresponds in region II of the adsorption isotherm. The range of DTAB concentration between 500 and 5,000 $\mu\text{mol/l}$ is close to the zeta potential charge equal zero millivolt at approximately DTAB concentration 1,500 $\mu\text{mol/l}$.

For the range of DTAB concentrations between 5,000 and 15,000 $\mu\text{mol/l}$, the flotation efficiency is sharply decreased with increasing DTAB concentration. This range of surfactant adsorption is strong hydrophobic interaction. So the aggregation will be decreased. This range can be occurred

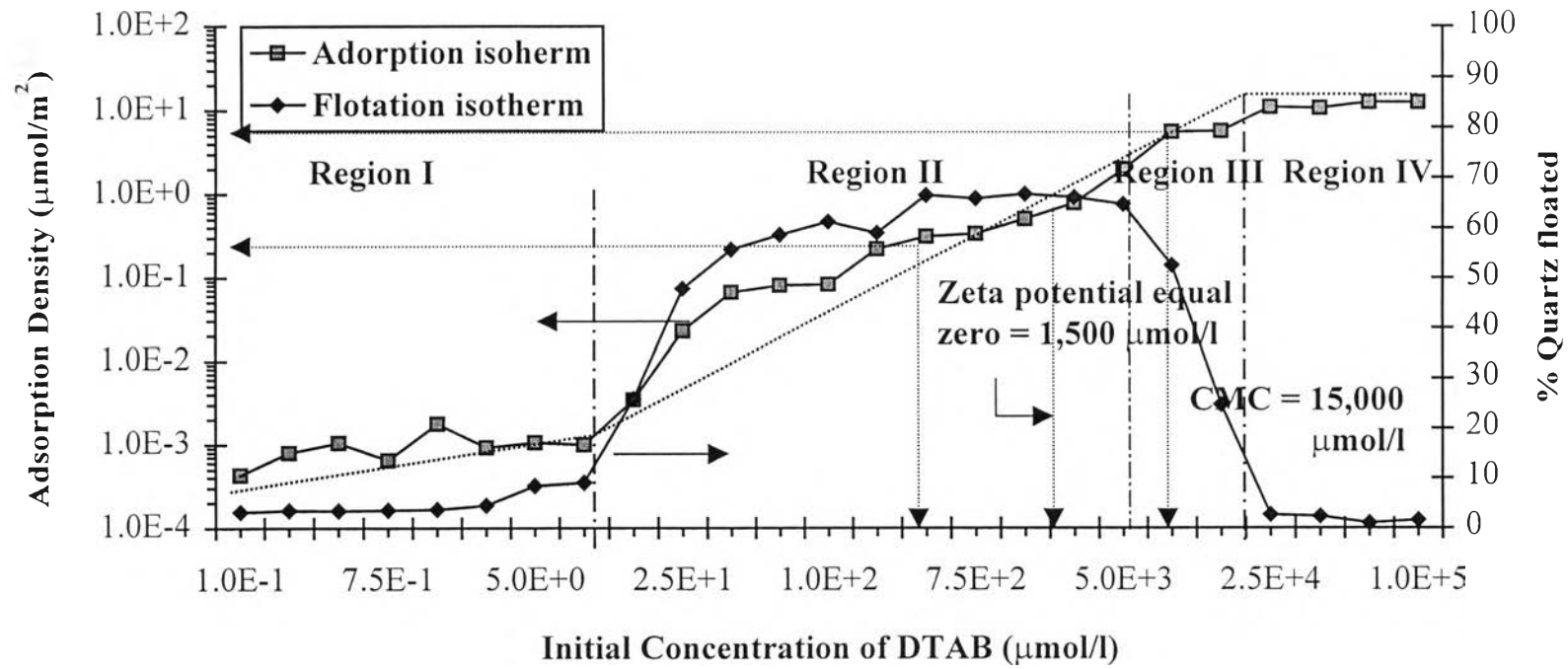


Figure 4.5 Comparison between adsorption isotherm and the flotation efficiency at air flow rate 5.7 ml/s.

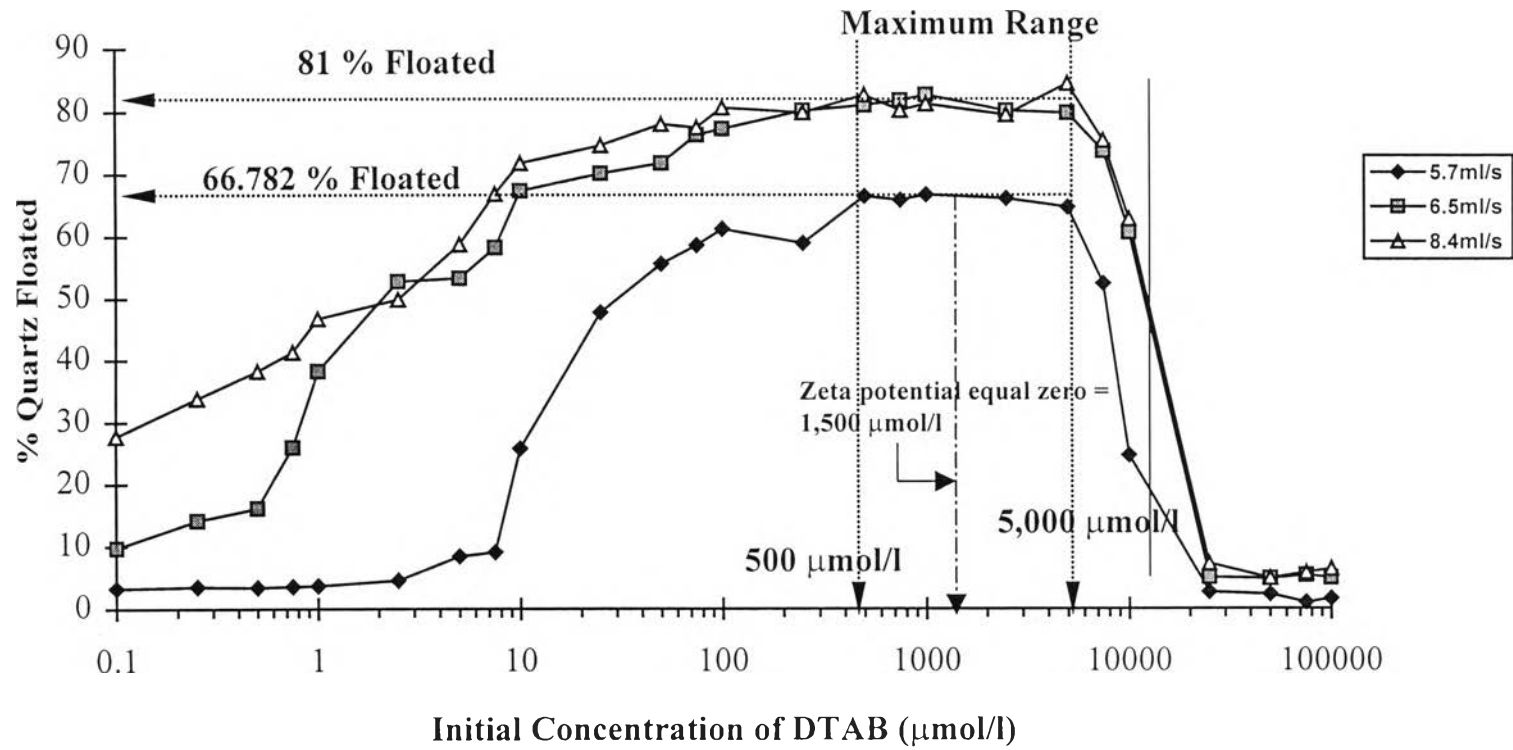


Figure 4.6 Relationship between flotation efficiency or percent quartz floated at different air flow rates versus DTAB concentrations.

reverse orientation model as well as to occur repulsion between the bubbles and the particle. On the basis of four-region model, flotation expected to exhibit a maximum at the transition point between region II/III. So, this range will correspond to region III of the adsorption isotherm.

For concentrations of DTAB solution more than 15,000 $\mu\text{mol/l}$, the flotation efficiency tends to be constant with increasing of DTAB concentration. This phenomenon can be explained by the complete bilayer structure of surfactant on the solid surface. The solid surface is hydrophilic patches. Thus the flotation efficiency will be constant and low.

4.4.2 Effect of Air Flowrate

Figure 4.6 illustrates the relationship between the quartz removal efficiency and the DTAB concentration with different air flowrates. As can be seen from Figure 4.6, at the equilibrium concentration of DTAB solution in the range of 0.1 to 500 $\mu\text{mol/l}$, the percentage of quartz floated was increased with increasing of the air flowrate from 5.7 to 8.4 ml/s. This phenomenon occurred because the hydrophobic patches on solid surface which can be exposed increase with increasing of the bubbles at air flowrate increased.

For concentrations of DTAB between 500 and 5,000 $\mu\text{mol/l}$, the flotation efficiency tend to be constant and a maximum for all three air flowrates. The flotation efficiency was increased with increasing of the air flowrate form 5.7 to 6.5 ml/s. When the air flowrate increased form 6.5 to 8.4 ml/s the flotation efficiency stayed constant, however. This is because of the flotation system is limited by such factors as flotation cell type pH, type of surfactant, etc. The values of percent quartz floated at the maximum are approximately 67% at the air flow rate 5.7 ml/s and approximately 81% at the air flowrates 6.5 and 8.4 ml/s.

For concentration of DTAB between 5,000 and 15,000 $\mu\text{mol/l}$., the percent of quartz floated sharply decreases with increasing DTAB

concentration for all three air flowrates. But the flotation efficiency increases with increasing of the air flowrate.

For DTAB concentrations exceeding 15,000 $\mu\text{mol/l}$, for all three air flowrates, the flotation efficiency tends to be constant but the flotation efficiency is slightly increased with increasing air flowrate.

4.5 Sizes of Quartz Aggregates

Sizes of the quartz aggregates formed at different DTAB concentrations were measured by an optical microscope as described in Chapter III. Photographs of quartz aggregates formed at different DTAB concentration are shown in Figure 4.7-4.12; other photographs are shown in Appendix B. Cumulative percentage of quartz aggregate size can be seen from Figure 4.13. As can be seen from Figure 4.7, under the absence of surfactant, almost all quartz particles are highly dispersed as a result of the electrostatic repulsion between the negatively charged quartz particles; the average particle size was approximately 28.3 μm and the maximum particles size was approximately 56.6 μm .

Aggregation of quartz particles occurred when the DTAB concentration is as low as 1.0 $\mu\text{mol/l}$ as shown in Figure 4.8, and the adsorption as low as one molecule/5,000 \AA^2 . This concentration corresponded to region I of the adsorption isotherm. Some quartz particles remained dispersed while other were aggregated. The average particle size of quartz was still approximately 28.3 μm but the maximum particle size was 96 μm . Since the solid surface is slightly increased in hydrophobicity, the hydrophobic patches cause the particles quartz to stick together and form aggregates. The percentage of particles aggregate is 67.5. Figure 4.9 shows a significant increase in the aggregate size when the DTAB concentration increase to 100 $\mu\text{mol/l}$.

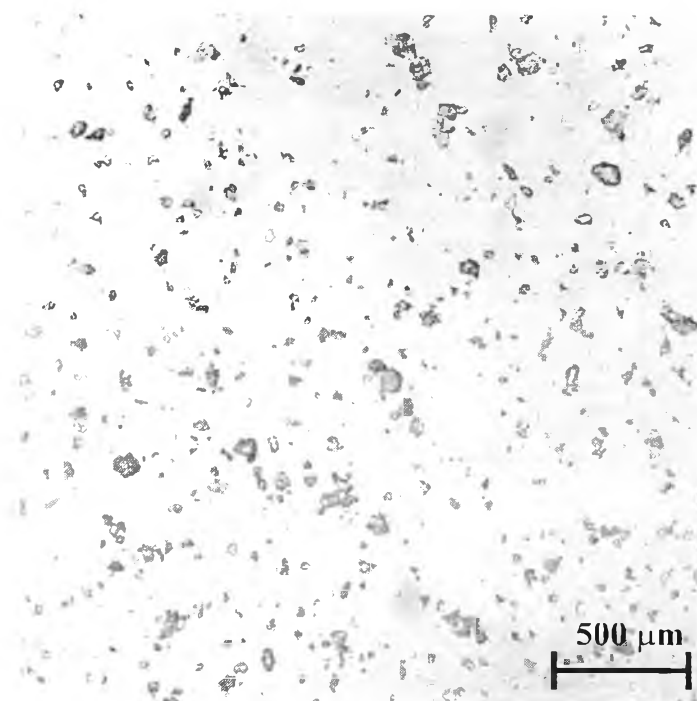


Figure 4.7 The smallest size aggregates of quartz particles as without surfactant.

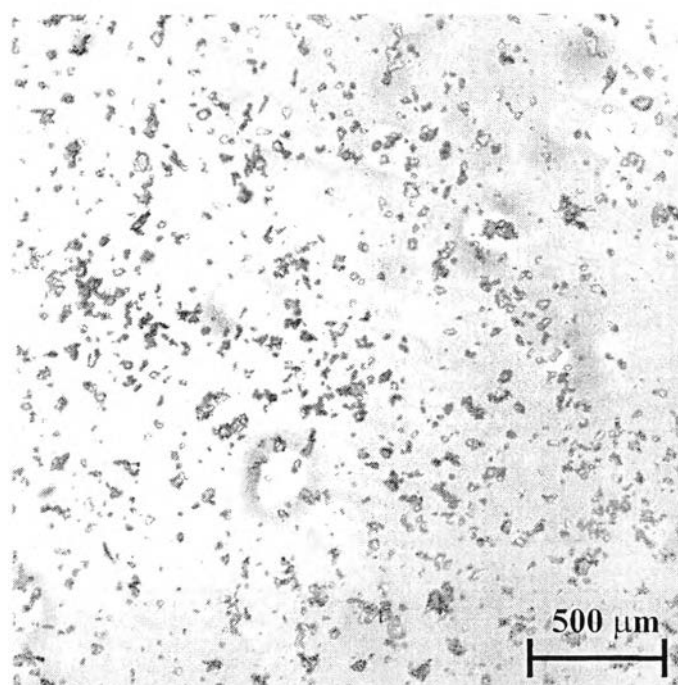


Figure 4.8 Aggregates of quartz particles at DTAB concentration 1.0 $\mu\text{mol/l}$ initial concentration.

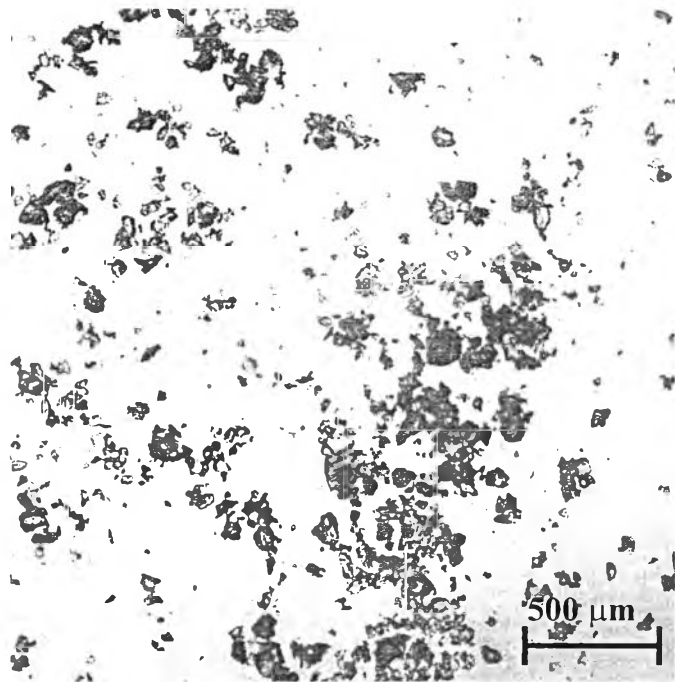


Figure 4.9 Aggregates of quartz particles at DTAB concentration 100 $\mu\text{mol/l}$ initial concentration.

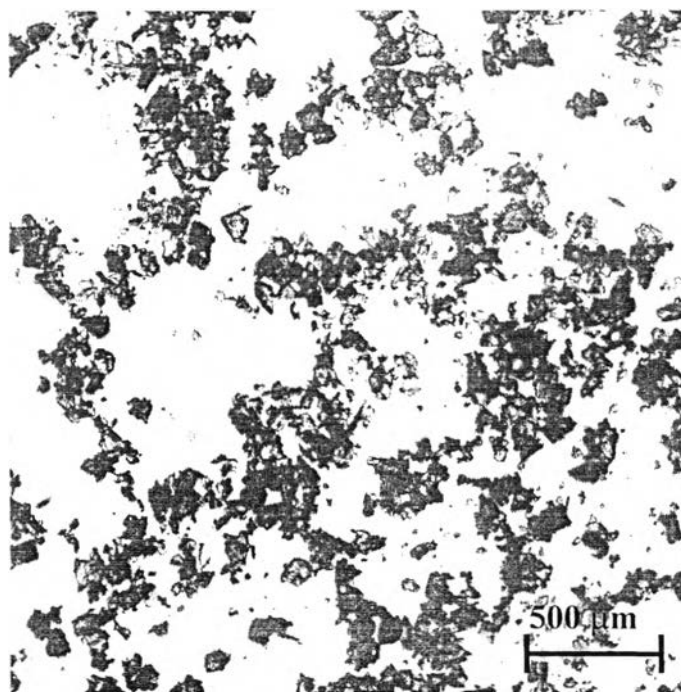


Figure 4.10 The largest size aggregates of quartz particles at DTAB concentration of 5000 $\mu\text{mol/l}$ initial concentration.

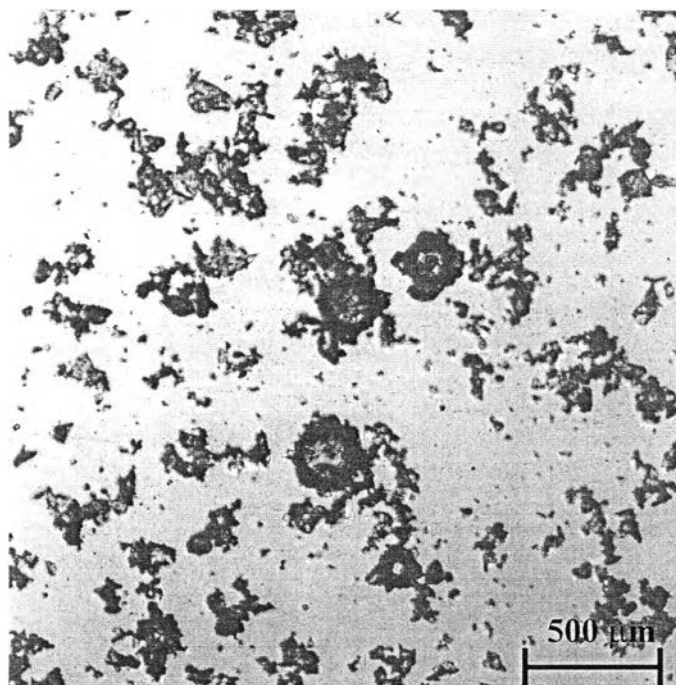


Figure 4.11 Aggregates of quartz particles at DTAB concentration of 10,000 $\mu\text{mol/l}$ initial concentration.

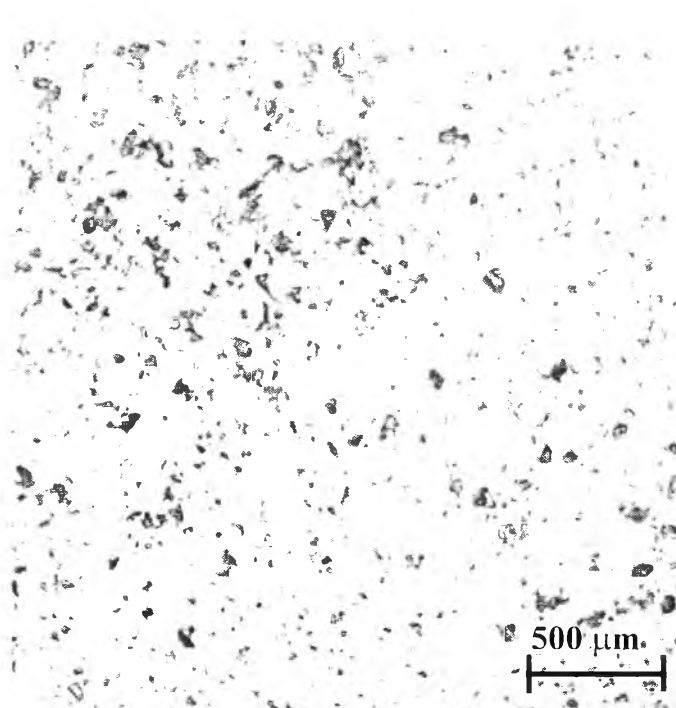


Figure 4.12 Aggregates of quartz particles at DTAB concentration of 100,000 $\mu\text{mol/l}$ initial concentration.

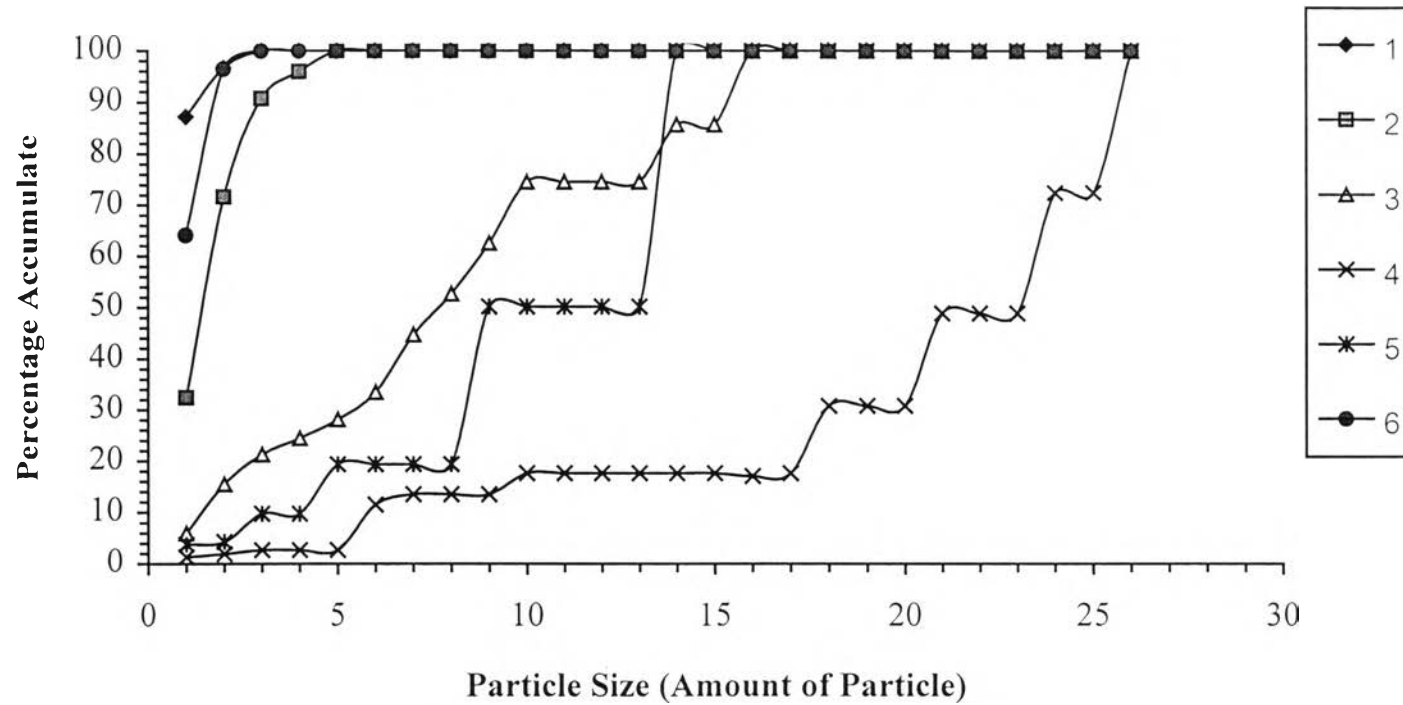


Figure 4.13 Commutative aggregate size distribution.

1 = without surfactant , 2 =at concentration for 1.0 $\mu\text{mol/l}$, 3 =at concentration for 100 $\mu\text{mol/l}$
 4= at concentration for 5,000 $\mu\text{mol/l}$, 5 = at concentration for 10,000 $\mu\text{mol/l}$, 6= at concentration
 for 100,000 $\mu\text{mol/l}$

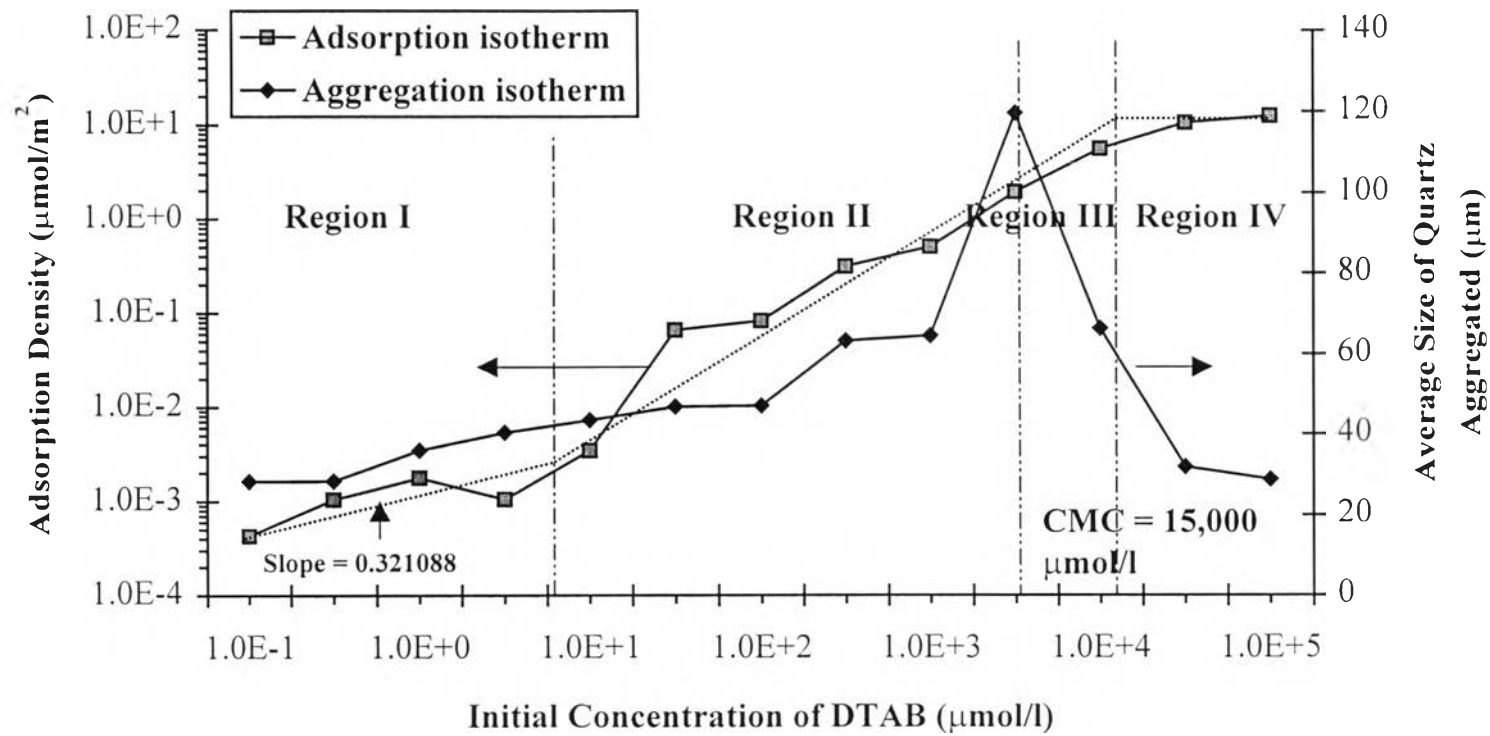


Figure 4.14 Correlation between adsorption isotherm and average size of quartz aggregates at different DTAB concentrations.

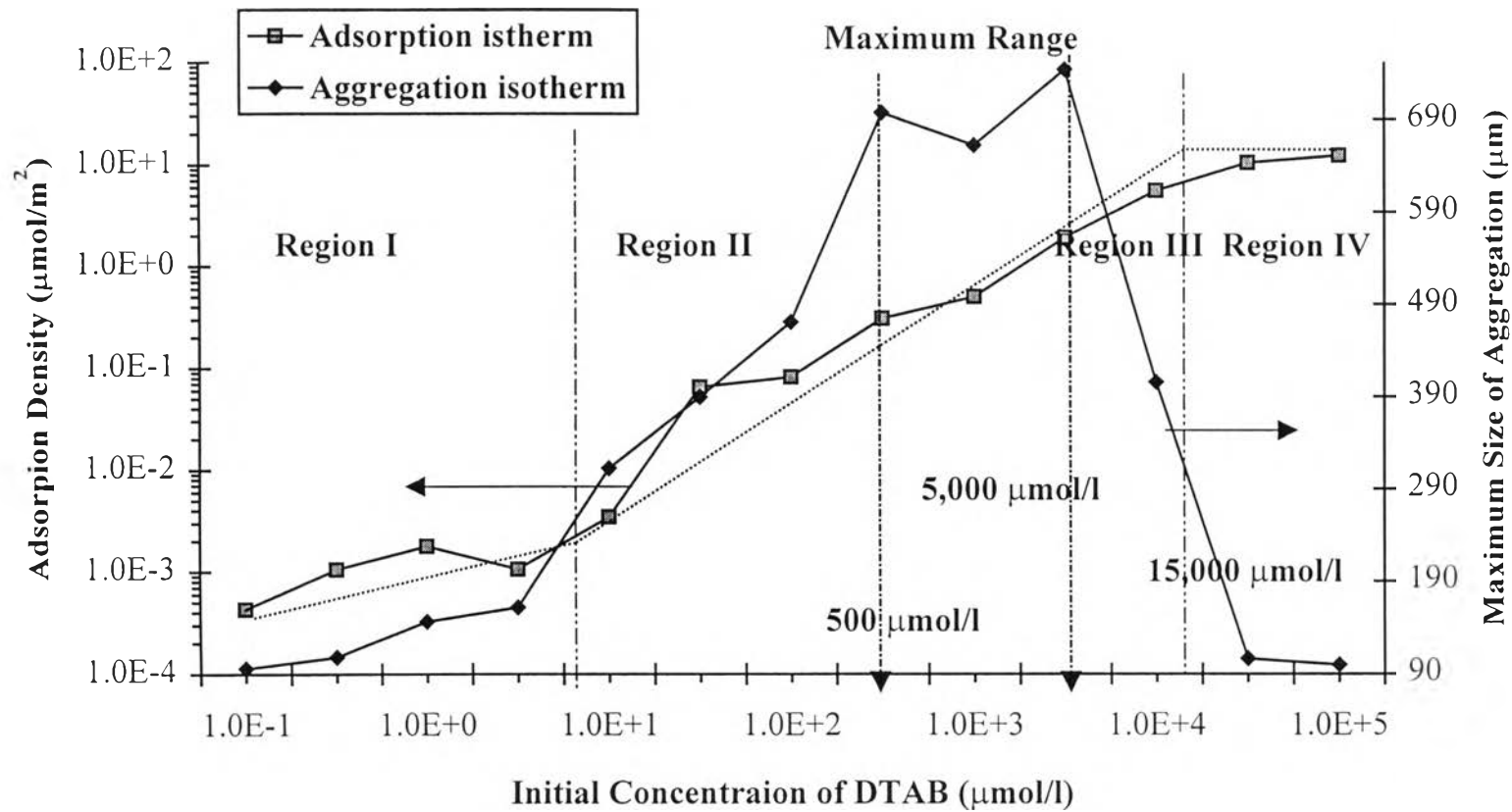


Figure 4.15 Correlation between adsorption isotherm and maximum size of quartz aggregates at different DTAB concentrations.

This DTAB concentration was now the range of region II of the adsorption isotherm. From the figure, however, some quartz particles are still completely dispersed. The average size of the quartz aggregates was now approximately 47 μm but the maximum particle size was 470 μm . Surfactant adsorption density is still quite low at less than 1/100 bilayer. The percentage of particles aggregated is 94.0. The largest size of the quartz aggregates appears when the DTAB concentration is 5,000 $\mu\text{mol/l}$, as shown Figure 4.10. This DTAB concentration was still in the range of region II of the adsorption isotherm. The average size of quartz particle aggregates was now approximately 120 μm and the maximum particle size was 743 μm . From the figure, however, some quartz particles are still completely dispersed and some quartz particles are aggregated. The percentage of particles aggregate is 98.7. This concentration gives less dispersion and more aggregation when compared to DTAB concentration of 100 $\mu\text{mol/l}$.

Particle aggregation at a DTAB concentration of 10,000 $\mu\text{mol/l}$, is shown Figure 4.11 This concentration is in the range of region III which is explained in next paragraph. The average size of quartz aggregates is approximately 66.3 μm and the maximum aggregate size is 406 μm . The percentage of particle aggregate is 96.2. This concentration gives less aggregation and more dispersion when compared to DTAB concentration 5,000 $\mu\text{mol/l}$. The aggregation of quartz particles as DTAB concentration of 100,000 $\mu\text{mol/l}$ is shown in Figure 4.12. This concentration is in the range of region IV of the adsorption isotherm. From the figure, almost all quartz particles are redispersed, though a few quartz particles are still aggregated. The particle size average is approximately 29 μm and the particle size maximum is 96 μm . The percentage of particle aggregated is 35.4. This phenomenon occurs because the solid surface is hydrophilic with a complete the bilayer surfactant structure.

Figure 4.14 and Figure 4.15 compare size of quartz aggregates and surfactant adsorption. In the range of DTAB concentration between 0.1 and

5,000 $\mu\text{mol/l}$, the particles size of quartz aggregated is increased with increasing of DTAB concentration as corresponded in the adsorption isotherm region I and II. The maximum particle size of quartz aggregated occurs in the adsorption isotherm region II. From Figure 4.15, the size of quartz aggregate was maximum in the range of DTAB concentrations between 500 and 5,000 $\mu\text{mol/l}$. This range is close to the zero zeta potential at a DTAB concentration of 1,500 $\mu\text{mol/l}$. On the basis of the four-region model, flotation is expected to exhibit a maximum at the transition point between regions II and III (Fan, et al., 1996). This range of concentration is corresponds in the flotation results. So, at the maximum particle size it corresponds to the II/III transition. For range of DTAB concentrations between 5,000 and 15,000 $\mu\text{mol/l}$ the size of quartz aggregates is decreased with increasing of DTAB concentration. This phenomenon corresponds to region III of the adsorption isotherm. This extent of region III in the present system can hence be concluded on the basis of aggregation. When the DTAB concentration excess the CMC, the size of quartz aggregates, becomes the small again and tends to be constant. This phenomenon correspond the adsorption isotherm in region IV. The average aggregate size now almost the sane as in when no surfactant was added. But the largest particle are now much larger.