

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Salt

The increase of particle floc size with time was observed for all salt concentrations. As shown in Figure 4.1, the floc size increased rapidly at the beginning and then leveled off. In general, the rate of flocculation increased with the increase in electrolyte concentration. The addition of salt led to the increase in the concentration of ion screening surface charge and, therefore, suppressed the repulsion and allowed irreversible flocculation. It might cause a compression of the diffuse part of the double layers around the particle. The flocculation of particles occurred when the repulsive forces were reduced to the value that particles came close enough until van der Waal force was predominant. Conversely, at low salt concentration, the electrostatic repulsion among silica particles was strong so that particles remained dispersing in the solution. Figure 4.2 showed that when salt concentration exceeded 0.5 m/l, silica particles started to be destabilized. The floc size increased with increasing the electrolyte concentration. The higher the amount of electrolyte concentration, the more difficulty to stabilize the silica system would be.

4.2 Effect of Polymer

Stability of the silica particles in the low molecular weight polymers was investigated (Figure 4.3). It was found that the particle size kept increasing with increase in the polymer concentration. The results showed that the low molecular weight polyacrylamide was not effective to stabilize the silica suspension.

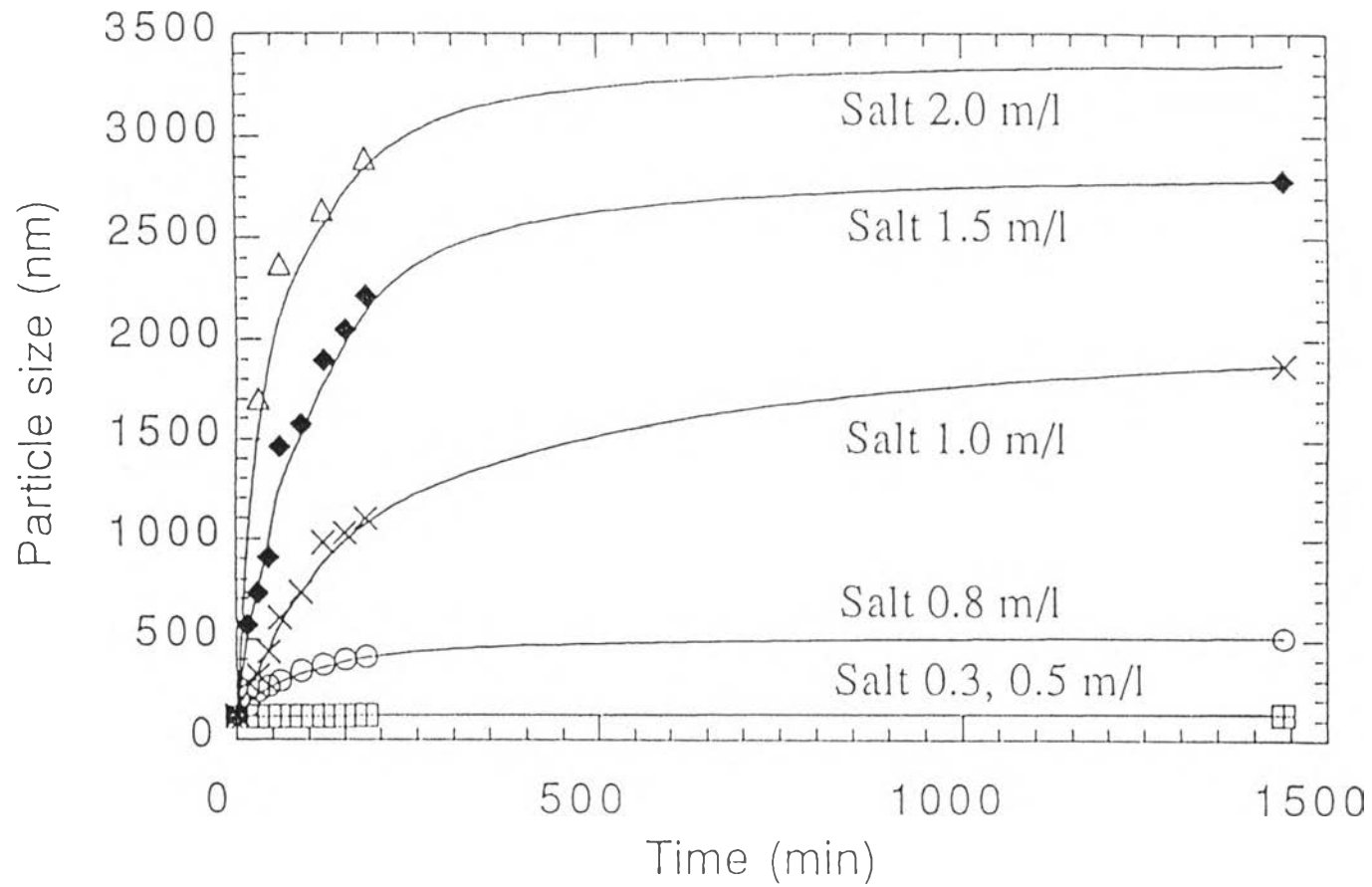


Figure 4.1: Effect of the electrolyte concentration on particle growth of silica suspension. The silica particle concentration was fixed at 7000 ppm. The high shear rate was made by magnetic stirrer.

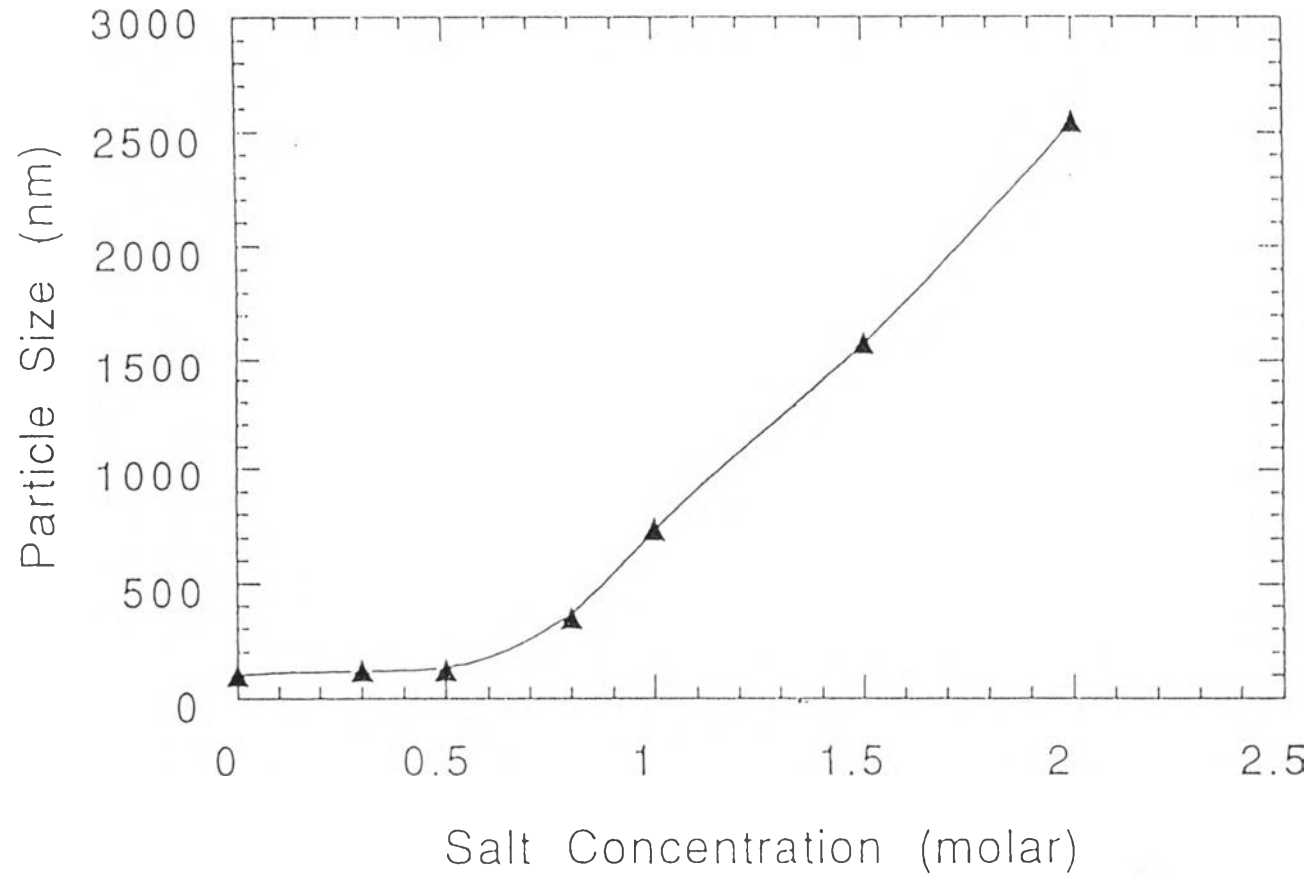


Figure 4.2 : The correlation between particle size at different electrolyte solution.

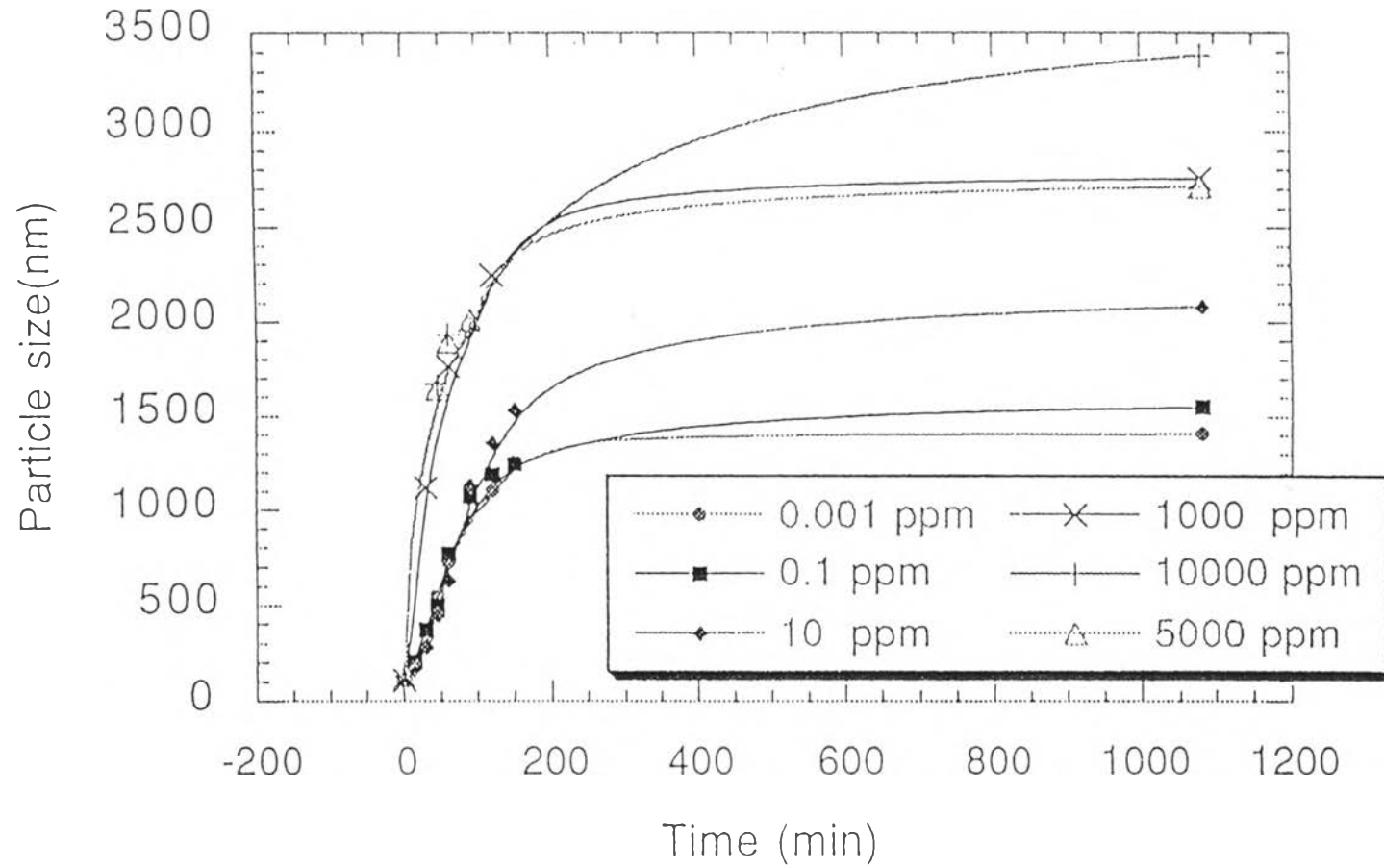


Figure 4.3: Effect of low molecular weight of nonionic polymer on the stability of silica particle at salt contraction 2 mol/l.

The effects of high molecular weight polyacrylamide and its concentration on stability of silica system were shown in Figure 4.4. Silica particles started flocculating as the concentration of polymer increased, due to the large amount of electrolyte concentration and the bridging phenomena. The increase in concentration of CTAB made the floc size increase until it reached maximum at about 10 ppm of polymer then it started to decrease. When the concentration of polymer was further increased, the particles were completely stabilized at the concentration of 50 ppm. These results showed that high molecular weight polyacrylamide (Mwt. 5,000,000-6,000,000) would stabilize the silica system. This kind of behavior could be explained by the complete and incomplete surface coverage of silica particles by polymers⁽³⁶⁾. As silica particles were not completely covered by polymer, polymer-polymer interaction led to particle bridging, but, at the full surface coverage, polymers repelled each other because of steric stabilization. The bridging phenomenon was due to the following interactions as follows

- (1.) Bridging among particle-polymer-particle (polymer bind particle together)
- (2.) Bridging between polymer and polymer (polymers interact with each other).

Low molecular weight polyacrylamide (Mwt 10,000) could not stabilize the silica particles as shown in Figure 4.5. Increase in the concentration of low molecular weight polyacrylamide led to the increase of the particle floc size. However, the stabilization of the flocs would occur at sufficiently high concentration of polymer while the effect of viscosity on the retardation of particle flocculation became significant.

The difference between high and low molecular weight polyacrylamides on stabilizing silica particles could be attributed to the viscous effect. For the same concentration (ppm) of polymer, the fluid with high molecular weight polymer was more viscous than that with low molecular weight. The experiment was performed to support the idea that viscous effect was more important than the effect of polymer concentration

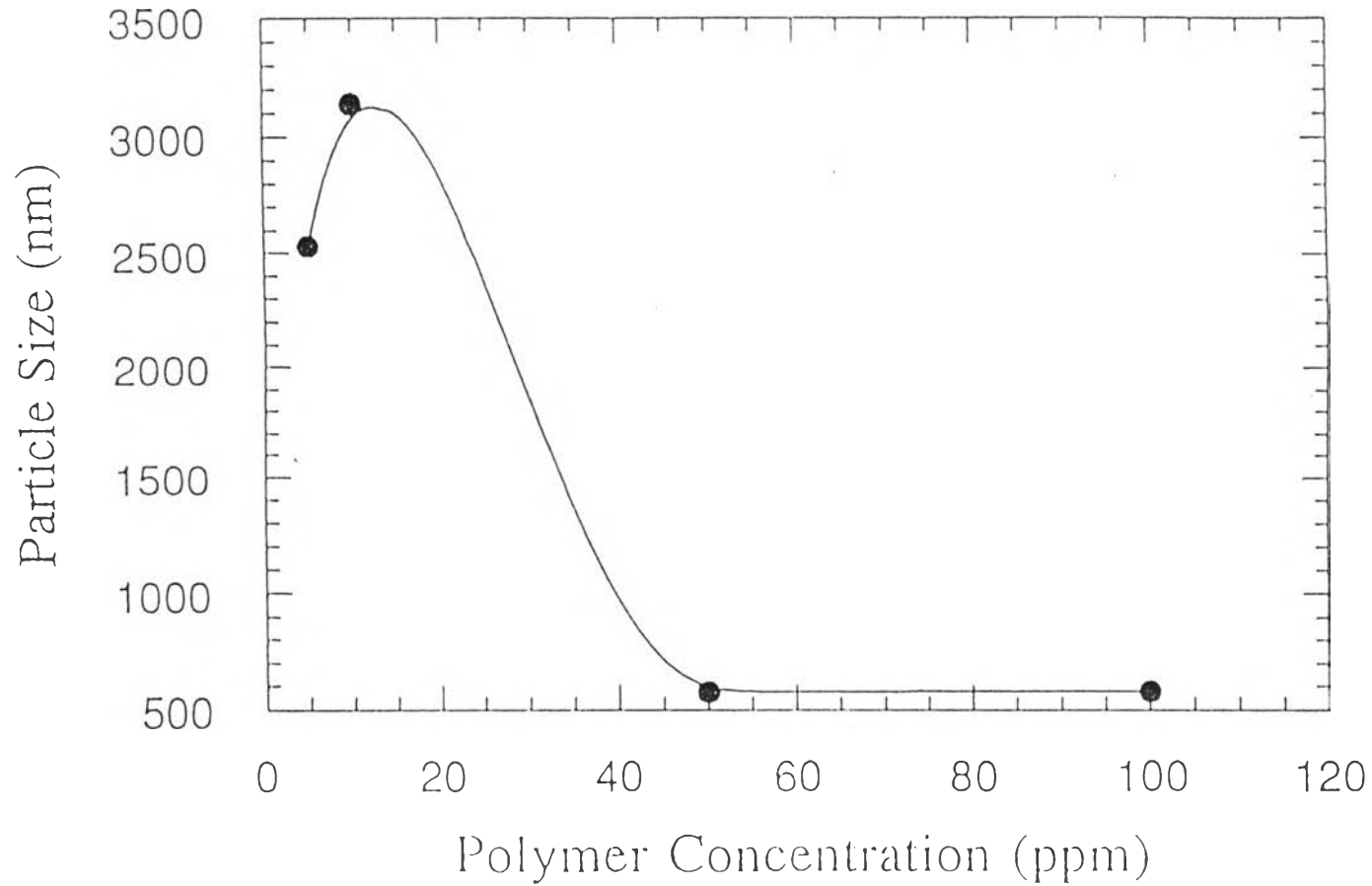


Figure 4.4: Effect of high molecular weight polymer(polyacrylamide) at salt concentration 2 mol/l on controllin the size of silica particles.

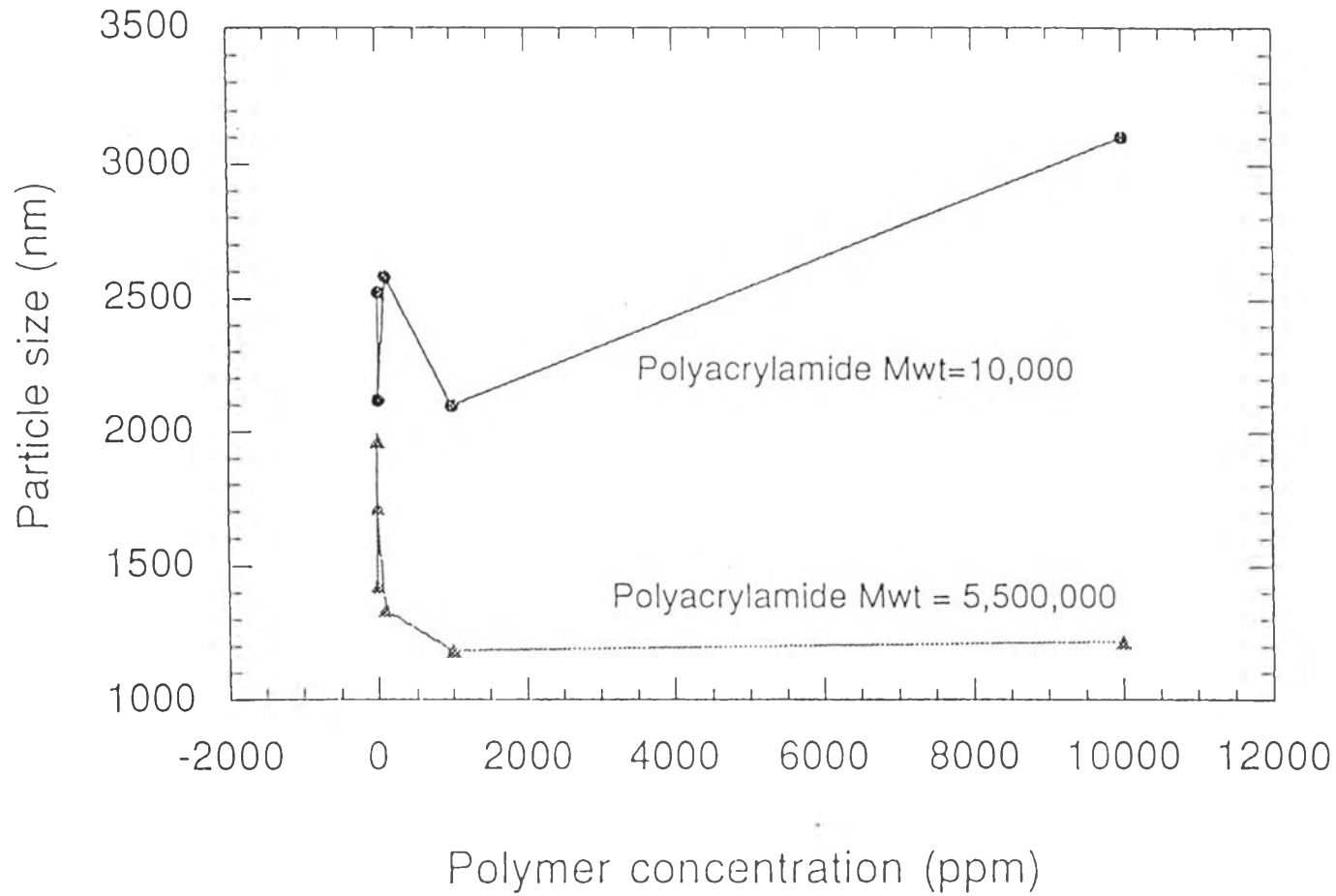


Figure 4.5: The effect of molecular weight of polymer on the silica floc at salt concentration 2 mol/l. The shear rate was applied by magnetic stirrer.

on the stability of silica particles. The results were shown in Figure 4.6.

As shown in Figure 4.6, the effect of viscosity in the silica floc experiment is significant. For different solutions with the same viscosity, the floc size should be similar in case of the system stabilization. By comparison of 3 different compositions : pure polymer, polymer with glycerol, and pure glycerol, all of which have the same viscosity, one observed (Figure 4.6) that the floc size did not change significantly. It showed that viscosity played a significant role on the stabilization of silica particles. At viscosity 9.63 cp., the solution was highly viscous and the particle size was much larger when pure polymer was added to the system than when pure glycerol was added (Figure 4.6). This trend could be explained on the basis of the polymer size in the pure solution. The particle of polymer at concentration 1000 ppm was large (400-800 nm) compared to silica particle (100 nm). Thus the measured particle size was in fact the size of polymer. The decrease in the rate of particle flocculation at high viscosity was due to the less mobility of particles in the solution.

There were some experimental errors which came from the impurity of the sample. The dust in the sample can cause an error in measurement using DLS. Moreover, the principle on which DLS works was “the light transmitted to the colloidal sample and the particle size was found from the angle of the scattered light, the intensity, sample time etc.”. For particles size measurement, sample solution had to be diluted to a very low concentration of silica particles. If the particle flocs were too large, it easily sank to the bottom of the tube leading to the difficulty in controlling the size distribution of the sample. The Coulter Counter could be used to determine the particle size distribution in the particle size range 0.4 - 30000 micron, but in this study Coulter Counter could not be used to measure the initial floc size which was as small as 0.1 micron.

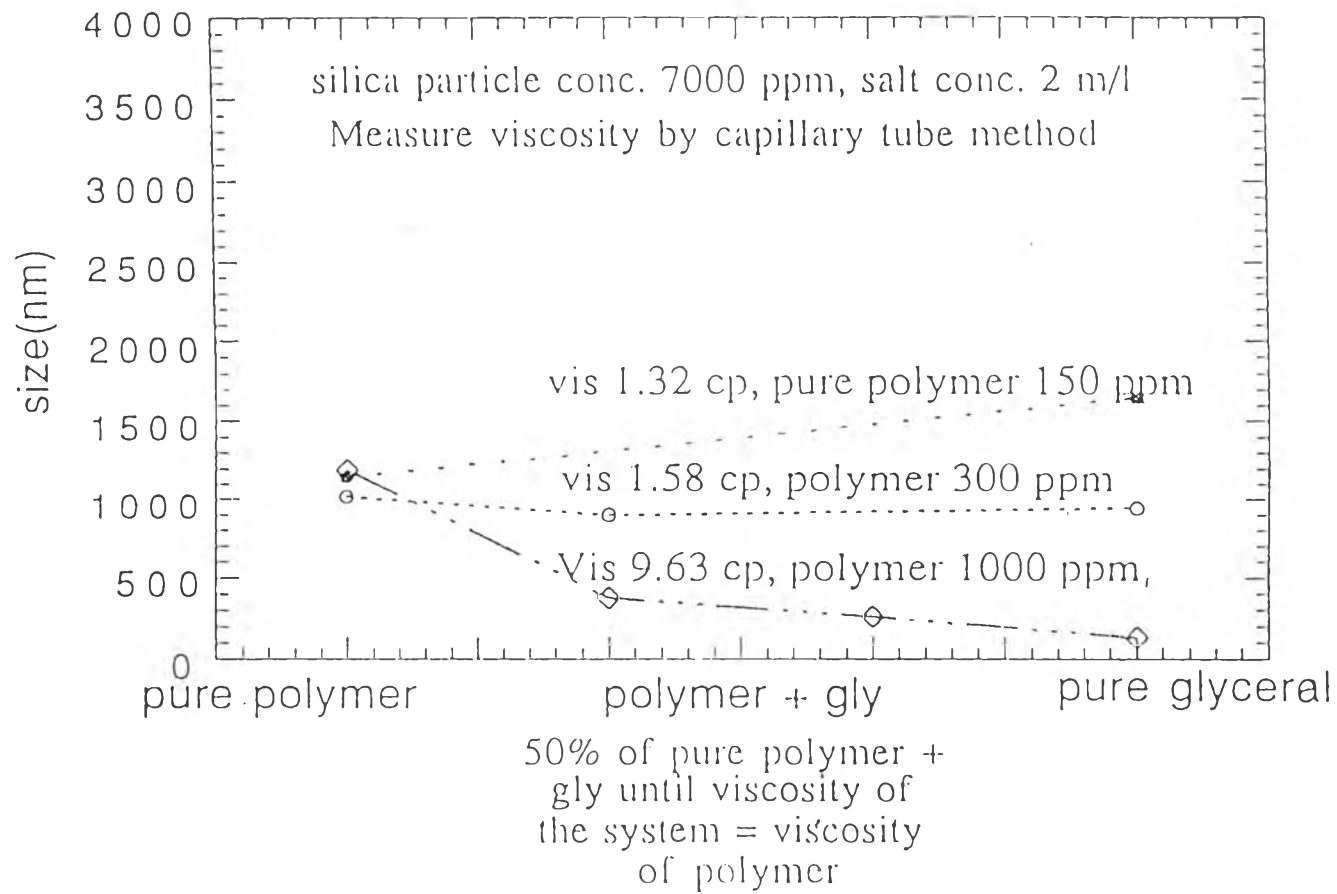


Figure 4.6: Effect of viscosity in the flocculation experiment.
Y - axis show the floc size at time 90 min after mixing.
X - axis stands for; "Pure polymer", "Polymer + Glycerol", "Pure Glycerol".

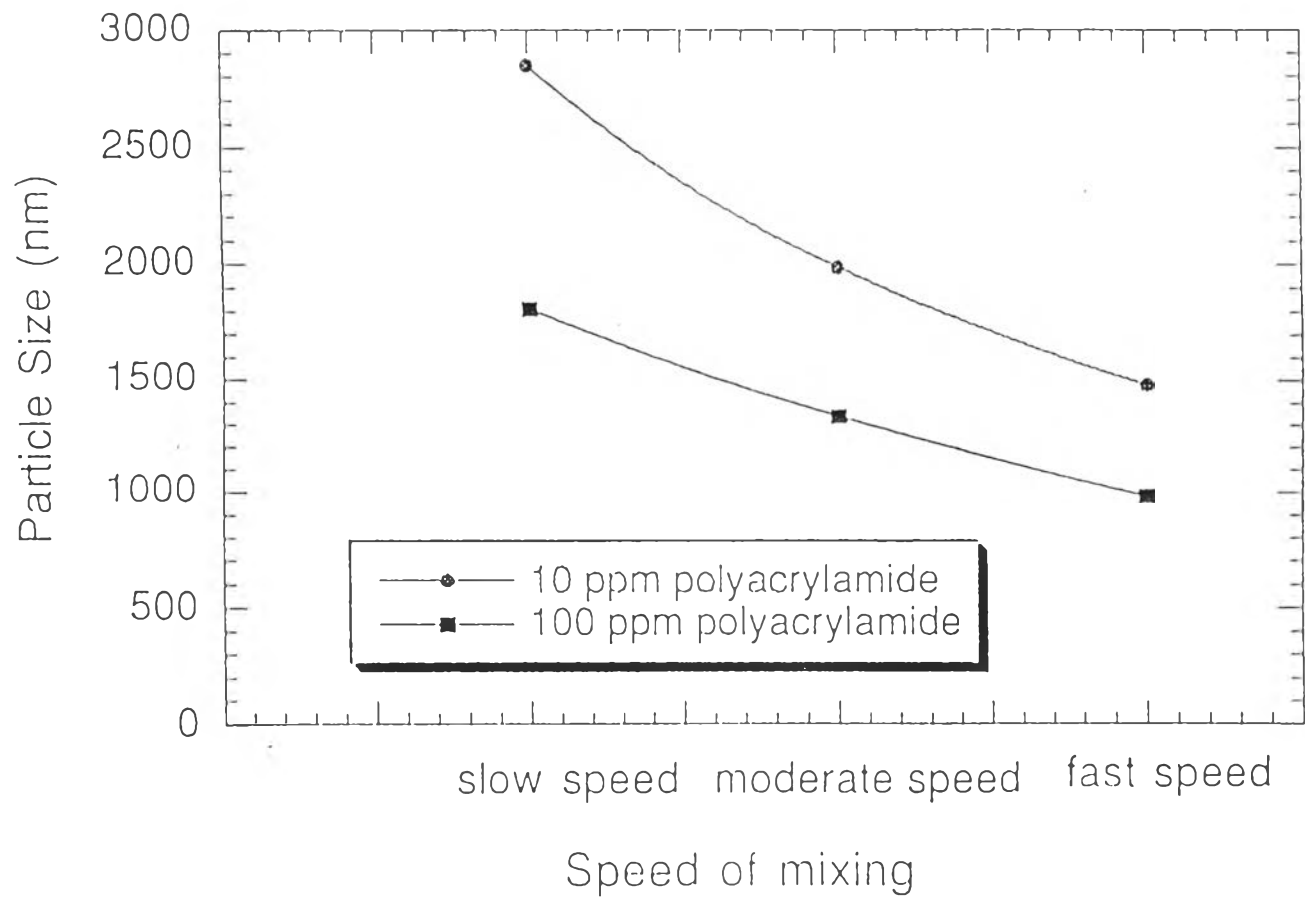


Figure 4.7: Effect of shear rate on different concentration of high molecular weight polymer at salt 2 mol/l. The magnetic stirrer was used for controlling the shear rate.

The speed of mixing was also an important parameter in controlling floc size as shown in Figure 4.7. When the mixing speed increases, the particle size was decreased. The figure showed that at high polymer concentration (100 ppm), the particle size was smaller than that at low polymer concentration (10 ppm). This trend might not be due to the effect of concentration alone because viscosity also had an effect on particle size as described earlier. The particle size decreased when the speed of mixing was increased because the high shear rate broke the attraction force among the particles. In the study, the shear rate applied to the solution was controlled by magnetic stirrer which did not give an exact value of shear rate. However it showed the trend that shear rate broke the bonds or the attraction among silica particles.

4.3 Effect of Surfactant

The effect of CTAB concentration on the size of silica flocs in aqueous solution at pH 8 was shown in Figure 4.8. Interestingly, one observed that the extremely large flocs occurred immediately after 7000 ppm silica particles being mixed with 100 ppm. The CTAB concentration from 0 to 100 ppm CTAB, the sizes of flocs increased with increasing CTAB concentration until the size peaks at 100 ppm CTAB was reached. However, the floc size stopped decreasing at 1000 ppm of CTAB and stayed the same even though the CTAB concentration was increased beyond 1000 ppm.

The result of pH 8 were founded as illustrated in Figure 4.9.

1. Low CTAB Concentration:

- Before CTAB was added, silica particles were completely stabilized by double layer repulsion. When the small amount of silica were added, this amount of CTAB was adsorbed in the silica surface. However, surfactant concentration was not high enough to fully cover the entire silica surface.

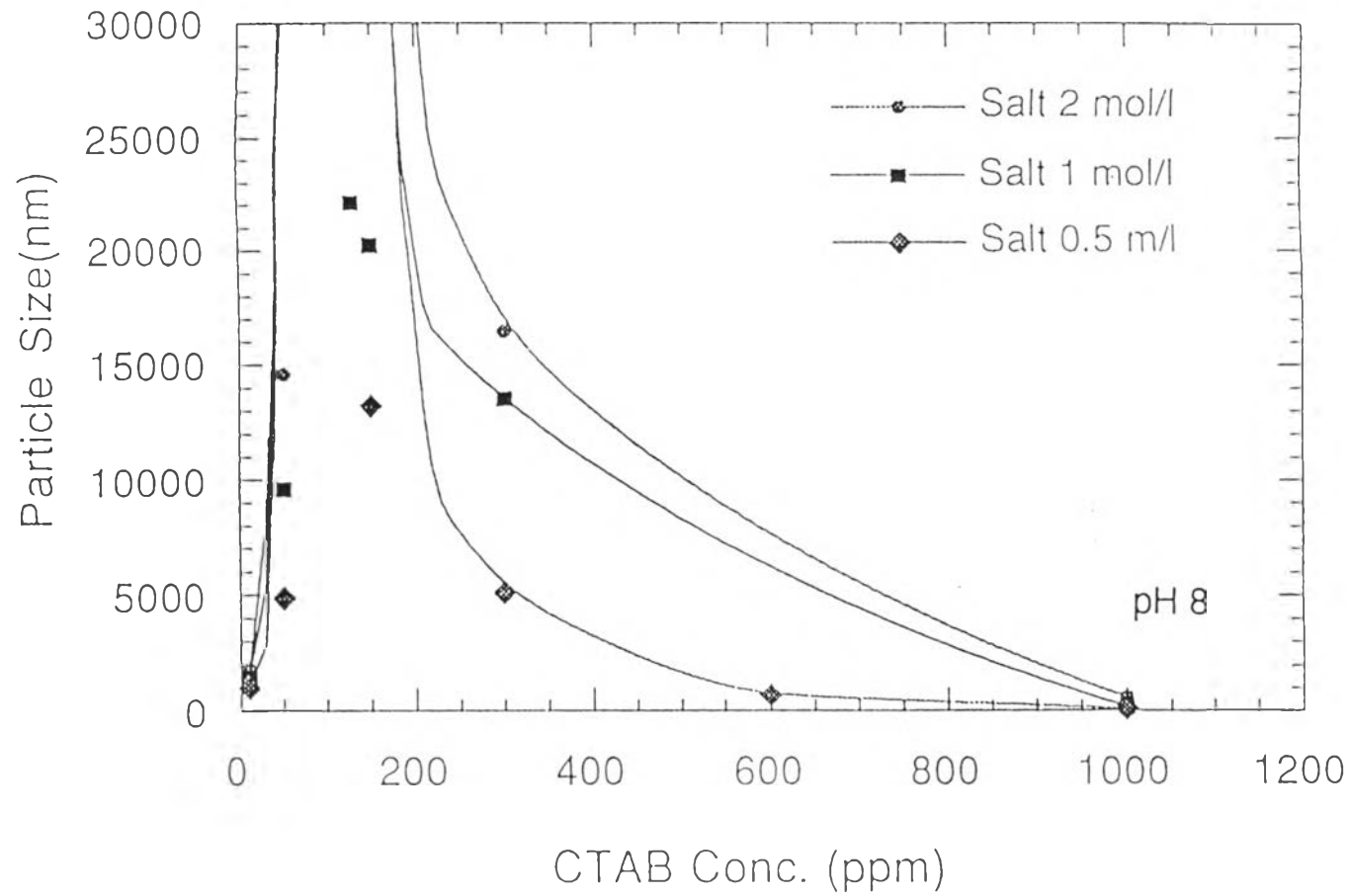


Figure 4.8 Effect of surfactant (CTAB) on the flocculation of silica particle at three different salt concentration. This experiment were performed at pH 8 and the high shear rate was applied by magnetic stirrer. The particle size was plotted at time 90 min after start mixing the sample.

The tail group of CTAB was hydrophobic so it tended to move away from the water by forming a bilayer as shown in Figure 4.9A. In this case, the silica particles aggregated due to the formation of CTAB bilayer.

- When a sufficient amount of electrolyte solution was added, the electrostatic repulsion among silica particles reduced. Therefore the attraction force among the particles became significant. The silica particles aggregated by direct contact with each other instead of bridging through surfactant molecules shown in Figure 4.9B.

2. High concentrations of CTAB:

- As more CTAB was added, the silica particles became completely covered with CTAB bilayer and the steric repulsion among them became significant. Moreover, the electrostatic repulsion also stabilized the system due to the charge on the surface of surfactant which was shown in Figure 4.9C

A similar study was performed at pH 4 and the results were shown in Figure 4.10. The floc size was still the largest at 100 ppm but the rate of formation of the flocs was not as fast as that at pH 8. In addition, the floc size at pH 4 was smaller than that at pH 8. The present study showed that CTAB could be used as stabilizer to disperse silica particles in the solution with pH 4 and 8, if the CTAB concentration were sufficiently high.

Comparing the results of the pH 4 and 8 experiments, we found that the pH played a significant role in the aggregation of silica particles. The effect of pH on the surface charge of colloidal silica in aqueous was well known⁽³⁷⁾. Silica particles were negatively charged in the range of pH 4 to 10. Consequently, this was the most effective range for CTAB adsorption. Above pH 10, the silica particles dissolve and at below pH 3, silica particles were positively charged. At a zero surface charge, the CTAB

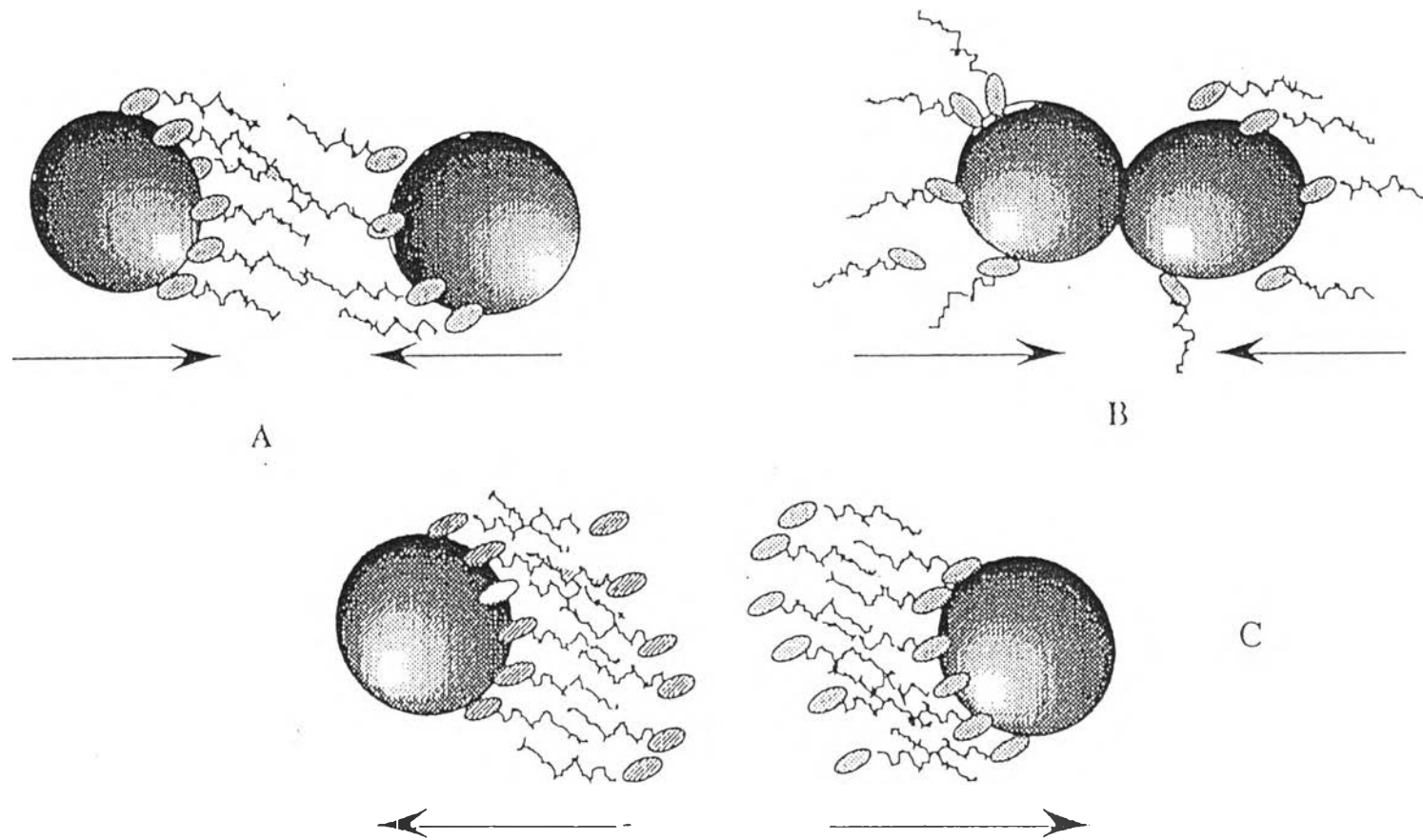


Fig 4.9 : Mechanism of CTAB on silica particle at different concentration.

* Low CTAB conc., there are two mechanisms explain the aggregation.

A. CTAB aggregate together. B. Silica particle aggregate together.

* High CTAB conc., the particle was surrounded by bilayer (C).

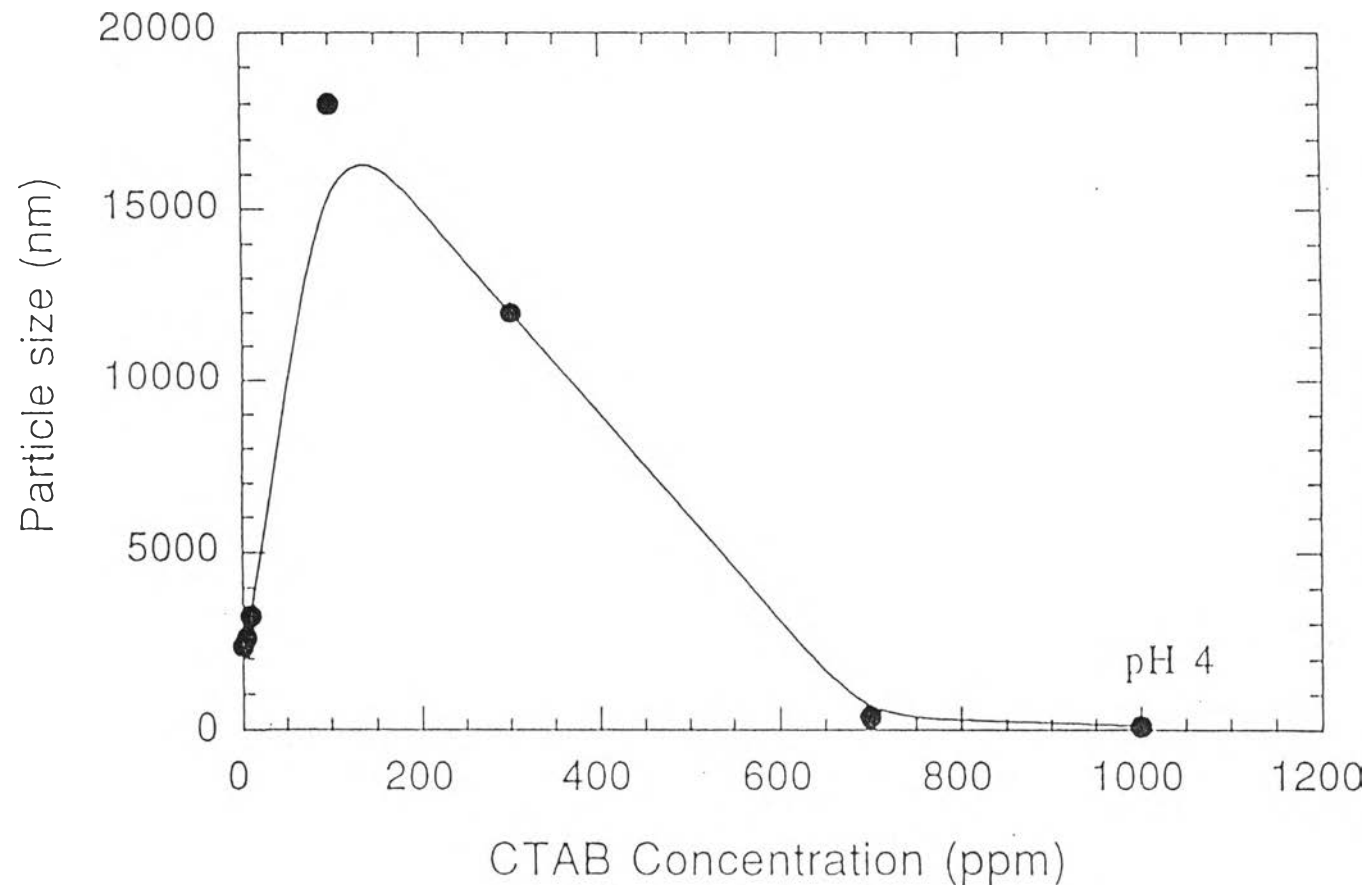


Figure 4.10 Effect of CTAB on the flocculation of silica particle at salt 2 molar. All of the conditions were fixed at the same as that in Figure 1 except this experiment was done at pH 4.

adsorption still occurred but it was not as strong as the ionic charge attraction. The silica sols showed an increase in negative zeta potential with further increasing of pH⁽³⁸⁾. Correspondingly, the adsorption of CTAB and other cationic surfactants to silica particle increased as the solution pH value increased⁽³⁹⁾.

The comparison of the floc size at pH 4 and pH 8 was shown in Figure 4.11. The largest floc size occurred at 100 ppm CTAB concentration in the solution of both pH 4 and pH 8. However, the floc size at pH 8 was significantly larger than that at pH 4 because of the dependence of the surface charge on the solution pH. At high pH (pH 8), the silica particles formed negative charge on Si-O⁻ groups which could strongly associate with positively charged molecules. At pH 4, the electrostatic attraction between silica particle and the CTAB was weaker than that at pH 8 because of the formation of a molecule Si-OH group which did not attractively interact with CTAB. As a consequence, the size of silica aggregated at pH 8 is larger than at pH 4.

The effects of a short tail surfactant, TMAB, (C₄H₁₂NBr) was compared with the longer tail surfactant (CTAB) in Figure 4.12. The results showed that even TMAB concentration up to 10,000 PPM, the floc size was virtually constant. The size of a CTAB molecule is about 2 nm and it has 19 carbon atoms in the hydrocarbon tail chain; however, TMAB had only 4 carbon atoms in the hydrocarbon tail chain. Due to the significantly shorter tail group, TMAB could not sterically stabilize the size of silica aggregates effectively. From this experiment, the longer the chain length of the stabilizer, the more influence it has on the size of silica aggregation.

In Figure 4.13, the low shear rate was applied by rotator which gently tumbled the sample. At high concentration of CTAB, it showed that when sufficient amount of CTAB concentration was added, the system could be stabilized. From this experiment, it also showed that the stability of the system occurred due to the amount of surfactant, not the shear rate.

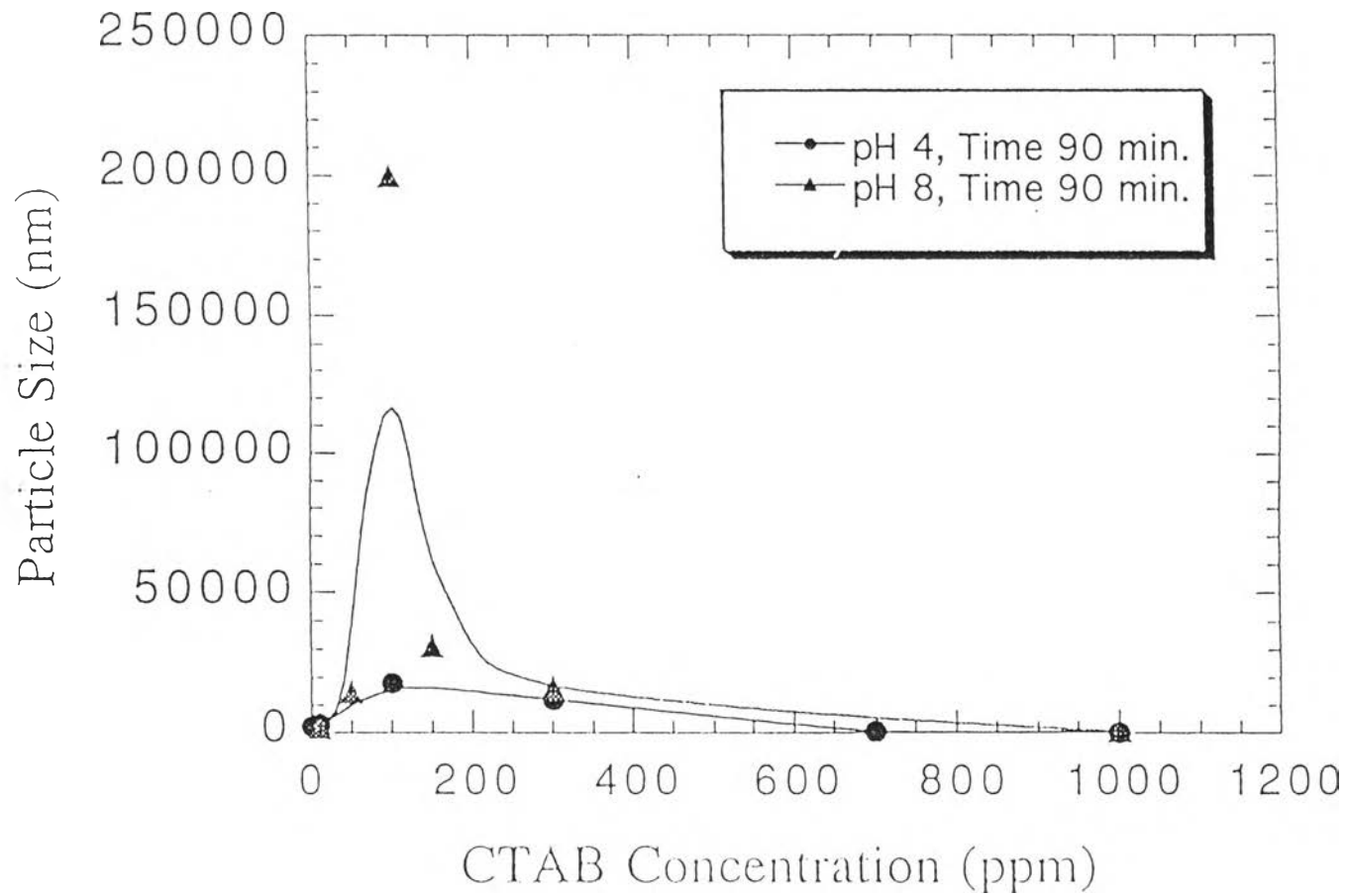


Figure 4.11 Comparison between the floc size of silica particle at pH 4 and pH 8. The salt concentration is 2 molar and the experiments were performed at high shear rate by magnetic stirrer.

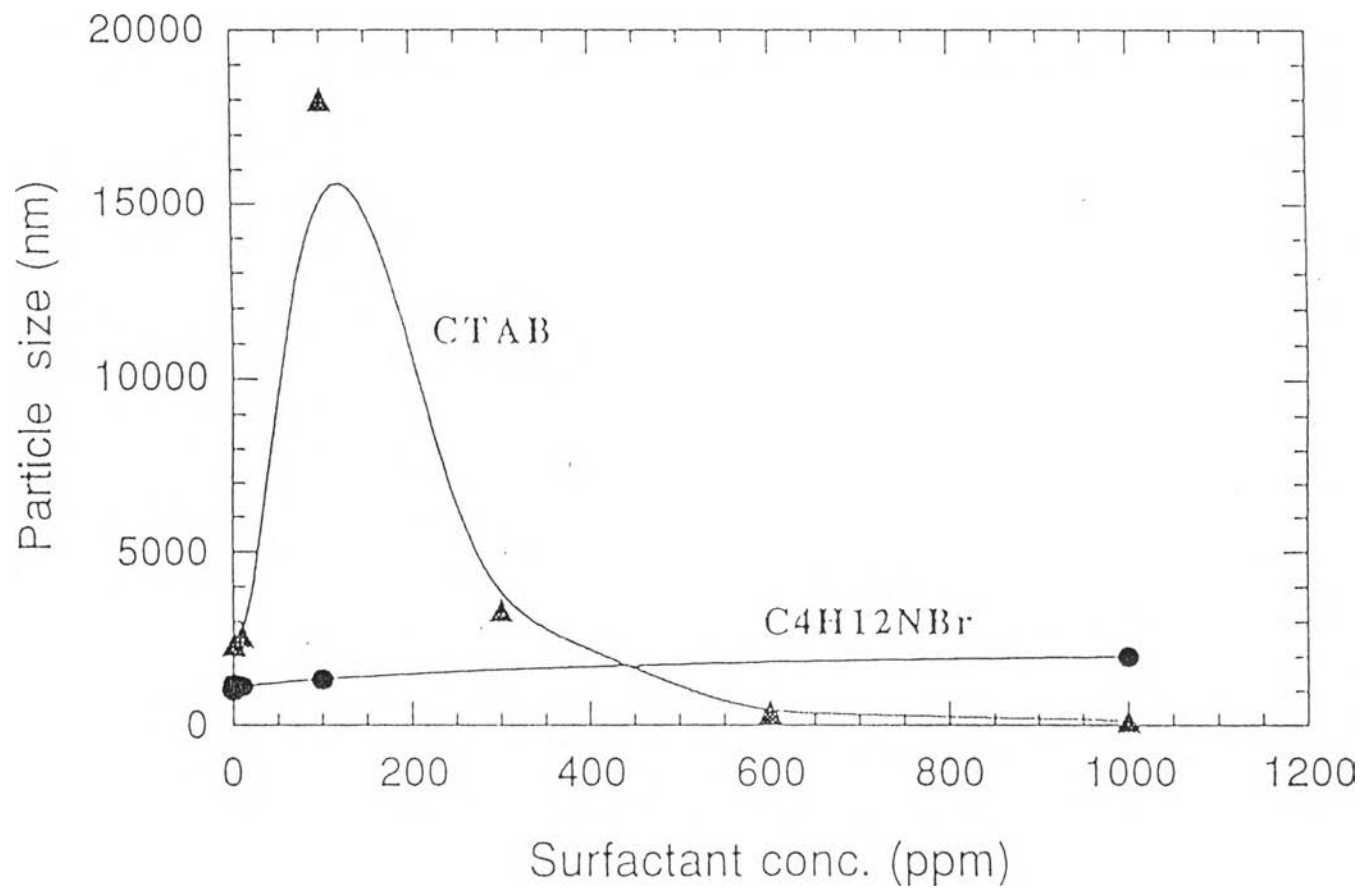


Figure 4.12 Effect of hydrocarbon chain length on the flocculation of silica particles. The long chain surfactant is CTAB which has 19 carbon and the short chain is TMAB which has 4 carbon.

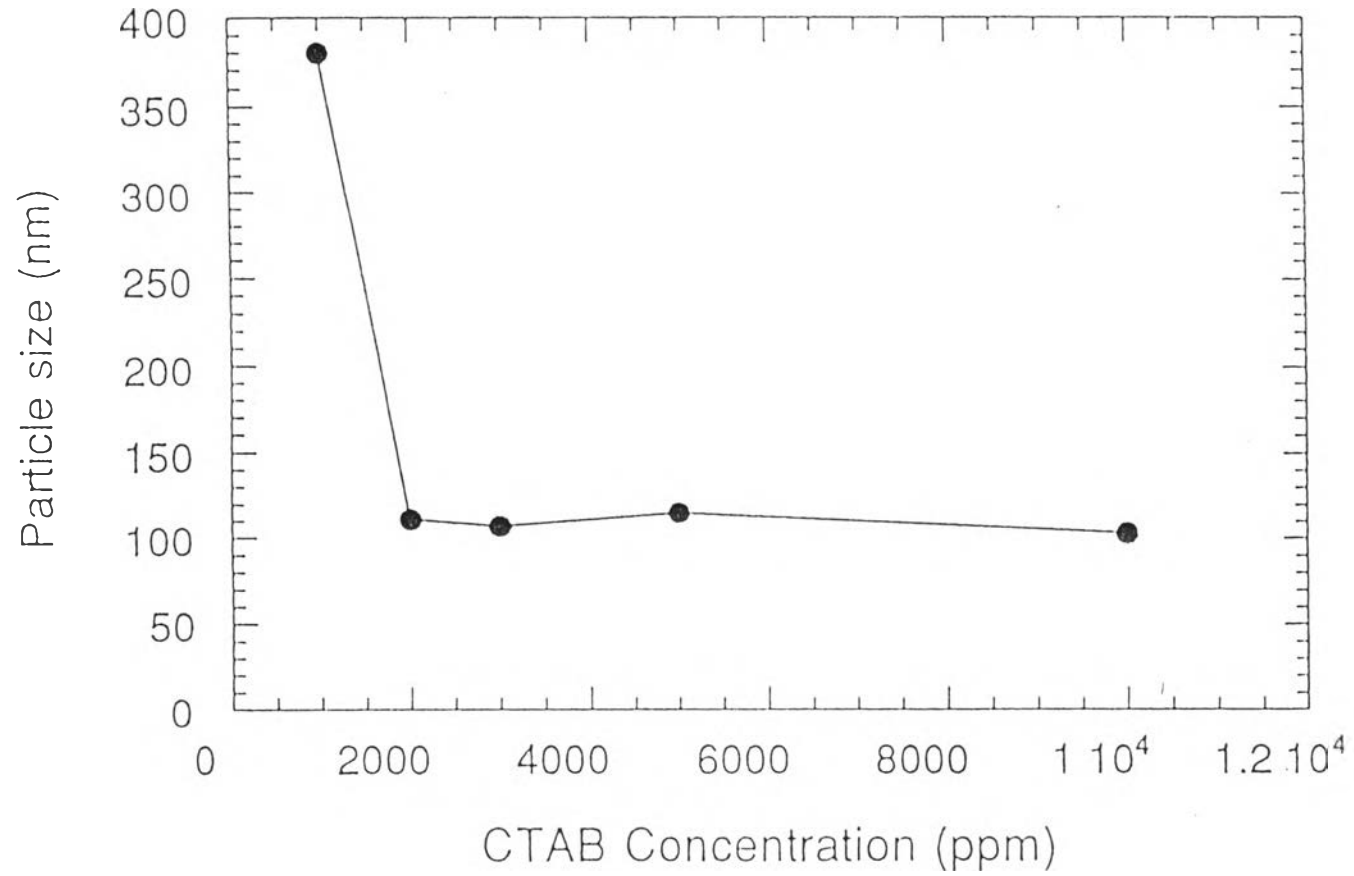


Figure 4.13 The particle stabilization at very low shear rate which is applied by rotator was plotted at time 90 min.

The difference between high and low shear rate was the minimum amount of surfactant that has to be added in the system (Table 4.1). Especially, one observed that under gentle tumbling (i.e. at very low shear rates), silica particles were completely stabilized by 2000 ppm CTAB. The results indicated that the stabilization of silica particles occurred through the adsorption of CTAB. Table 1 compared the minimum amount of CTAB necessary to completely stabilize the system at two different shear rates.

Table 4.1 The minimum amount of CTAB for stabilized the system

<i>Shear Rate</i>	<i>Conc. of CTAB that stabilize the system</i>
Fast rate	1000 PPM
Very slow rate	2000 PPM

The higher the shear rate, the smaller the amount of CTAB was necessary to be added for redispersing the floc and for stabilizing the system by keeping a certain extent of aggregation. The CTAB adsorption isotherm was shown in Figure 4.14 for different salinity levels. CTAB molecules continuously adsorbed on the silica particles up to CTAB concentrations of 1000 PPM. Above 1000 ppm, the amount of CTAB adsorption on particles remained constant. This trend could be explained by the charge neutralization of silica particle by CTAB. The complete adsorption could be explained by the charge-charge interaction which were negative charge from silica particles (O^-) and positive charges from surfactant (N^+). From the experiment, the largest floc size occurred immediately after mixing silica 7000 ppm with CTAB 100 ppm. At that point (Table 4.2), the charge of silica particle surface was calculated and compared with the charge of CTAB at CTAB concentration 100 ppm. The number of charges on the silica surface was close to the number of the opposite charges from the CTAB, so the charges of the particles are stabilized.

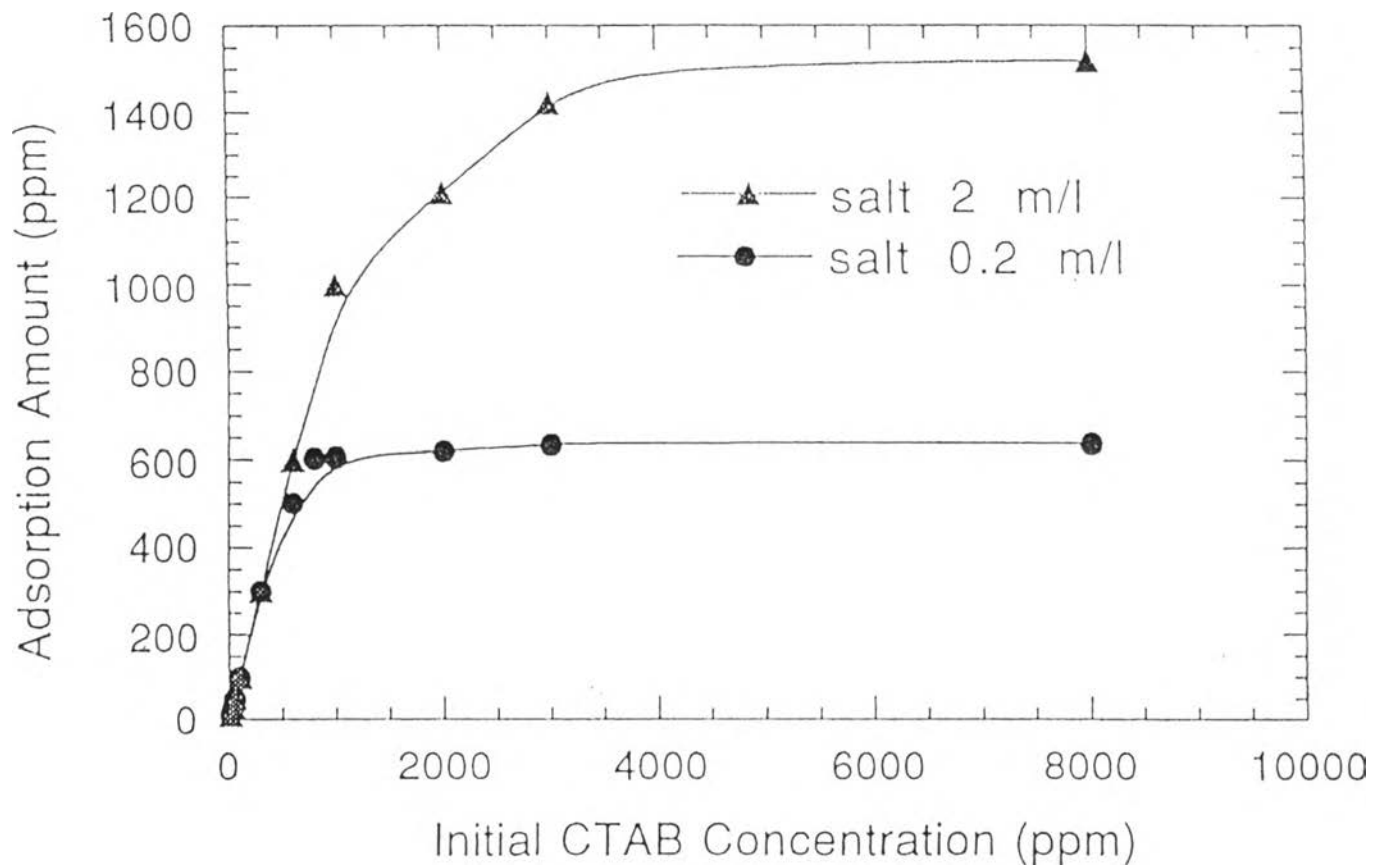


Figure 4.14 The amount of adsorption of CTAB on silica particles were shown at two differences salt concentration. The rotator which is very low shear rate was used for mixing samples.

On the other hand, the amount of CTAB adsorbed on silica particles reached 1000 ppm that was significantly higher than that at maximum silica flocculation. The reasons were that CTAB could adsorb on the silica surface such as ion pairing, ion exchange, acid base interaction etc.⁽⁴⁰⁾. Another possible way in this case was the H-bonding between N⁺ ion of CTAB and O ion on silica surface. Besides, CTAB might form extra molecular layers above the CTAB bilayer on silica surface.

Table 4.2 Number of charges on the silica particles and on the CTAB

<i>Component</i>	<i>Number of charges per liter</i>
Silica 7000 ppm	1.20E20 to 1.72E20
CTAB 100 ppm	1.34E20

The average number of CTAB molecules adsorbed per silica particle was calculated and was shown in Table 4.3. The amount of adsorbed CTAB increased with increasing the concentration of sodium chloride salt. At low CTAB concentration, the number of adsorbed CTAB molecules increased linearly with the concentration of CTAB in solution. As CTAB concentrations in solution was increased, the number of CTAB adsorbed also increased until it reached 120,000 CTAB molecules per silica particle for salt concentration of 2 mol/l and reached 30,000 CTAB molecules per silica particle 0.2 mol/l, respectively (Table 4.3). The difference in the amount of CTAB adsorption at different salt concentration could be explained by the decrease in the electrostatic repulsion among surfactant molecules so that CTAB molecule could pack with each other more densely on silica particle surfaces. At high salt (2 mol/l) and high CTAB concentration, it was also clear the peptization of silica particle was established a bilayer of CTAB molecules on particle surface. Therefore, the number of CTAB molecule in Table 4.3 showed the adsorption concentration of CTAB monolayer which directly adsorbed on silica particle. The amount of CTAB monolayer could

be calculated by halving the number of CTAB on the silica particles from Table 4.3.

Table 4.3 The adsorption concentration and the number of surfactant on the silica particle

CTAB initial concentration	SALT 0.2 mol/l		SALT 2 mol/l	
	CTAB adsorption concentration (ppm)	Number of CTAB per silica sphere	CTAB adsorption concentration (ppm)	Number of CTAB per silica sphere
10	10	2006	10	2006
30	30	6017	30	6017
50	50	10028	50	10028
100	100	20056	100	20056
300	300	60168	300	60168
600	501	100569	600	120336
800	603	120913	-	-
1000	606	121491	1000	200560
2000	620	124379	1212	242982
3000	635	128267	1423	285404
8000	608	121940	1520	314851

It was found that, the CTAB monolayer on the silica surface was 60,000 and 150,000 CTAB molecules per silica particle at 0.2 and 2 mol/l NaCl, respectively. The theoretical number of CTAB molecules covering the entire silica surface was approximated by two different assumptions. One assumed that the alkyl tail chain of CTAB was parallel to the silica surface and the calculated number of CTAB molecules per silica particle was 18,470. The other assumed that tail was perpendicular to the silica surface; consequently, the number of monolayer CTAB molecule per silica was 125,000. The experimental number of CTAB particles was close to the

number from the theoretical assumption which the CTAB forming bilayer on the silica surface.

To confirm the effect of charge neutralization, zeta potential at the surface was measured as shown in Table 4.4.

Table 4.4 Zeta potentials of the silica particle at bare silica surface comparing with CTAB on its surface

<i>Composition of sample</i>	<i>Zeta potential (mv)</i>
Pure Silica particles	- 50
Silica + 3000 ppm CTAB	+ 32

Note: The zeta potential cannot be measured for large flocs because they are rapidly sediment to the bottom of the cell.

Zeta potential measurement shows that the bare silica surface was negatively charged with the measured Zeta potential of +50 mv. However, the surface of silica particle becomes positive charge in the present of 3000 ppm CTAB in the solution. The possible explanation shown in Figure 4.15 was the mechanism of charge reversal on the silica particle when CTAB was adsorbed on the surface. The charge on the surface of silica particle in water was negative charge when CTAB was applied. The charge of CTAB would attack on the silica particle and would neutralize the charge. If the CTAB concentration were still increased, the charge, the silica surface would turn to positive charge because of CTAB micelle formation.

The redispersion of silica particles from large floc was studied by the presence of shear which was carried out using a solution containing 2000 ppm CTAB (Figure 4.16). The size of silica floc decayed very fast within 50 min. and the floc size stabilizes at 600 nm, while the high shear rate was performed by magnetic stirrer.

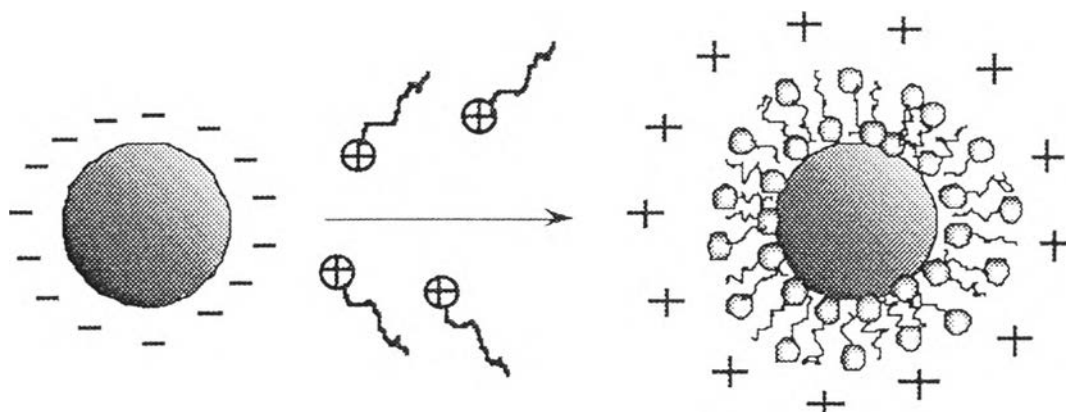


Figure 4.15 The illustration showing the schematic diagram of charge reversal on the silica surface due to the surfactant adsorption.

Figure 4.17 showed the size of silica flocs as the function of the shear rate. The particle size decreased with increasing the shear rate. Moreover, a given floc size can be obtained reproducibly by controlling the shear rate. The rupture of silica flocs under shearing resulted from the breakage of the attractive bridges among silica particles. As soon as the flocs were ruptured, CTAB in the solution would adsorb on the silica surface and would form a CTAB bilayer (this situation would occur only at high CTAB concentrations) to stabilize the resultant aggregates. At low CTAB concentration, the shear force could break the floc. However, as soon as the shearing was stopped, the particles started aggregating into large flocs. The aggregation occurred on the silica surfaces which were not completely covered by the CTAB bilayer.

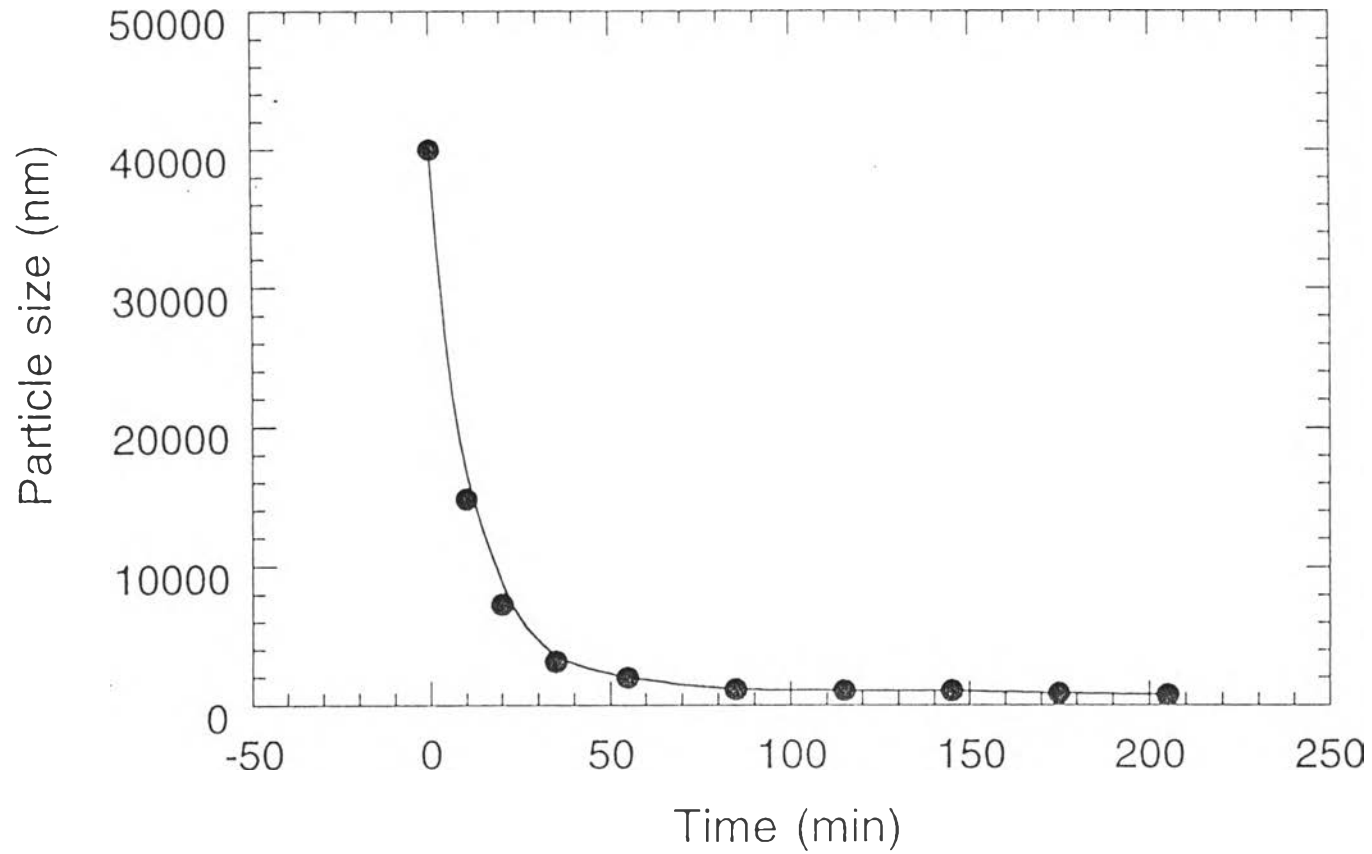


Figure 4.16 Particle redispersion in 2000 ppm CTAB. The redispersion experiment was performed by using the magnetic stirrer to apply the high shear force.

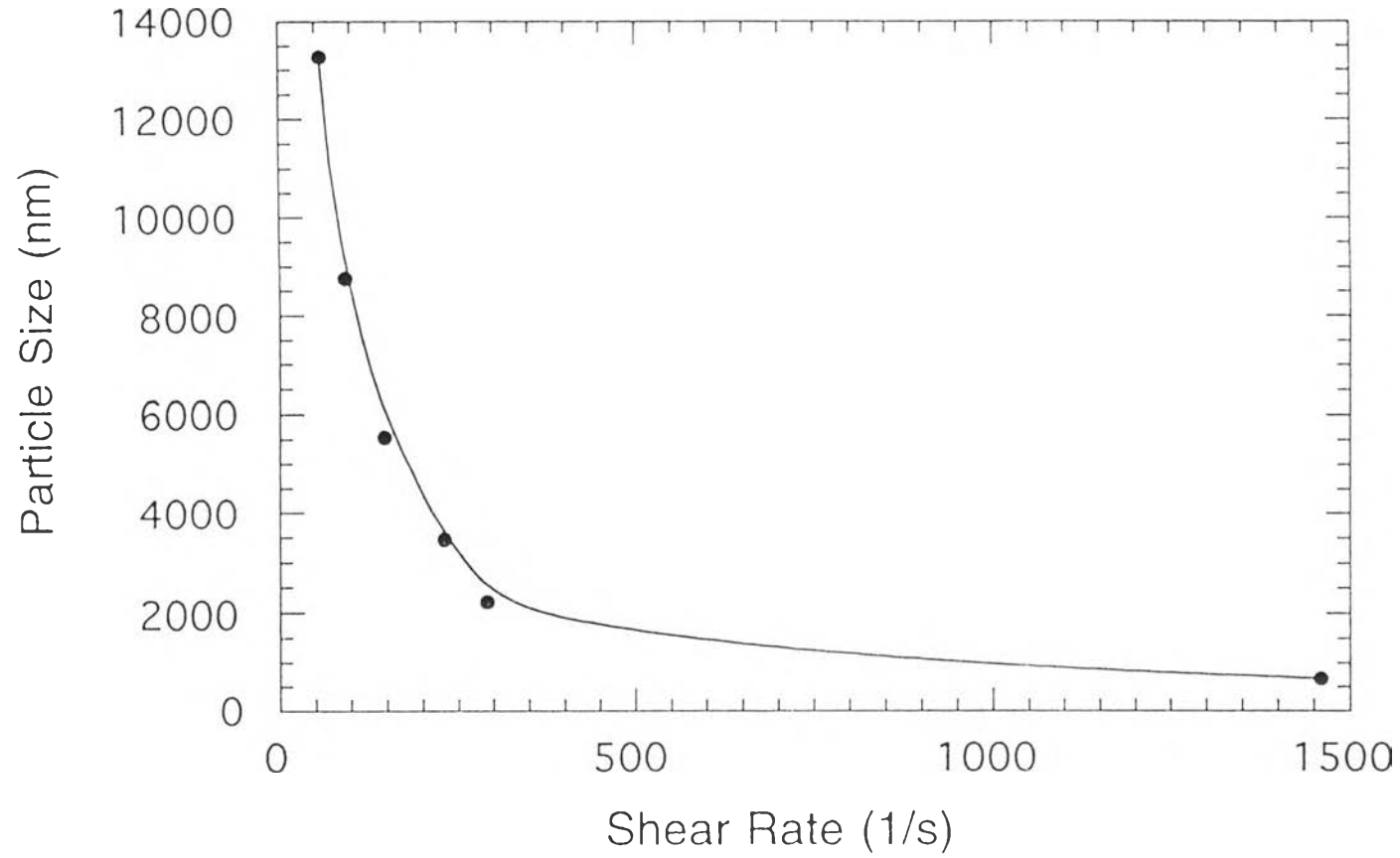


Figure 4.17 The correlation between the decrease of particle size with shear rate. The shear rate was controlled by Rheometer.

The floc of silica particles at high CTAB concentration could not be redispersed unless shear rate was applied. In cases of no shear rate, CTAB will form micelle and will remain in the solution because CTAB cannot break the floc of the silica particles by itself.

Figure 4.18 The mechanism of shear rate in breaking the silica floc.

