# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Talcum Powder Characterization

Table 4.1 shows the chemical composition of talcum powder by XRF technique. Talcum powder or hydrous magnesium silicate was found to contain 64.59% $SiO_2$ and 33.26% $MgO$ which was close to its chemical formula ($3MgO$ $4SiO_2.H_2O$), indicating that the talcum powder was pure enough for using as a model of this study. Figure 4.2 shows the XRD pattern to indicate the crystals of magnesium silicate and it has a monoclinic crystal structure.

**Table 4.1** Chemical composition of talcum powder

| Compound | Composition (%) |
|---|---|
| $SiO_2$ | 64.59 |
| $MgO$ | 33.26 |
| $Al_2O_3$ | 1.18 |
| $CaO$ | 0.50 |
| $Fe_2O_3$ | 0.43 |
| $P_2O_5$ | 0.04 |
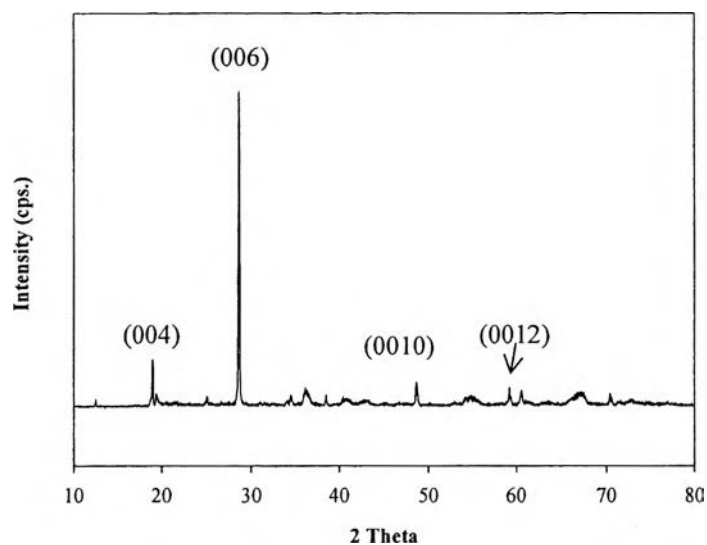
**Figure 4.1** XRD pattern of talcum powder.

The specific surface area of talcum powder is 4.169 $m^2/g$ which was determined by nitrogen adsorption BET measurement with a surface area analyzer. The mean diameter of talcum powder measured by laser technique using particle size analyzer is 86.83 µm. The surface morphology and the shape of talcum powder were shown in Figure 4.2, which have lamellar surface at the edge of particle and talcum powder particles are heterogeneous and large size which responsible for the low surface area.
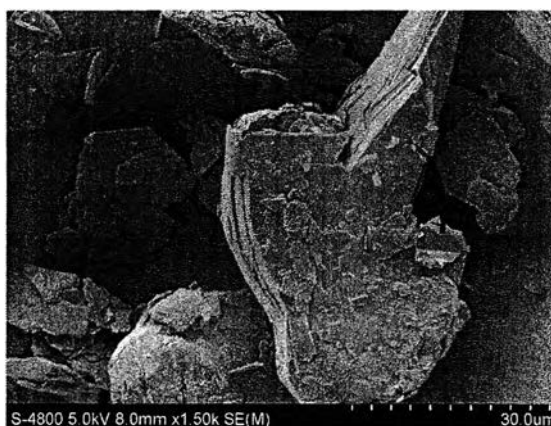


**Figure 4.2** SEM image of talcum powder.

## 4.2 Surfactant Adsorption Isotherm Results

Surfactant adsorption at liquid-solid interface can alter the dispersion properties by changing the Van der Waals attraction, electrostatic repulsion, and the steric forces between the particles. The extent of the modification depends on the adsorption density (surface coverage), packing, and orientation of molecules at the interface, and the nature of charges on the molecule (Somasundaran, 2009). Therefore, surfactant adsorption is an important part to first discuss.

The surfactant adsorption is calculated in the terms of adsorption density, $\Gamma$ ($\mu mol/m^2$) as shown in Eq. 6.1, and the adsorption isotherm is generally plotted on $\log - \log$ scale.

$$\Gamma = \frac{(C_0 - C)V}{W a_s} \qquad (4.1)$$

where $\Gamma$ is the surfactant adsorption; $\mu mol/m^2$, $C_0$ is the initial surfactant concentration, $\mu mol/l$; C is the equilibrium surfactant concentration, $\mu mol/l$; V is the volume of a surfactant solution, $l$ ; W is the weight of a powder sample, g; and $a_s$ is the specific surface area of a powder sample; $m^2/g$ (Kharitonova $et\ al.$, 2005).

### 4.2.1 Adsorption Isotherm of Anionic Surfactant

The adsorption isotherm of SDS on talcum powder at various solution pHs is shown in Figure 4.3. In the range of 100-3,000 $\mu mol/l$, the adsorption density increased with increasing SDS concentration until the adsorption reached a plateau region at about 5,000 $\mu mol/l$ while the CMC value of SDS was 9,000 $\mu mol/l$ as shown in Figure 4.4. This result implies that there is favorable adsorption of SDS on the talcum powder surface leading to saturation of available surface below the CMC. The maximum adsorption density is about 22 $\mu mol/m^2$ at the initial pH of 5. Furthermore, the effects of solution pH were also studied, the results showed that as the pH solution increased, the amount of SDS adsorbing onto talcum powder decreased because the increase in solution pH caused the talcum powder surface become more negative, leading to less SDS adsorption.
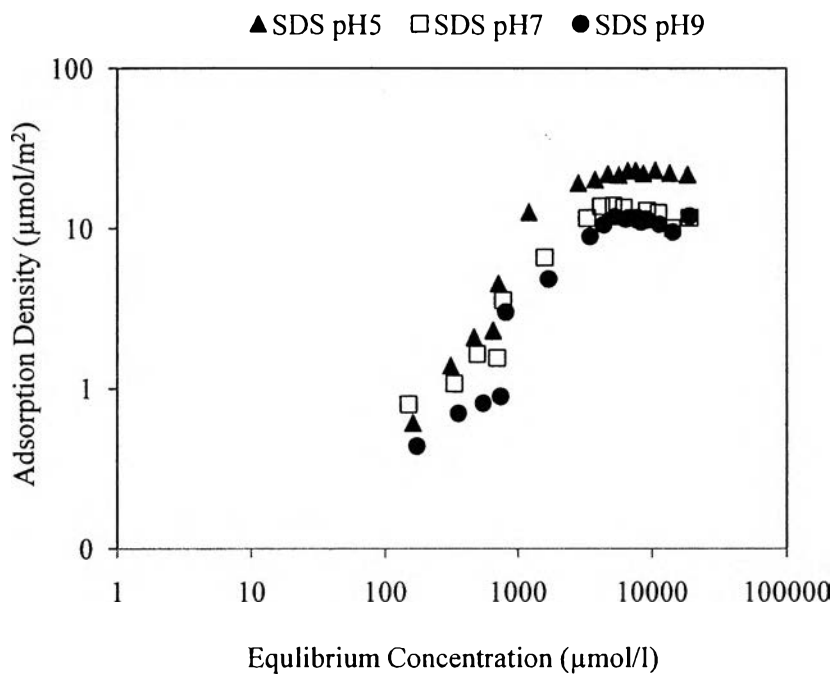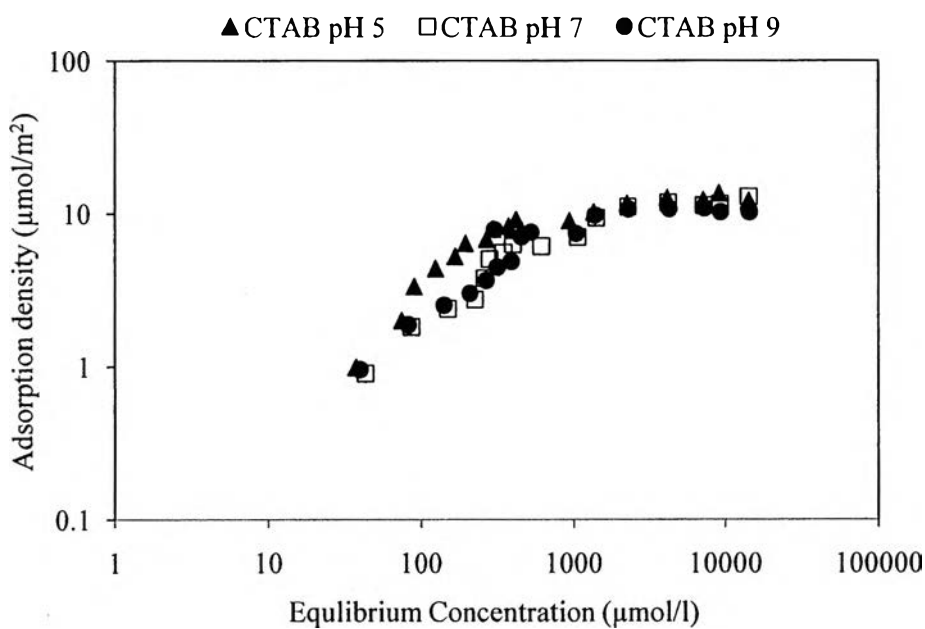
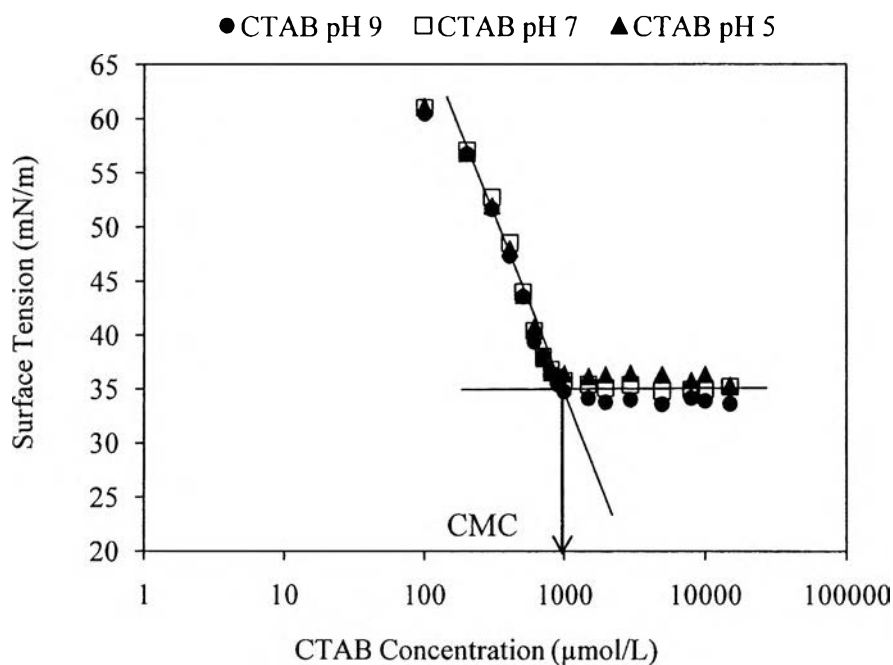**Figure 4.3** Adsorption isotherm of SDS on talcum powder at various pH values.
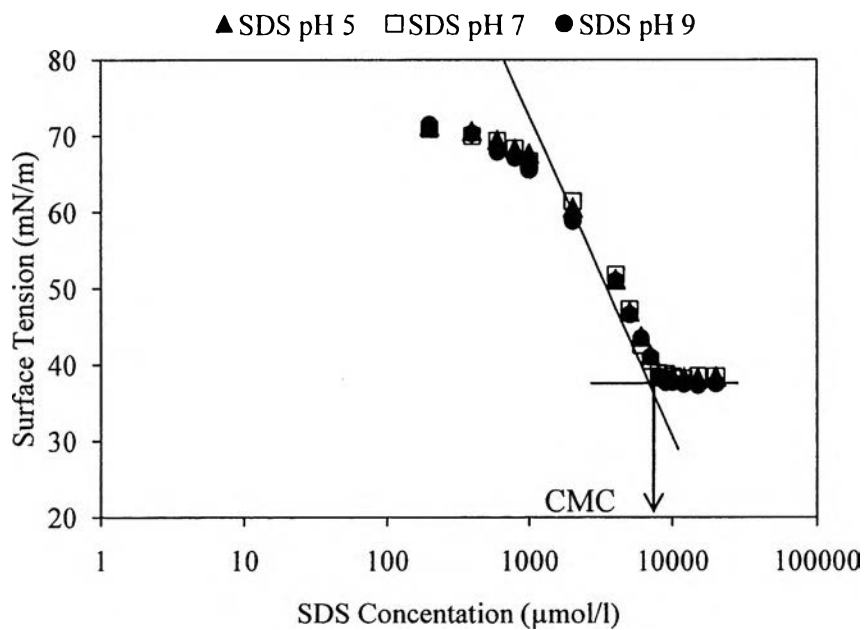


**Figure 4.4** Surface tension of SDS at various concentrations and pH values by pendant drop technique.

### 4.2.2 Adsorption Isotherm of Cationic Surfactant

Figure 4.5 shows the adsorption isotherm of CTAB on talcum powder at various solution pHs. In the range of 30-1,000 μmol/l, the adsorption density increased with increasing CTAB concentration until the adsorption reached a plateau region at 1,000 μmol/l which corresponds to the CMC value of CTAB at 1,000 μmol/l as confirmed by the surface tension results, as shown in Figure 4.6. In comparison between Figure 4.3 and Figure 4.5, the adsorption isotherm shape of CTAB shows similar trend as that of SDS while the maximum amount of CTAB surfactant adsorbed on talcum powder is about 12 μmol/m$^2$. The solution pH insignificantly affected on adsorption isotherm of CTAB on talcum powder
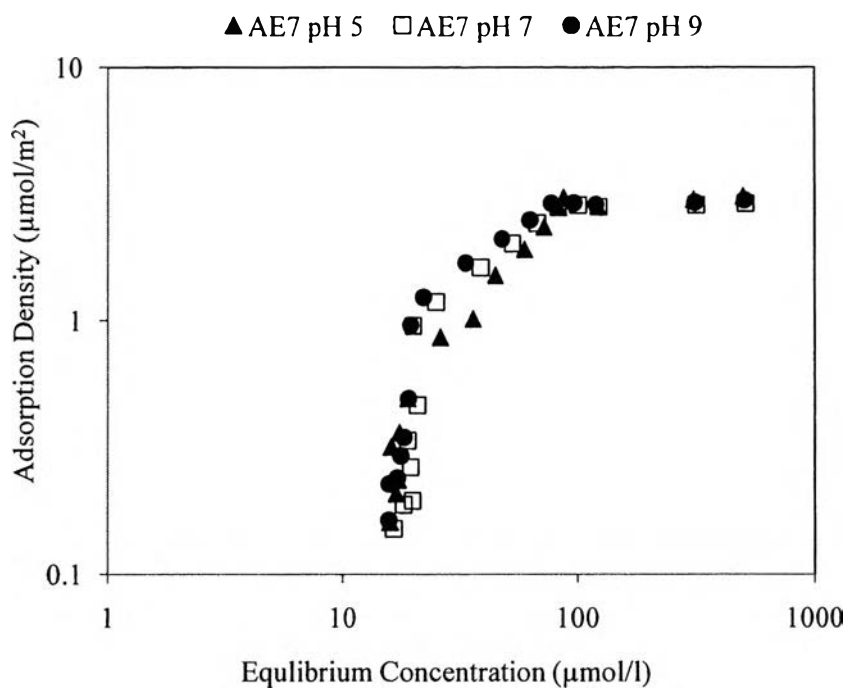


**Figure 4.5** Adsorption isotherm of CTAB on talcum powder at various pH values.
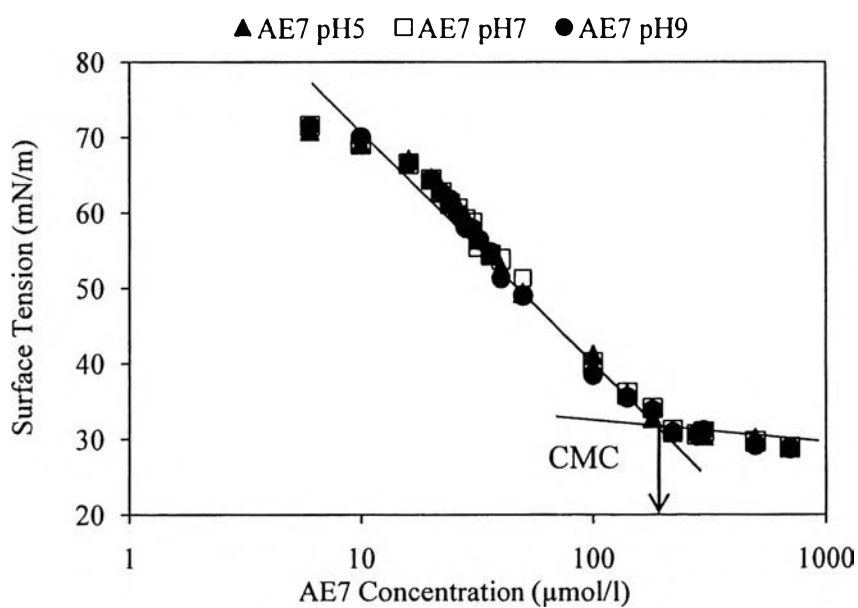
**Figure 4.6** Surface tension of CTAB at various concentrations and pH values by pendant drop technique.

### 4.2.3 Adsorption Isotherm of Nonionic Surfactant

The adsorption isotherm of AE7 on talcum powder at various solution pHs is shown in Figure 4.7. The adsorption density of AE7 on talcum powder sharply increased with increasing AE7 concentration in the range of 10-25 $\mu mol/l$ until the adsorption reached a plateau region at 100 $\mu mol/l$ which corresponds to the CMC value of AE7 at 200$\mu mol/l$ as confirmed by the surface tension results, as shown in Figure 4.8.In comparison of Figure 4.3, Figure 4.5 and Figure 4.7, the adsorption isotherm of AE7 on talcum powder was significantly different from that of the previous SDS and CTAB surfactant, it is also followed an L-shaped or Langmuirian pattern. The maximum adsorption density of AE7 on talcum powder is 3$\mu mol/m^2$. The surfactant molecules were adsorbed in a partial monolayer on the talcum powder surface by carbon chain attachment to the surface by hydrophobic bounding. In addition, the effect of solution pH, the adsorption isotherm showed that it insignificantly affected on the adsorption density.

**Figure 4.7** Adsorption isotherm of AE7 on talcum powder at various pH values.



**Figure 4.8** Surface tension of AE7 at various concentrations and pH values by pendant drop technique.

As compared in the type of surfactant, from Figure 4.3, Figure 4.5 and Figure 4.7 show the adsorption isotherm of SDS, CTAB and AE7 with various surfactant concentrations, talcum powder can adsorb either ionic or nonionic surfactant, indicated that talcum powder has heterogeneous surface. The maximum adsorption density of AE7 on talcum powder was much lower than of those of SDS and CTAB. SDS solution and CTAB solution have nearly value of maximum adsorption density. SDS surfactant (anionic surfactant) can adsorb on talcum powder even if its surfaces are negative charge (in the next discussion). Because of the heterogeneity of surface of talcum powder, there are some positively charge sites on the surface despite a net negative charge.

The adsorption area assuming close-packed monolayer at the liquid/vapor interface is calculated by using the Gibbs adsorption equation applied to surface tension data (Rosen, 1989)

$$\Gamma_{LV} = -\frac{1}{nRT}\frac{d\gamma_{LV}}{d\ln C} \tag{4.2}$$

Therefore, the surface area per surfactant molecule on the solid surface; $a_s$ in square angstroms is:

$$a_s = \frac{10^{23}}{N\Gamma_{LV}} \tag{4.3}$$

where $\Gamma_{LV}$ = surface excess concentration or surfactant adsorption at liquid/vapor
  interface; mmol/m$^2$;

  n = 1 for nonionic surfactant or ionic surfactant at a high salinity or

  = 2 for ionic surfactant and no added salt;

  R = gas constant (8.314 J/mol.K);

  T = constant temperature at 298 K;

  $\gamma_{LV}$ = surface tension; mN/m;

  N= Avogadro's number (6.02x10$^{23}$);

Equation 4.2 was applied to dilute solutions below the CMC. The vapor/liquid interface typically exhibits a constant adsorption ($\Gamma_{SL}$) or constant slope of $\gamma_{SL}$ vs.

$lnC_S$ from about 20% of the CMC to the CMC as a Gibbs close-packed monolayer is attained.

For SDS, CTAB and AE7 solution at pH7, the close-packed monolayer at liquid/vapor interface calculated by using the Gibbs adsorption equation is $51\text{Å}^2$/molecule, $56\ \text{Å}^2$/molecule and $61\ \text{Å}^2$/molecule, respectively. As compared with close-packed monolayer at liquid/vapor interface and occupied surface areas of all studied surfactant, the number layer of surfactant adsorption on talcum powder surface is 3.5, 3.8 and 1.04 for SDS, CTAB and AE7, respectively. Talcum powder consists of the layer of silicate tetrahedral and magnesium hydroxide and layers are held together by Van der Waals force so that the layers are capable of slipping easily (Wallqvis *et al*, 2006). AE7 adsorbed with the lowest adsorption density. It is possible that the steric effect from the largest head group of AE7. Because talcum powder has hydrophobic surface, AE7 adsorbed on surface of talcum powder as a monolayer which AE7 molecule absorbed at hydrophobic surface through hydrophobic interaction. In case of SDS and CTAB surfactants, surfactant molecules has smaller than AE7 molecule, surfactant molecule can diffuse into between the layer of talcum powder leading to increase surface area and surfactant adsorption.

## 4.3 Zeta Potential and PZC Results

### 4.3.1 PZC of Talcum Powder Results

The point of zero charge (PZC) is the pH at zero zeta potential. Figure 4.9 shows the zeta potential of talcum powder as a function of equilibrium pH. The zeta potential with pH is a positive value at low pH and an increasingly negative value as the pH increase. The PZC value of talcum powder is 3.4, indicating that talcum powder has negative charge surfaces and more negative charge surface with increasing solution pH.
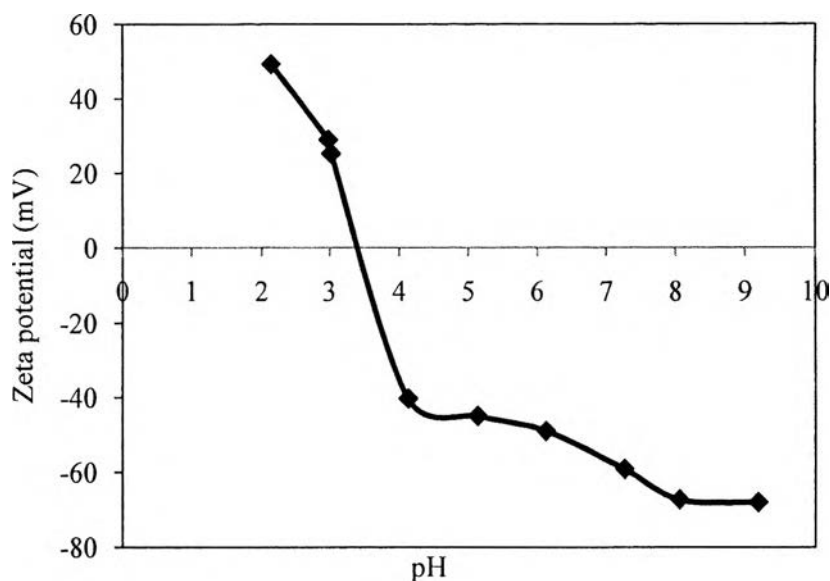
**Figure 4.9** Zeta potential of talcum powder in deionized water at various pH values.
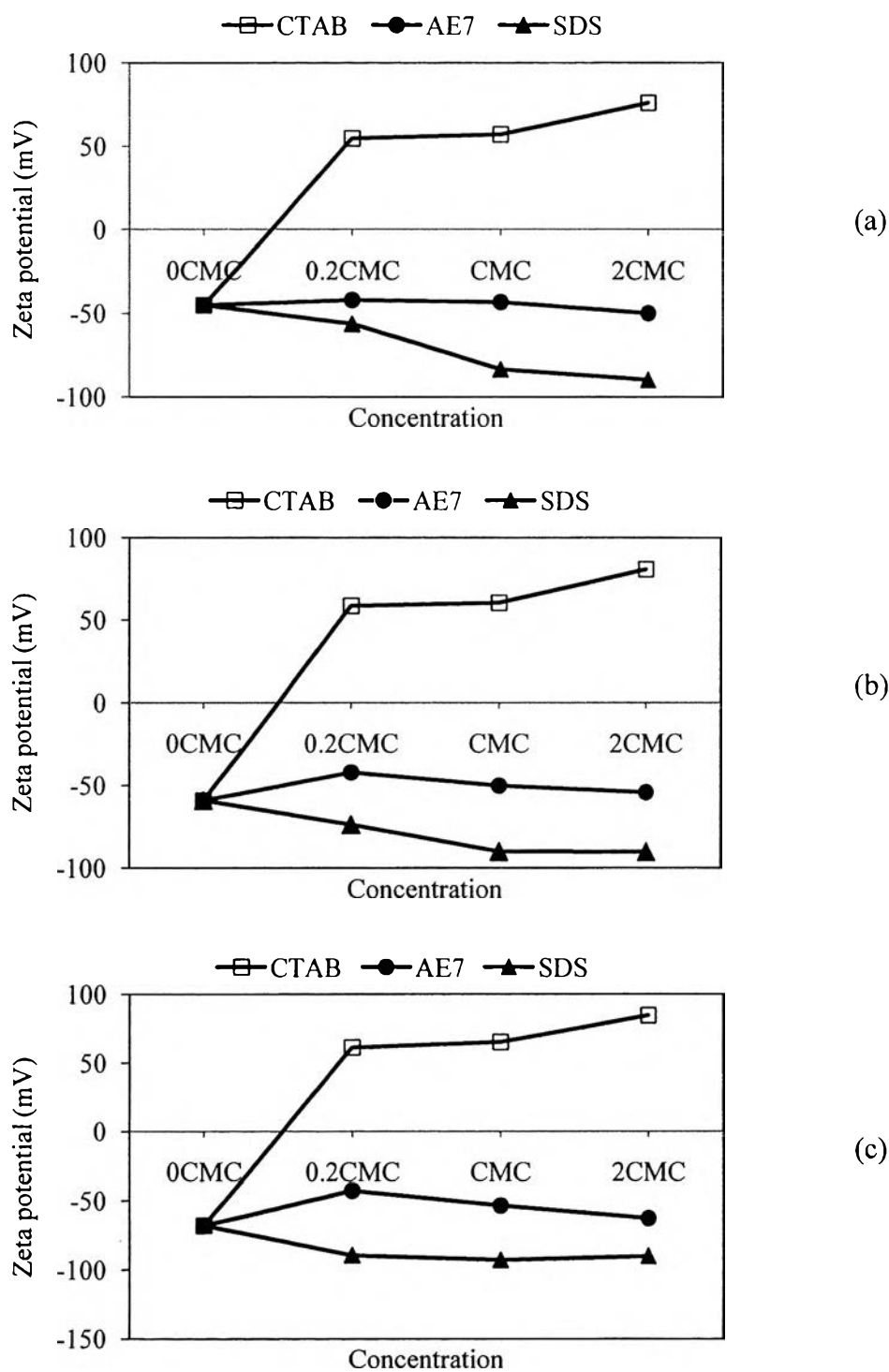
### 4.3.2 Zeta Potential of Talcum Powder in Surfactant Solution

Zeta potential is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other (Rosen, 1989). It is an important feature because zeta potential can be measured in a fairly simple manner, while the surface potential cannot. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. However, if the particles have low zeta potential values then there will be no force to prevent the particles coming together and flocculating (Malvern Instruments).In this study, the zeta potential of talcum powder is investigated in two effects which are effect of surfactant concentration and effect of solution pH.

#### 4.3.2.1 Effect of Surfactant Concentration

Figure 4.10 shows the zeta potential of talcum powder in surfactant solution with various surfactant concentrations at solution pH5, pH7 and pH9. The zeta potential of talcum powder in absence of surfactant for all solution pH has negative value but has changed in the presence surfactant solution. For all

solution pH of SDS solution, the zeta potential of talcum powder becomes more negative with increasing surfactant concentration which correlated to SDS surfactant adsorption increases and reaches a maximum when the adsorption reaches a plateau value. This indicated that when increasing surfactant concentration, more SDS molecules adsorbed on talcum powder surface with negative head group pointing toward solution which resulted in increasing negative value of zeta potential. On the other hand, the zeta potential of talcum powder in CTAB solution shows the positive value, indicated that CTAB changed the negative charge surface of talcum powder to positive charge surface. In addition, the zeta potential becomes more positive with increasing surfactant concentration for all solution pH because more CTAB molecules adsorbed on talcum powder surface with positive head group pointing toward solution which resulted in increasing positive value of zeta potential. For all solution pH of AE7, nonionic surfactant, the AE7 caused talcum powder to be negatively charged and surfactant concentration had insignificant effect on zeta potential. The nonionic surfactant would not be expected to have a significant effect on the electrostatic charge because nonionic surfactant has no charge at head group as ionic surfactant. The effect of AE7 on zeta potential is probably due to the bound water-more bound water with ethoxylate group. The maximum absolute value of zeta potential of talcum powder was found in SDS solution, followed by CTAB and AE7 respectively which correlated to the order of surfactant adsorption: SDS>CTAB>AE7. The increasing absolute value of zeta potential with increasing surfactant concentration leaded to the increase repulsion forces. This zeta potential can be related to the colloid stability in electrostatically stabilized systems (Jailani *et al.*, 2008).

**Figure 4.10** Zeta potential of talcum powder (a) at solution pH5, (b) at solution pH7, (c) at solution pH9.

*4.3.2.2 Effect of Solution pH*

Figure 4.11 shows the zeta potential of talcum powder in surfactant solution with various solution pH at 0.2CMC, CMC and 2CMC. Talcum powders in absence of surfactant have more negative zeta potential with increasing pH level. In SDS solution at 0.2CMC concentration, the zeta potential of talcum powder becomes more negative with increasing solution pH from 5 to 9 which similar trend as that in the absence of surfactant, indicating that SDS at low concentration behave as talcum powder in absence of surfactant. The repulsion force increases with increasing solution pH level. In SDS solution at CMC and 2CMC concentration, the zeta potential has negative value but it did not change with increasing solution pH from 5 to 9, so the solution pH does not affect on zeta potential at high concentration above CMC. For CTAB solution at all three concentrations, the zeta potential of talcum powder becomes more positive with increasing solution pH from 5 to 9. This indicated that the repulsion force increases with increasing solution pH level. Furthermore, for AE7solution at all three concentrations, the talcum powder has negative value of zeta potential and solution pH had insignificant effect on zeta potential. Thus, solution pH does not effect on the repulsion force in AE7 solution.
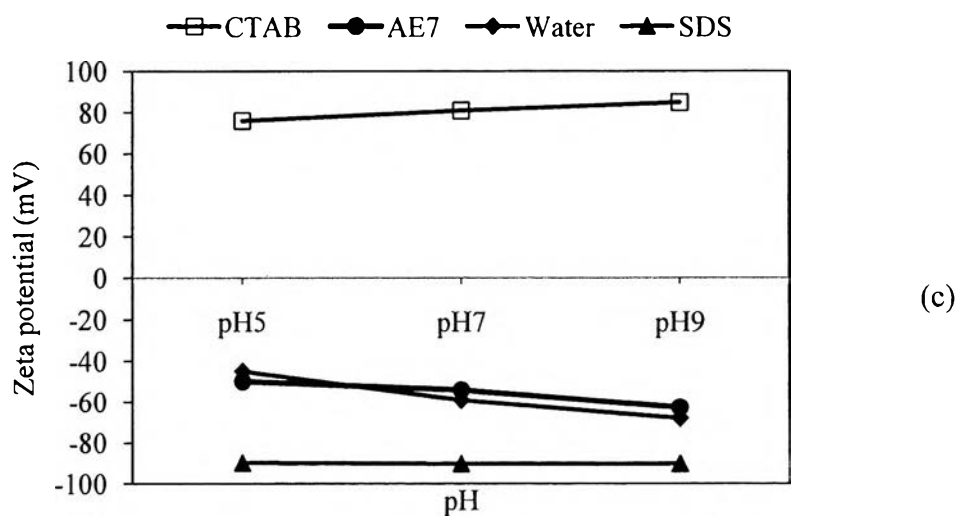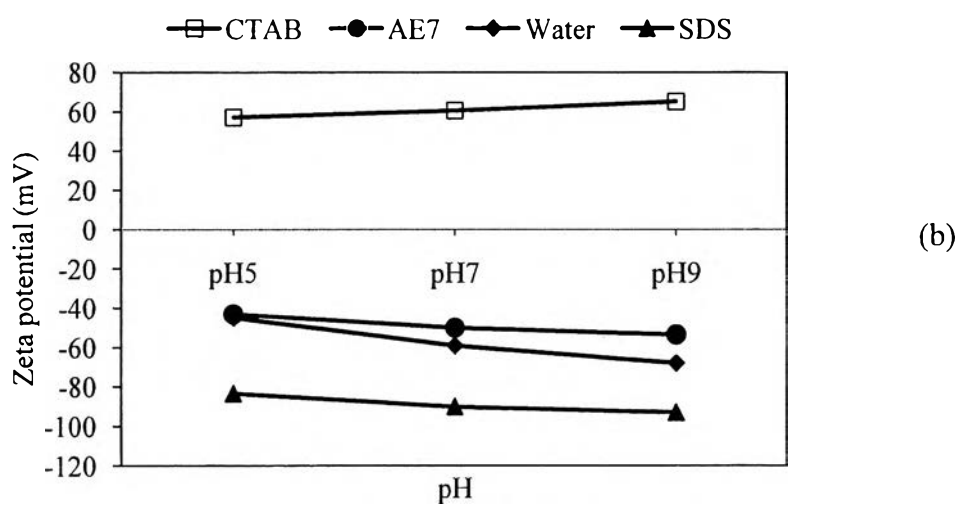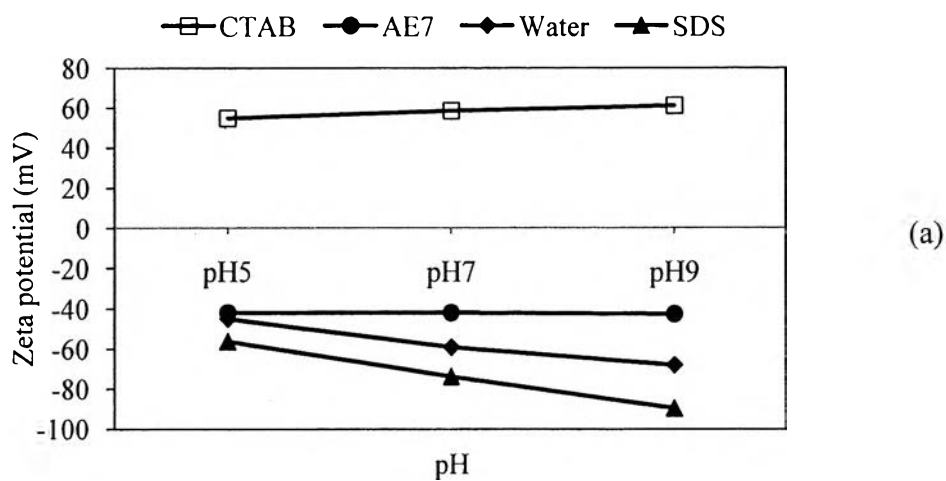
**Figure 4.11** Zeta potential of talcum powder (a) at 0.2CMC, (b) at CMC, (c) at 2CMC.

## 4.4 Dispersion Stability Results

The redeposition of particle is expected to relate the dispersion stability of particle in cleaning solution. In this study, the dispersion stability of talcum powder in absence and presence of surfactants was investigated as a function of time by using a UV-VIS spectrophotometer fixed wavelength at 550 nm. The light absorbance of talcum powder indicated the dispersion stability which high light absorbance means high particle density and high dispersion stability whereas low light absorbance means low particle density and low dispersion stability. The dispersion stability of talcum powder in surfactant solution at settling times of 12,000 sec was studied in two main effects which are the effect of surfactant concentration and solution pH.

### 4.4.1 Effect of Surfactant Concentration

The dispersion stability of talcum powder in absence and presence of surfactant with various surfactant concentrations for all solution pH represents in the Figure 4.12. The light absorbance of talcum powder in absence of surfactant is lower than in presence of surfactant for all surfactant concentrations, indicated that the dispersion stability of talcum powder in absence of surfactant is lower than in presence of surfactant because of the natural hydrophobicity of talcum powder. Thus, surfactant can improve the dispersion stability of talcum powder in solution because surfactant molecules adsorbed on the surface of talcum powder which increasing repulsive force between particles, this correlated to the surfactant adsorption and zeta potential. The dispersion stability drastically increased with increasing surfactant until above CMC the dispersion stability slightly increased that correlated to surfactant adsorption and zeta potential. Because more surfactant molecules adsorbed on the surface of talcum powder when increased surfactant concentration leading to increase repulsive force, talcum powder in surfactant solution with increasing surfactant concentration can enhance the increasing repulsive force that resulted in higher dispersion stability of particles.
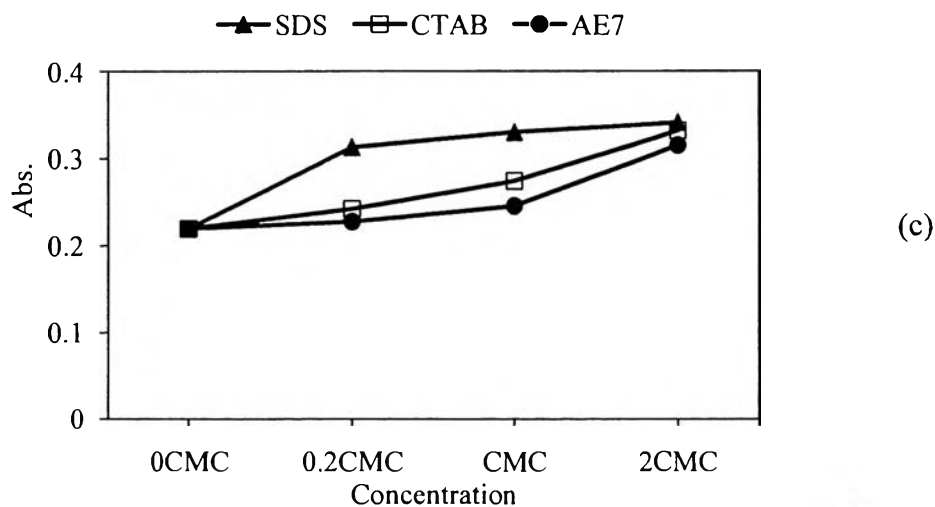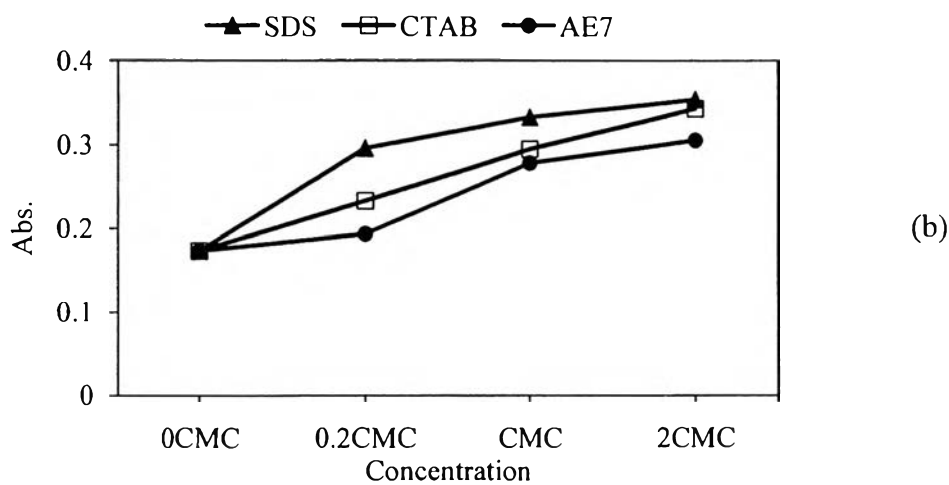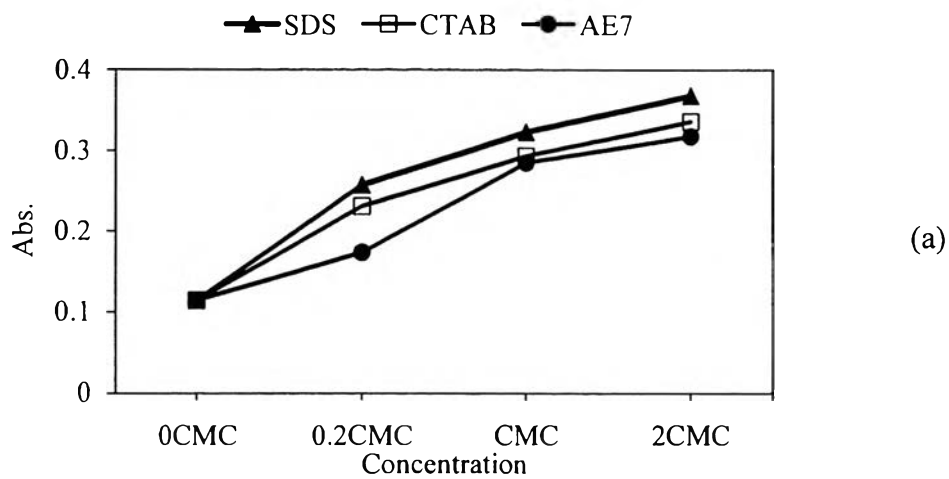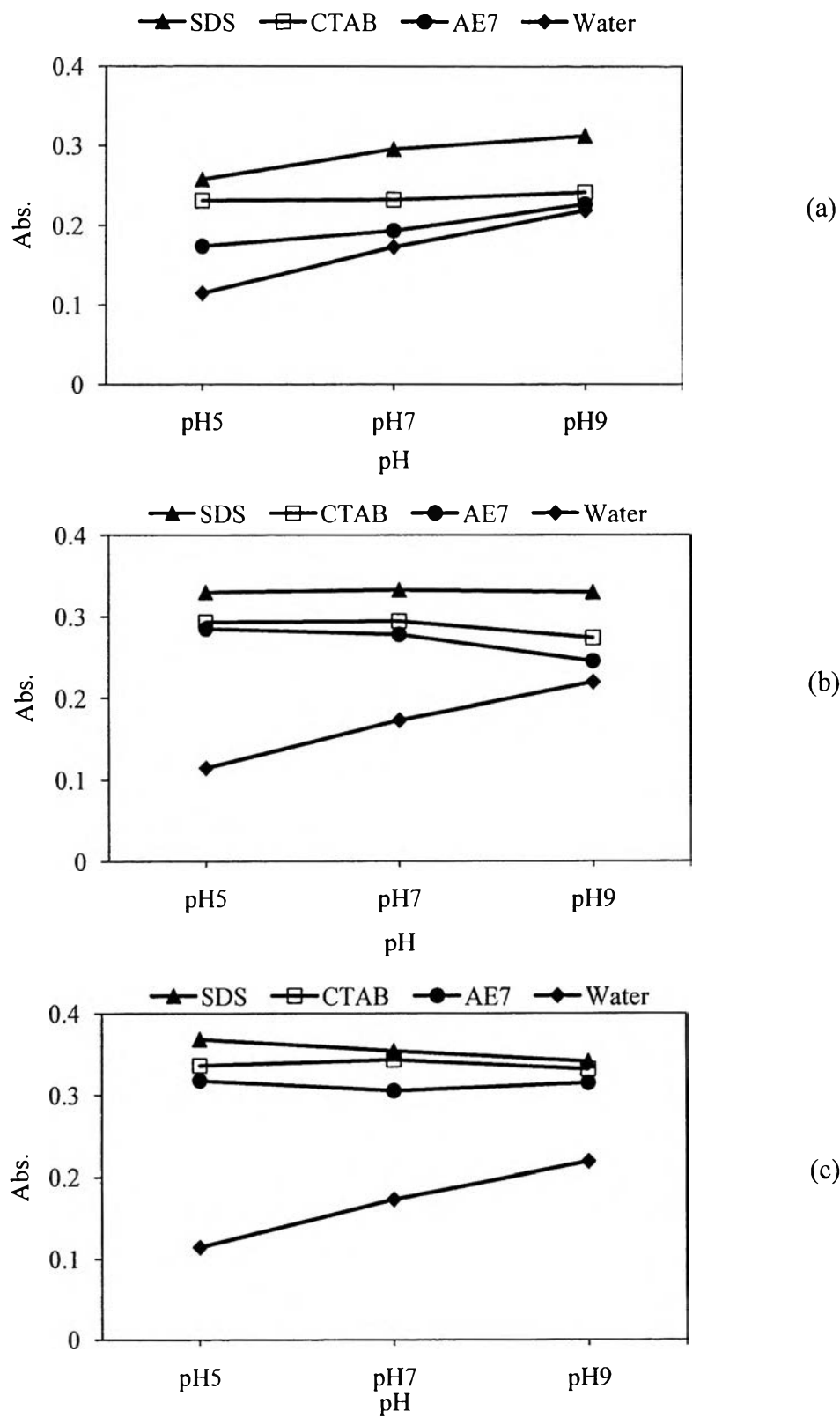
**Figure 4.12** Dispersion of talcum powder (a) at solution pH5, (b) at solution pH7, (c) at solution pH9.

As compared with type of surfactants for all solution pH, the increasing dispersion stability with increasing surfactant concentration is the highest in SDS solution, followed by CTAB and AE7 respectively. This correlated with maximum surfactant adsorption and absolute value of zeta potential in the order of SDS>CTAB>AE7. In case of AE7, nonionic surfactant, the dispersion stability of talcum powder is the lowest but higher than in absence of surfactant due to the lowest of surfactant adsorption and absolute value of zeta potential. Even though talcum powder in AE7 surfactant has the lowest absolute value of zeta potential, the steric effect of AE7 surfactant molecules adsorbed on the surface of talcum powder can enhance the dispersion stability of talcum powder.

### 4.4.2 Effect of Solution pH

Figure 4.13 represents the dispersion stability of talcum powder in absence and presence of surfactant with various solution pHs for all surfactant concentration. The light absorbance of talcum powder in absence of surfactant increased with increasing solution pH from 5 to 9, indicated that dispersion stability increased when increased solution pH, which correlated to increase negative value of zeta potential with increase in solution pH. The more negative zeta potential is the more repulsive force resulted in more dispersion stability. In surfactant solution at 0.2CMC concentration, the light absorbance of talcum powder has similar trend as in absence of surfactant, indicated that talcum powders have higher dispersion stability when increasing solution pH from 5 to 9 because increase in the absolute value of zeta potential leaded to increase repulsive force. In surfactant solution at CMC and 2CMC concentration, the light absorbance does not change much, indicated that solution pH insignificantly affected on the dispersion stability of talcum powder. Thus, the effect of solution pH at high surfactant concentration depended on the surfactant adsorption which solution pH has no effect on surfactant adsorption. However, in SDS surfactant at 2CMC, the trend of dispersion increased with decrease solution from 9 to 5 because of the effect of solution pH on surfactant adsorption.

**Figure 4.13** Dispersion of talcum powder (a) at 0.2CMC, (b) at CMC, (c) at 2CMC.

As compared with the type of surfactant, ionic surfactants which are SDS and CTAB have higher dispersion of talcum powder for all solution pH than in nonionic surfactant, it depended on the high surfactant adsorption and high absolute value of zeta potential. Ionic surfactant adsorbed on the surface has the charge at the head group that provided the repulsive force, leading to higher repulsive force than in nonionic surfactant. In SDS surfactant solution for all surfactant concentration, the dispersion stability of talcum powder is the highest and the best dispersion stability of talcum powder in 2CMC concentration at pH5 which related to maximum surfactant adsorption and absolute value of zeta potential resulted in the highest repulsive force between particles. In CTAB solution, surfactant adsorbed on the surface changed the negative charge to positive charge surface, provided the repulsive force that lead to stabilize talcum powder to disperse in solution. For nonionic surfactant, AE7, the lowest in dispersion of talcum powder that correlated to the lowest surfactant adsorption and absolute value of zeta potential. The dispersion of talcum powder in AE7 resulted from steric effect of surfactant adsorbed on surface.

In general, cleaning agent in cleaning process consists of surfactant. The dispersion stability is expected that related to prevent redeposition on the surface of slider in cleaning agent. As the discussion earlier, surfactant can enhance the dispersion of talcum powder because surfactant molecules adsorbed on the surface of talcum powder resulted in increased repulsive force and reduce hydrophobic attraction between particles. Thus, surfactant in cleaning agent can stabilize talcum powder particles to disperse in solution to prevent redeposition on the surface which depended on surfactant adsorption. In this study, SDS surfactant is the highest dispersion stability because of the highest repulsive force that related to highest surfactant adsorption and maximum absolute value of zeta potential.

## 4.5 Contact Angle Results

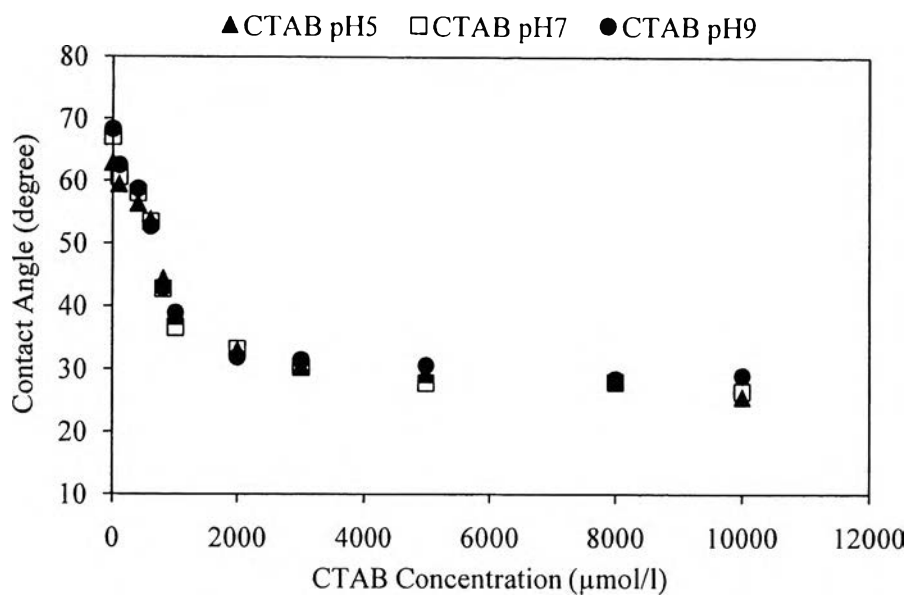### 4.5.1 Contact Angle Results of Anionic Surfactant

The contact angle of SDS solution on talcum powder is represented on Figure 4.14 for all solution pH, the contact angles decreased significantly with increasing SDS concentration until reaching the CMC of SDS at around 9,000 μmol/l. The contact angle at above the CMC concentration decreased with decreasing solution pH from 9 to 5 which correlated to surfactant adsorption of SDS that increased with decreasing solution pH.
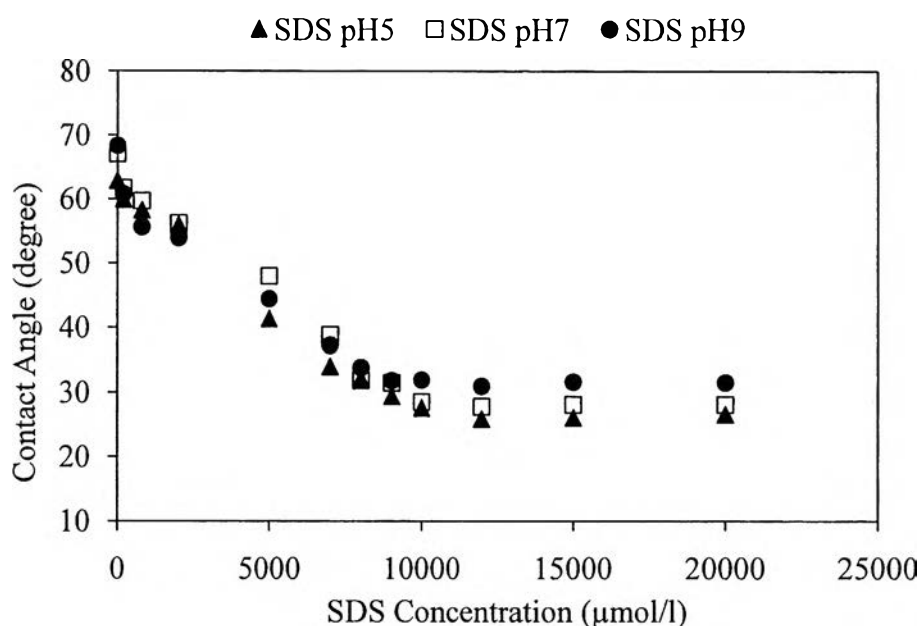


**Figure 4.14** Contact angle of SDS solution on talcum powder with various pH levels.

### 4.5.2 Contact Angle Results of Cationic Surfactant

Figure 4.15 shows the contact angle of CTAB on talcum powder. As increase in surfactant concentration for all solution pH, more surfactant adsorbed on the surface of talcum, resulted in contact angle decreased with increasing surfactant concentration until reached above CMC. The solution pH insignificantly affected on the contact angle because of its insignificant effect of surfactant adsorption on solution pH.

**Figure 4.15** Contact angle of CTAB solution on talcum powder with various pH levels.

### 4.5.3 Contact Angle Results of Nonionic Surfactant
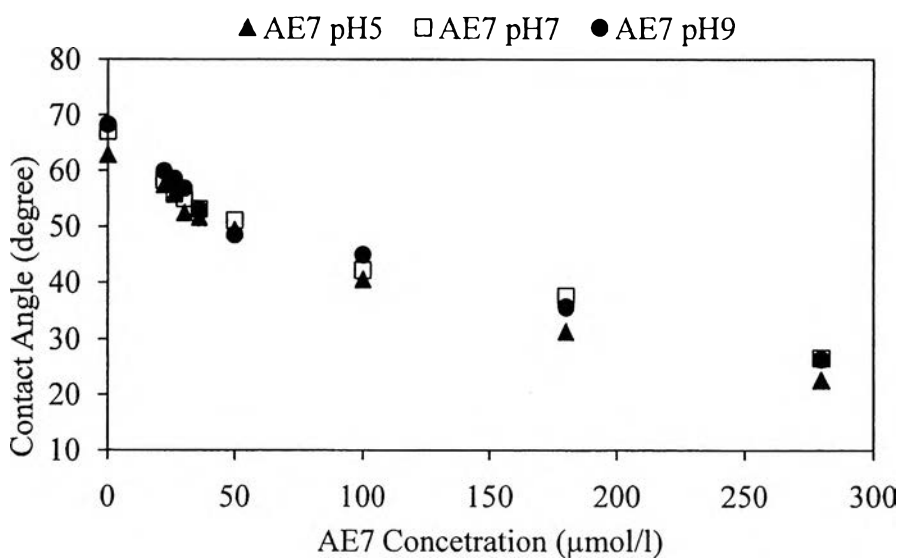


**Figure 4.16** Contact angle of AE7 solution on talcum powder with various pH levels.

Figure 4.16 represents the contact angle of AE7. The contact angle decreased with increasing surfactant concentration for all solution pH until at high concentration, the contact angle cannot measure. The solution pH insignificantly affected on the contact angle because of its insignificant effect of surfactant adsorption on solution pH.

Measurement of the contact angle of surfactant solution on talcum powder surface indicates the wetting of surface. A lower value of contact angle indicates better wetting whereas a higher value of contact angle indicates lower wetting. Thus, for all surfactant solution, the higher surfactant concentration, the higher surface wettability. As compared with type of surfactants, from Figure 4.14, Figure 4.15 and Figure 4.17, the contact angle value of talcum powder for all three surfactants is closely, indicated that wetting is not important factor for dispersion stability but important for enhancement aqueous solution to wet on the surface.