CHAPTER IV
RESULTS AND DISCUSSION

In all experiments the concentration of SDS and calcium ions remained below K_{sp} and CMC to prevent precipitation and formation of calcium didodecyl sulfate complex micelle. The value of concentration-based K_{sp} of calcium didodecyl sulfate at $30^O C$ was 6.0×10^{-3} M^3 (Riviello., 1997) and the activity-based K_{sp} was 5.02×10^{-3} M^3 (Stellner and Scamehorn 1989). The CMC of SDS at $30^O C$ was 8300 µM (Mukerjee and Mysel 1970). The conditions of pH chosen in experiments were of 7 and 9. The temperature of all experiments was constant at $30^O C$.

4.1 Effect of Calcium Ions on the Adsorption of SDS on the Paper Fiber

Adsorption isotherms were generated showing the relationship between the SDS and calcium ions. Figures 4.1 and 4.2 depicted the adsorption of calcium ions on the surface of paper fiber at pH 7 and pH 9. Both curves had similar shapes of adsorption and they were separated into 3 regions. In the first region, the calcium ions were attached by negatively charged sites of the paper fiber resulting from ionization of carboxyl and hydroxyl groups on paper surface and alkaline condition on shear layer of paper fiber (Riviello, 1997). After this region, in the second region, the curve was stable because the counterions chloride ions build up ionic strength of the system. In the third region, the dominant mechanism was the same as in the first region, the further addition of calcium ions resulted in electrostatic interaction with the adsorbed chloride ions. At equilibrium calcium concentration of 25,000 µM, the calcium loading on surface was 15 $\mu mol/m^2$.
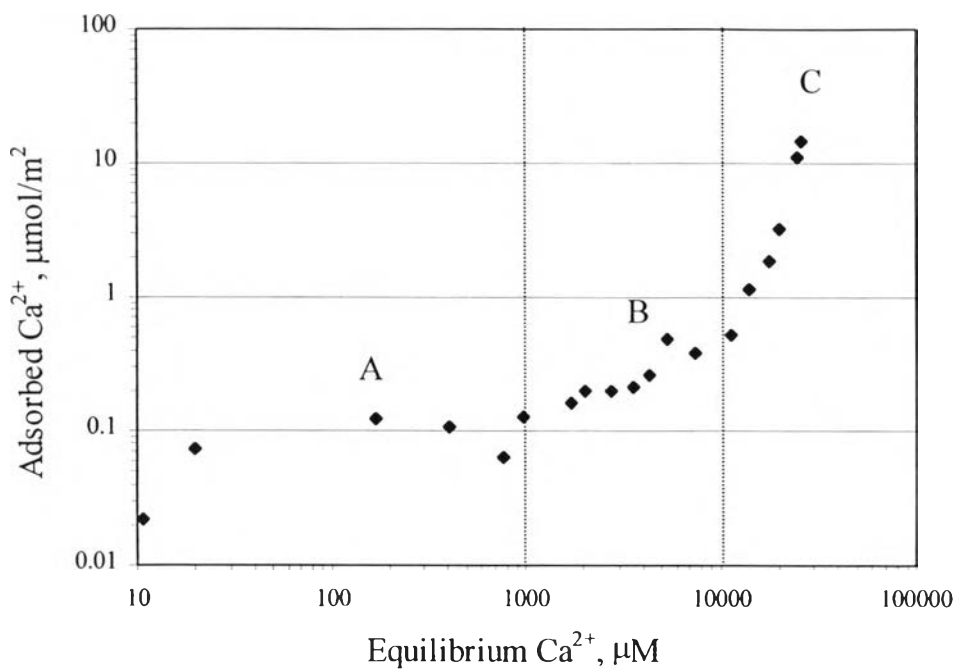
Figure 4.1 Adsorption isotherm of calcium on paper fiber with no SDS at pH 7 at $30^{O}C$; varying initial calcium concentration.
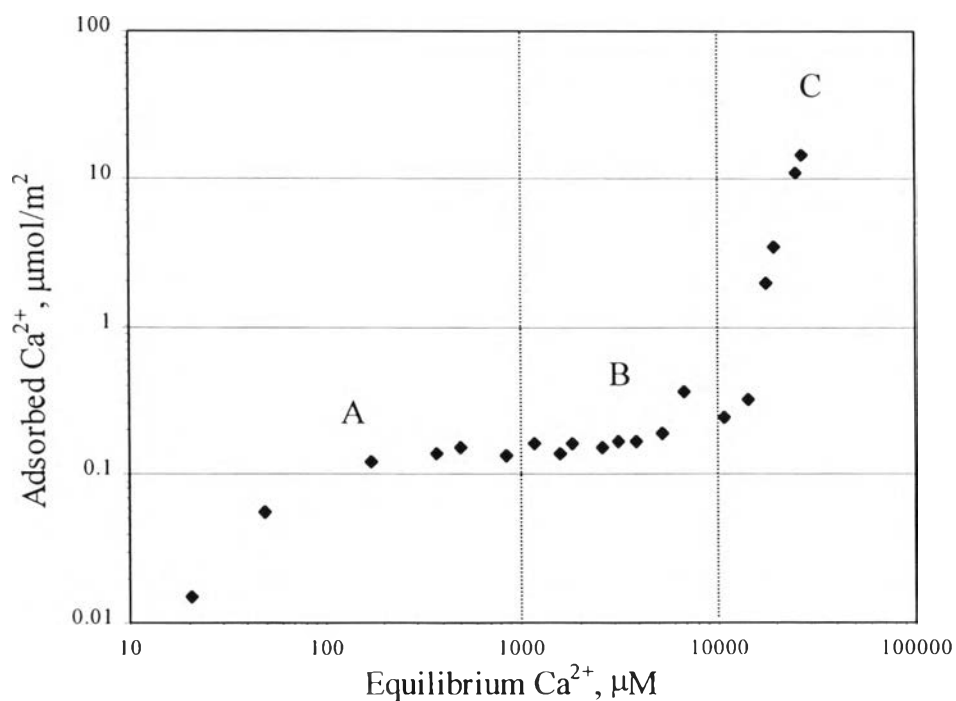

Figure 4.2 Adsorption isotherm of calcium on paper fiber with no SDS at pH 9 at $30^{O}C$; varying initial calcium concentration.
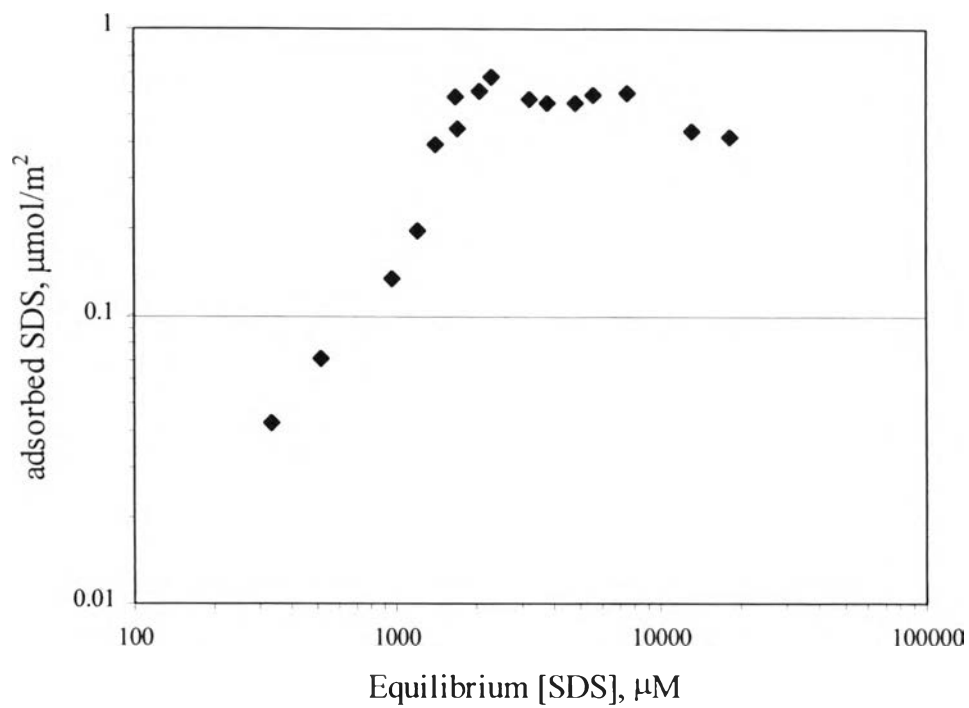
Figure 4.3 Adsorption isotherm of SDS on paper fiber with no calcium at pH 7 at 30°C; varying initial SDS concentration.
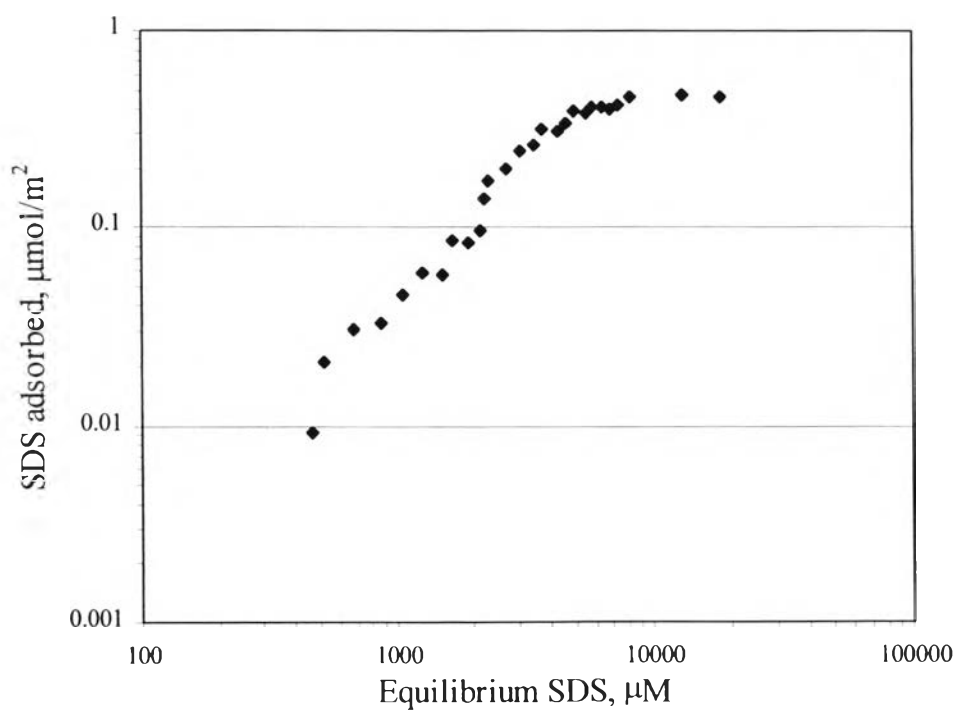

Figure 4.4 Adsorption isotherm of SDS on paper fiber with no calcium at pH 9 at 30°C; varying initial SDS concentration.

It appeared that surface was not completely covered by calcium. If there were more calcium added, the paper fiber would be capable of better adsorption.

The adsorption isotherm of SDS on paper fiber at pH 7 was shown in Figure 4.3 and one at pH 9 was shown in Figure 4.4. Both curves appeared to be S-shape according to Rosen (1989). At higher pH, paper fiber carried more negative charged sites and the head groups of SDS were also negative, so the adsorption of SDS on paper fiber should be tail down orientation, leaving the negative head groups outward to the solution, so called hydrophobic interaction. The result showed that the plateau adsorption of SDS at pH of 7 was approximately 0.5 μmol/m^2 corresponding to 3,000 μM (less than CMC of SDS) but the plateau adsorption of SDS at pH 9 corresponding to 8,000 μM (near CMC of SDS).

Figure 4.5 is a replot between the adsorption isotherms of SDS and calcium on paper fiber at pH 7 shown previously in Figure 4.1 and 4.3. At equilibrium SDS concentration at approximately 3,000 μM, the plateau adsorption of SDS was approximately 0.5 μmol/m^2. But calcium adsorption curve denoted by diamond showed that fiber had more adsorption capacity on calcium than on SDS. At the equilibrium SDS concentration between 800-3,000 μM, the curve of SDS had higher slope than the calcium curve which meant the SDS preferred to adsorb on paper fiber higher than calcium ions. After the equilibrium SDS concentration at 3,000 μM, the calcium adsorption continued to increase while SDS curve leveled off. It could be concluded that the paper fiber had more capacity to adsorb calcium than SDS was.
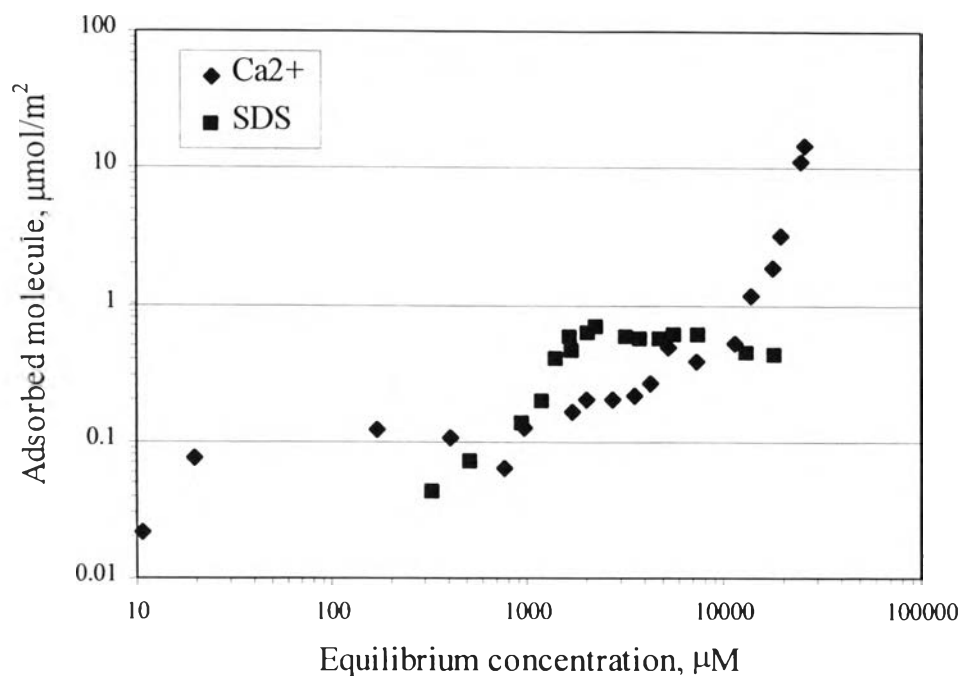
Figure 4.5 Adsorption isotherms of SDS and calcium on paper fiber at pH 7 at $30^{\circ}C$; (■) varying initial SDS concentration, (◆) varying initial calcium concentration.

Figure 4.6 shows relationship between adsorbed SDS and equilibrium SDS in the presence of various initial calcium concentrations at pH 7. The same relationship was obtained at pH 9 as shown in Figure 4.7. Both curves in Figures 4.6 and 4.7 revealed that addition of various amounts of calcium did not have much change in adsorbed SDS. Because the calcium concentrations of 100 and 1,000 µM were not high enough to be cooperative adsorption for increasing the SDS adsorption capacity. Figures 4.8 and 4.9 show the relationship of SDS and calcium adsorbed on paper fiber at pH 7 and 9. At initial calcium concentration of 100 µM, the initial SDS concentration was varied but calcium surface loading still remained constant at 0.015 µmol/m². Likewise, at initial calcium concentration of 1,000 µM, SDS adsorption could not reach the full adsorption capacity on paper fiber and the calcium loading was constant at 0.15 µmol/m² with various SDS concentration. It is suggested

that the amount of calcium was not high enough to induce bridging mechanism with SDS on paper fiber, because some adsorbed SDS remained unreacted and not participating in calcium adsorption. However, there are several possible adsorption mechanisms for calcium and anionic surfactant on the layer of fiber in high saline condition depending on the solution conditions and concentration of surfactant and calcium (Rutland and Pugh 1997).
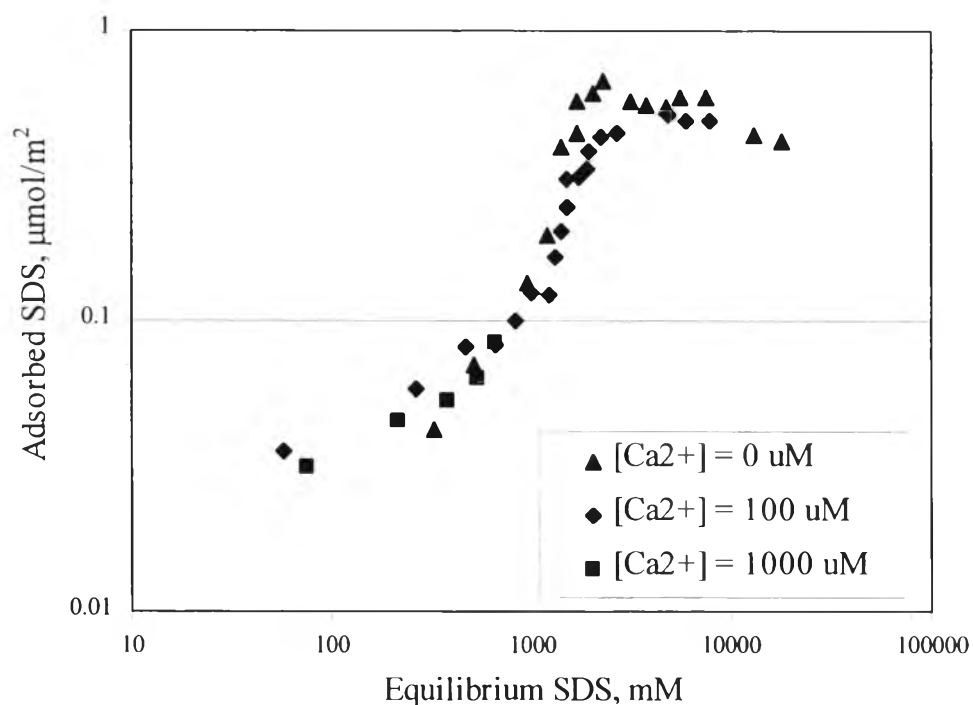

Figure 4.6 Adsorption isotherms of SDS with varying initial calcium concentration at pH 7 at 30°C; (▲) varying initial SDS concentration, (◆) varying initial SDS concentration and constant initial calcium concentration 100 μM, (■) varying initial SDS concentration and constant initial calcium concentration 1,000 μM.
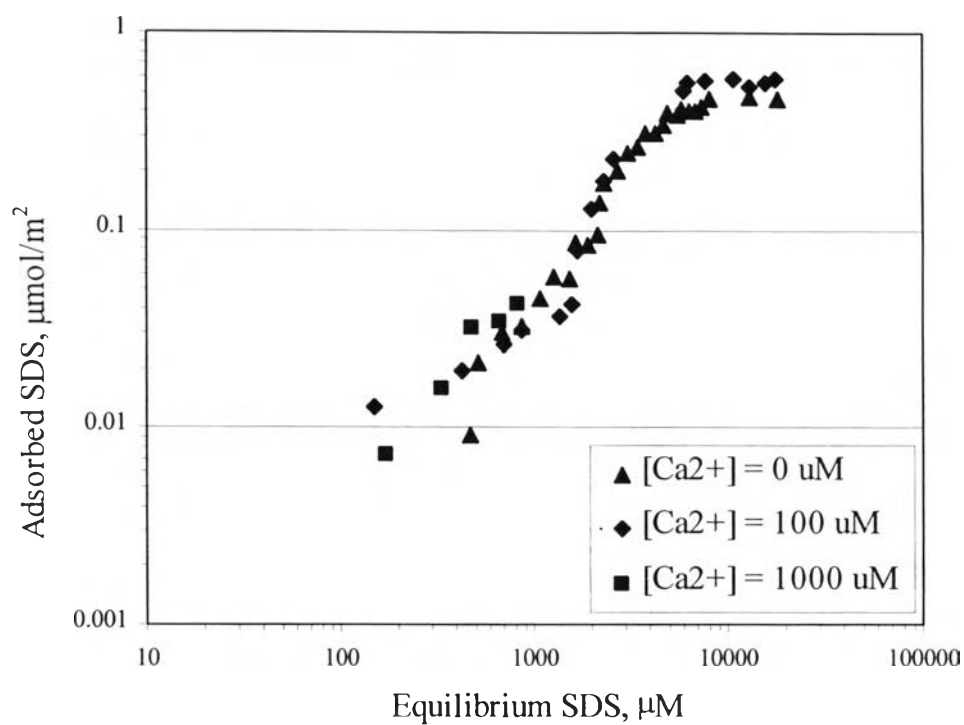
Figure 4.7 Adsorption isotherms of SDS with varying initial calcium concentration at pH 9 at $30^{\circ}C$; (▲) varying initial SDS concentration, (◆) varying initial SDS concentration and constant initial calcium concentration 100 μM, (■) varying initial SDS concentration and constant initial calcium concentration 1,000 μM.
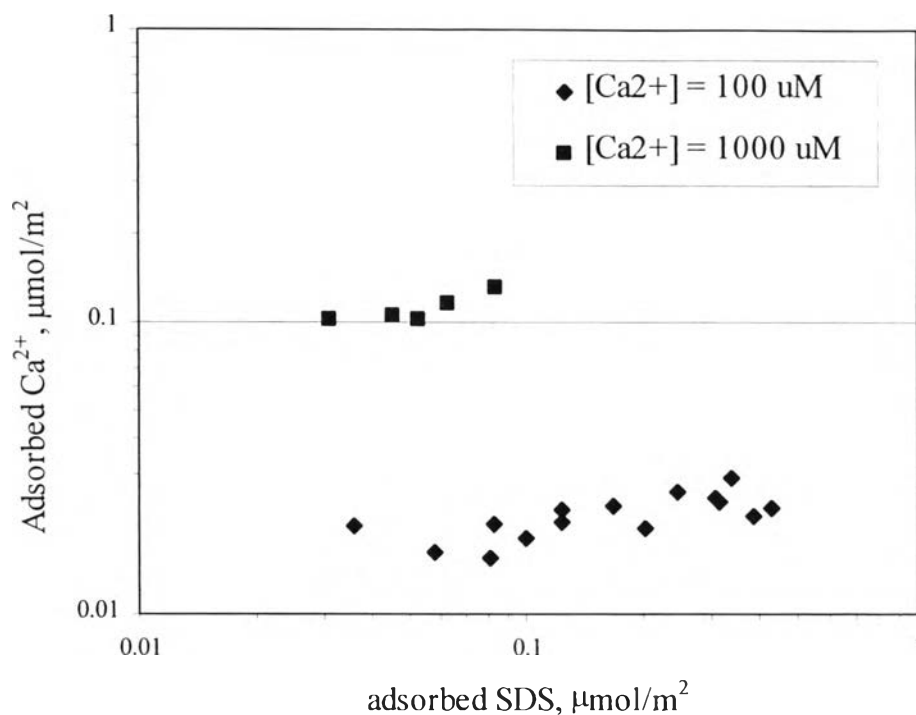
Figure 4.8 Adsorption isotherms of calcium and SDS with varying initial calcium concentration at pH 7 at 30°C; (◆) varying initial SDS concentration and constant initial calcium concentration 100 μM, (■) varying initial SDS concentration and constant initial calcium concentration 1,000 μM.
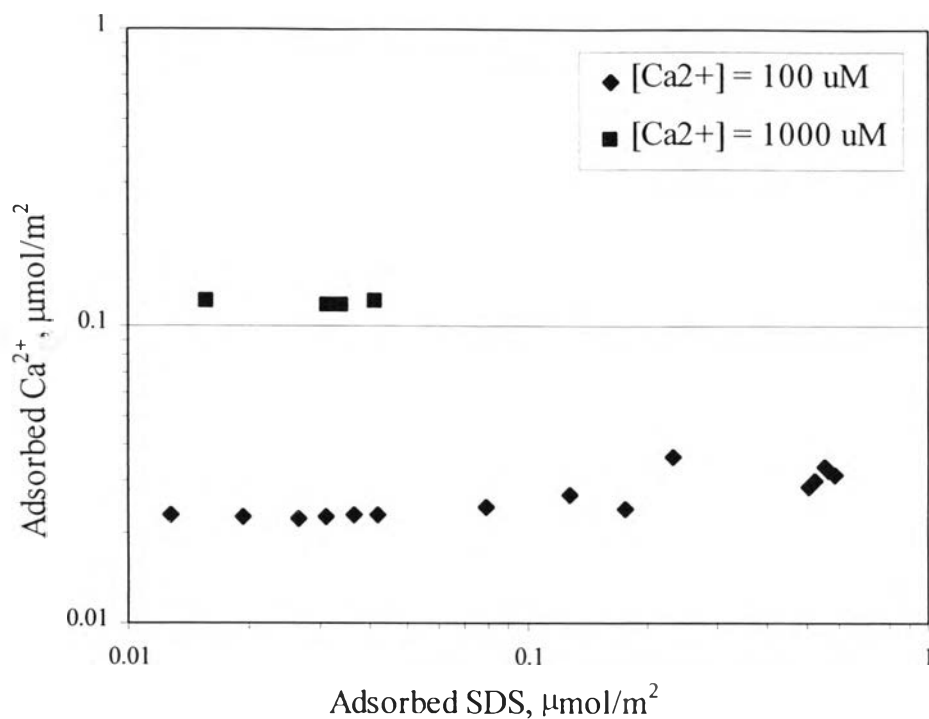
Figure 4.9 Adsorption isotherms of calcium and SDS with varying initial calcium concentration at pH 9 at $30^{O}C$;(◆) varying initial SDS concentration and constant initial calcium concentration 100 μM, (■) varying initial SDS concentration and constant initial calcium concentration 1,000 μM.

4.2 Effect of pH on the Adsorption of SDS and Calcium Ions on Paper Fiber

When pH of system was changed, H^+ and OH^- were the potential determining ions for the paper fiber surface. Figure 4.10 illustrates the comparison of the SDS adsorption on paper fiber at pH 7 and 9. These data also suggested that the surfactant had greater affinity for fiber in solution at pH 7 than one at pH 9. This is probably due to OH^- ions covering more on surface at pH 9, in turn, causing increase in electrostatic repulsion between SDS and surface. It should be noted that at the SDS equilibrium concentration below CMC (8300 μM), the SDS adsorption capability at pH 7 was twice as

much as one at pH 9. At equilibrium SDS concentration beyond CMC, both adsorption isotherms approached the same capacity of 0.5 μmol/m² for both pH.
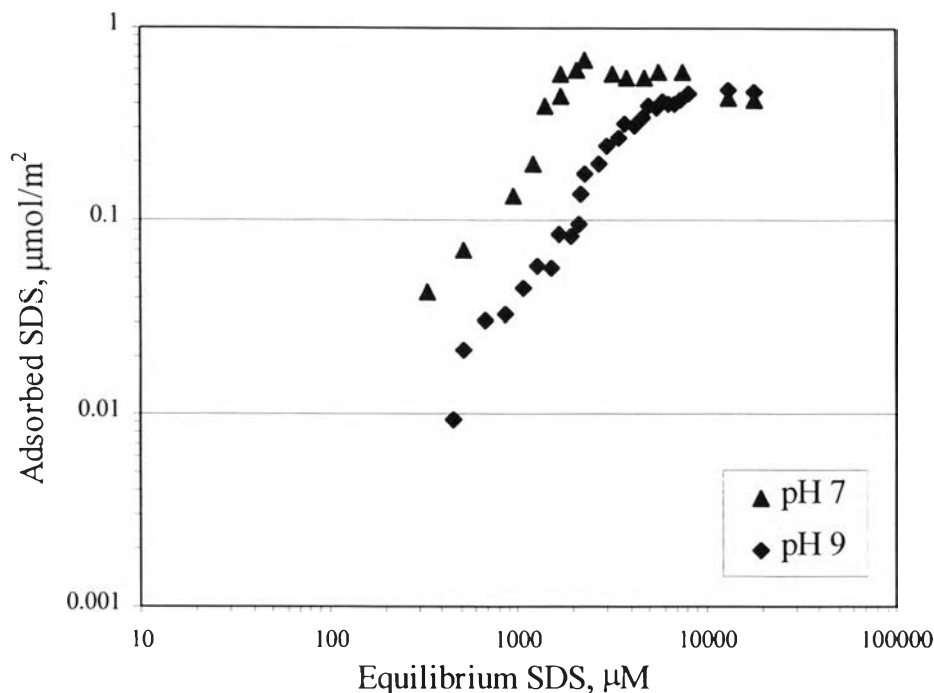

Figure 4.10 Adsorption isotherms of SDS with no calcium and varying pH at 30°C ; (▲) varying initial SDS concentration at pH 7, (◆) varying initial SDS concentration at pH 9.

Figure 4.11 shows the relationship between calcium adsorption and equilibrium calcium concentration at both pH conditions. Both curves were similar and almost superimposed, which suggested that pH had no effect to calcium adsorption on paper fiber. Because the electrostatic force between calcium ions and paper surface was greater than the effect from OH⁻ ions. SDS adsorption on paper fiber in the presence of varying initial concentration of calcium ions and varying pH were shown in Figures 4.12 and 4.13. In all cases, increasing pH from 7 to 9 caused a decrease in SDS adsorption by half due to OH⁻ ions covering more on surface at pH 9.

The adsorption isotherm of calcium in the presence of initial SDS concentration of 100 μM and 1000 μM were shown in Figures 4.14 and 4.15. From both Figures, changing pH had no effect on calcium adsorption, but had direct effect on SDS adsorption.
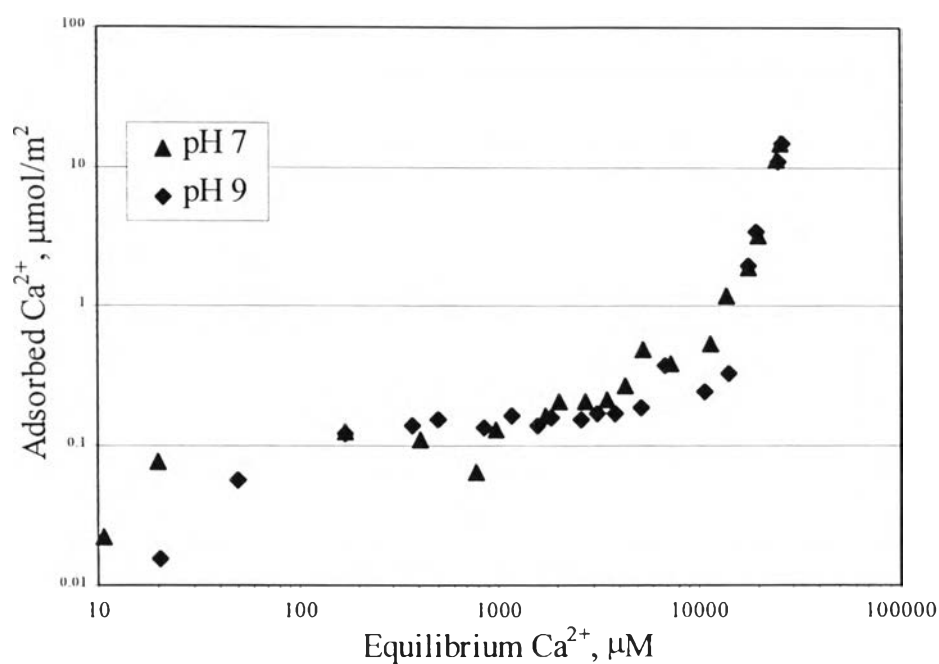

Figure 4.11 Adsorption isotherms of calcium with no SDS and varying pH at 30°C; (▲) varying initial calcium concentration at pH 7, (◆) varying initial calcium concentration at pH 9.
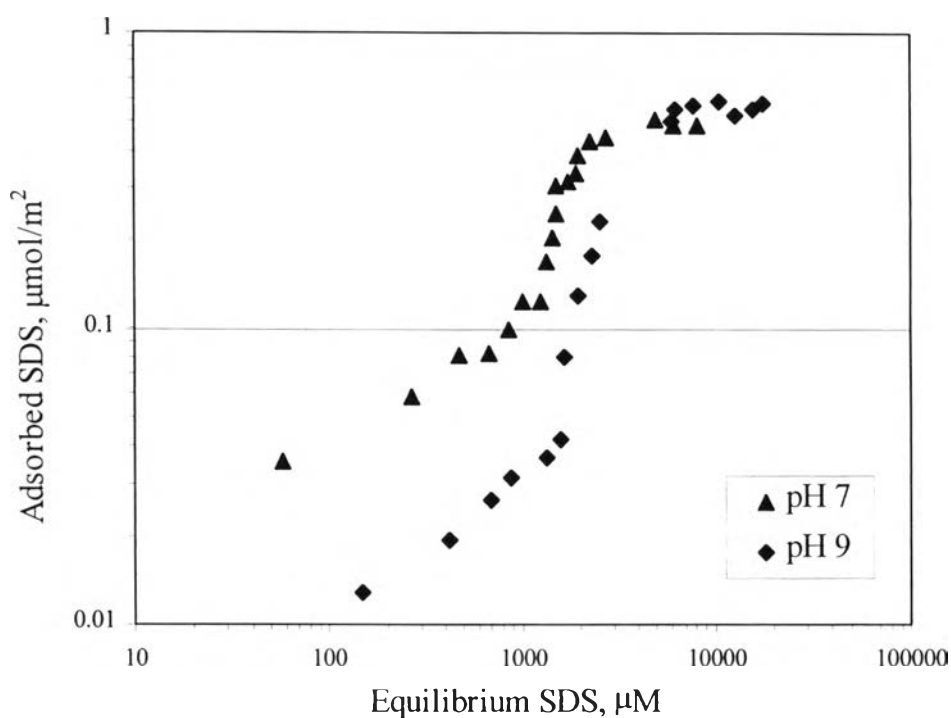
Figure 4.12 Adsorption isotherms of SDS with initial calcium concentration 100 μM and varying pH at 30^OC; (▲) varying initial SDS concentration and constant calcium concentration 100 μM at pH 7, (◆) varying initial SDS concentration and constant calcium concentration 100 μM at pH 9.

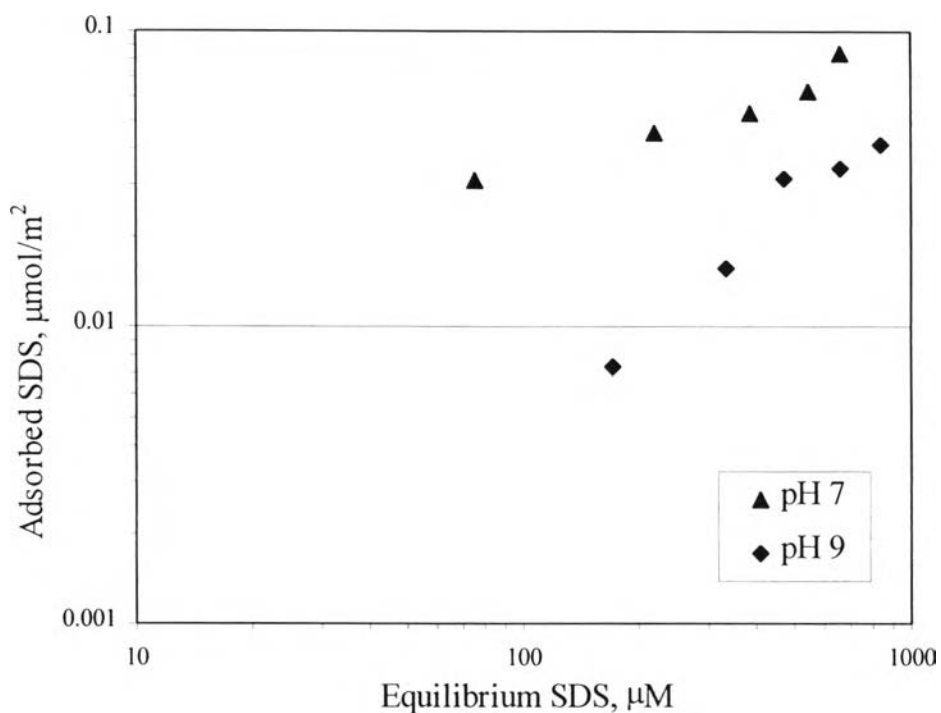**Figure 4.13** Adsorption isotherms of SDS with initial calcium concentration 1,000 μM and varying pH at 30°C; (▲) varying initial SDS concentration and constant calcium concentration 1,000 μM at pH 7, (◆) varying initial SDS concentration and constant calcium concentration 1,000 μM at pH 9.
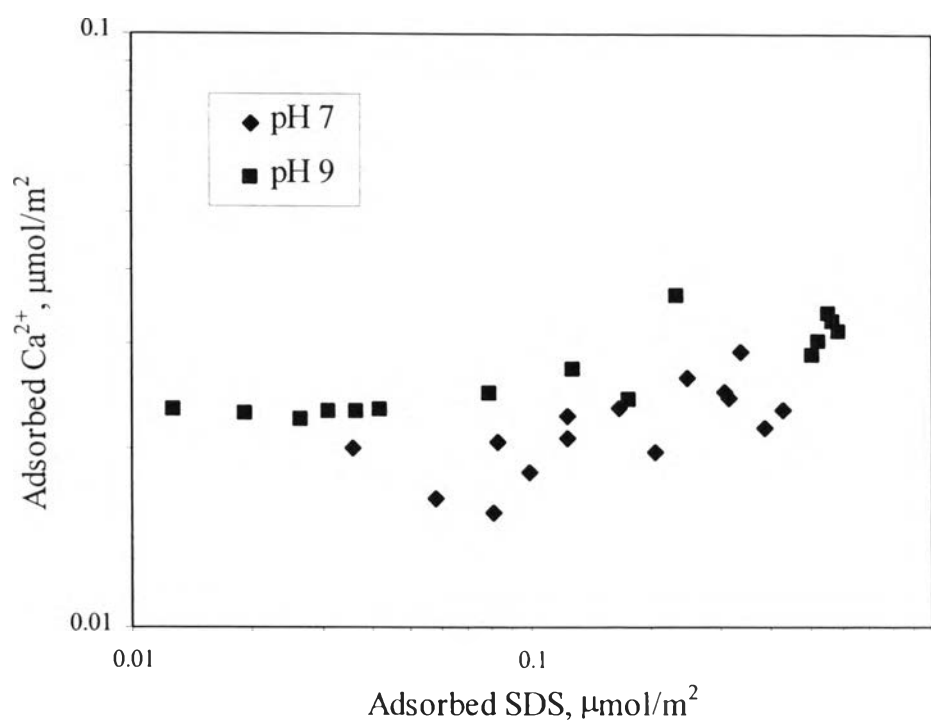
Figure 4.14 Adsorption isotherms of calcium and SDS with initial calcium concentration 100 μM and varying pH at 30°C; (◆) varying initial SDS concentration and constant calcium concentration 100 μM at pH 7, (■) varying initial SDS concentration and constant calcium concentration 100 μM at pH 9.
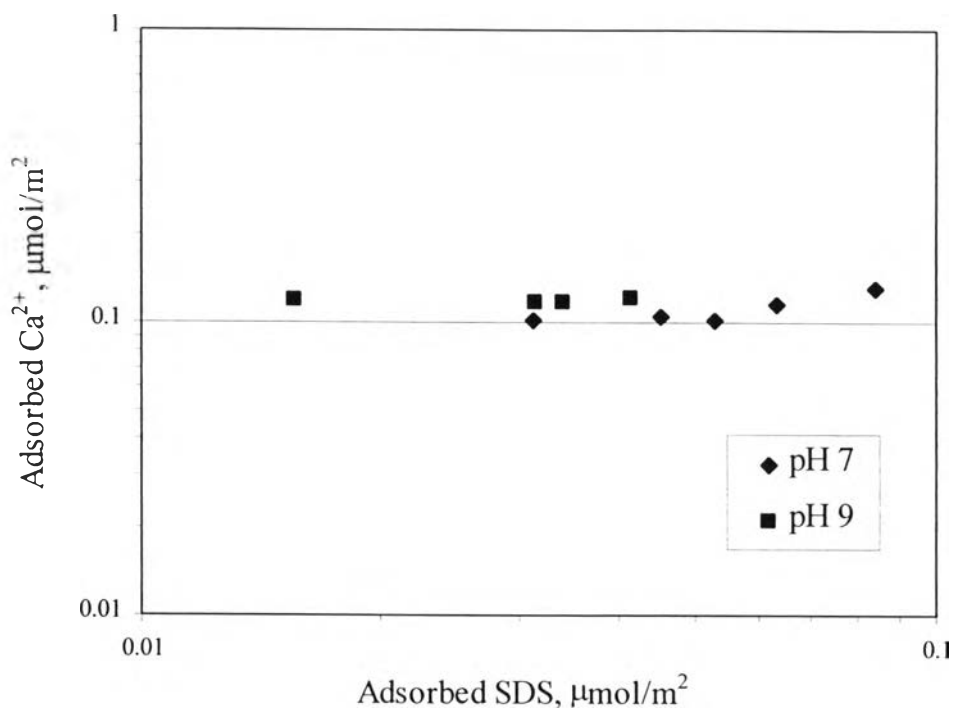
Figure 4.15 Adsorption isotherms of calcium and SDS with initial calcium concentration 1,000 μM and varying pH at 30°C; (◆) varying initial SDS concentration and constant calcium concentration 1,000 μM at pH 7, (■) varying initial SDS concentration and constant calcium concentration 1,000 μM at pH 9.

4.3 Effect of SDS and Calcium Ions to the Zeta Potential of Paper Fiber

Figure 4.16 illustrates the zeta potential of the paper fiber in the absence of calcium at pH 7. Adding SDS caused the absolute magnitude of negative zeta potential decrease by approximately 7 mV, from 28 to 21 mV, with SDS adsorption on the surface even though the adsorbed molecules carried a negative charge. Because SDS adsorbed on the fiber with the configuration as shown in Figure 4.17 (Scamehorn *et al.*, 1997). This configuration was horizontal lay-down which made the hydrophobic part of SDS molecules cover on the negatively charged sites of the fiber resulting in decrease of zeta potential. In all cases, increasing calcium concentration at pH

7 further decreased the absolute magnitude of zeta potential as shown in Figure 4.18 because the presence of calcium ions made the electrical diffuse double layer around the negatively charged particles more compressed. The compression of electrical diffuse double layer resulted in diminishing electrostatic repulsion between the particles. Adding 100 μM of calcium to system made the absolute magnitude of zeta potential decrease approximately 1 mV. Increasing calcium concentration up to 1,000 μM to system caused the absolute magnitude of zeta potential decrease by approximately 2.5 mV and 5 mV at equilibrium SDS concentration less than 600 μM and higher than 600 μM, respectively.
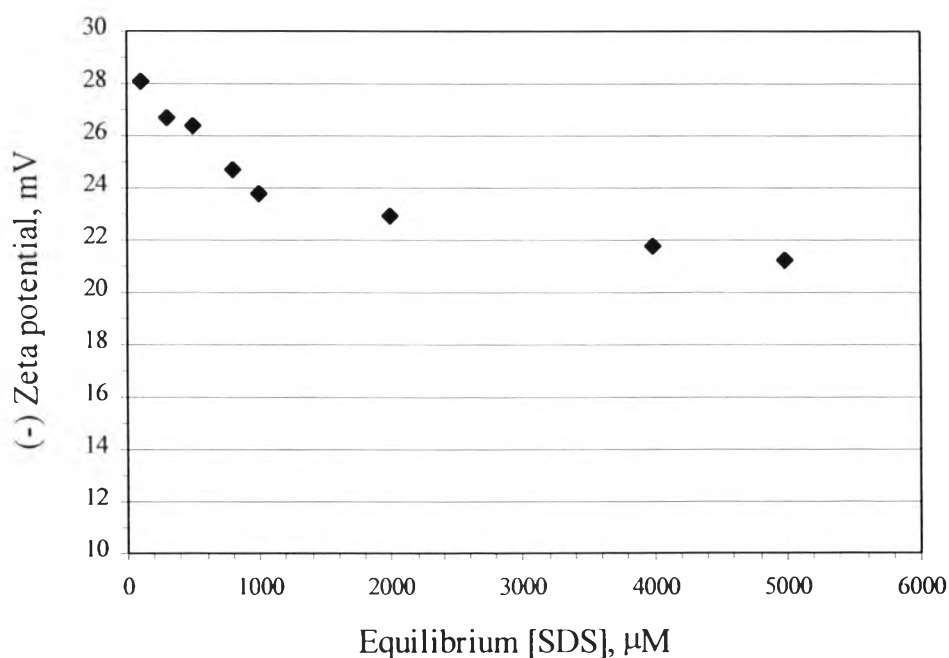

Figure 4.16 Zeta potential of paper fiber as a function of equilibrium SDS concentration with no calcium at pH 7 at 30°C; (♦) varying initial SDS concentration.
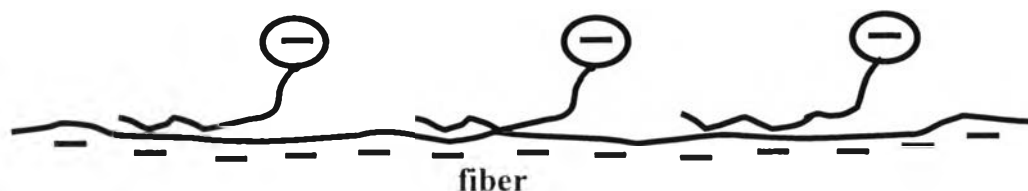

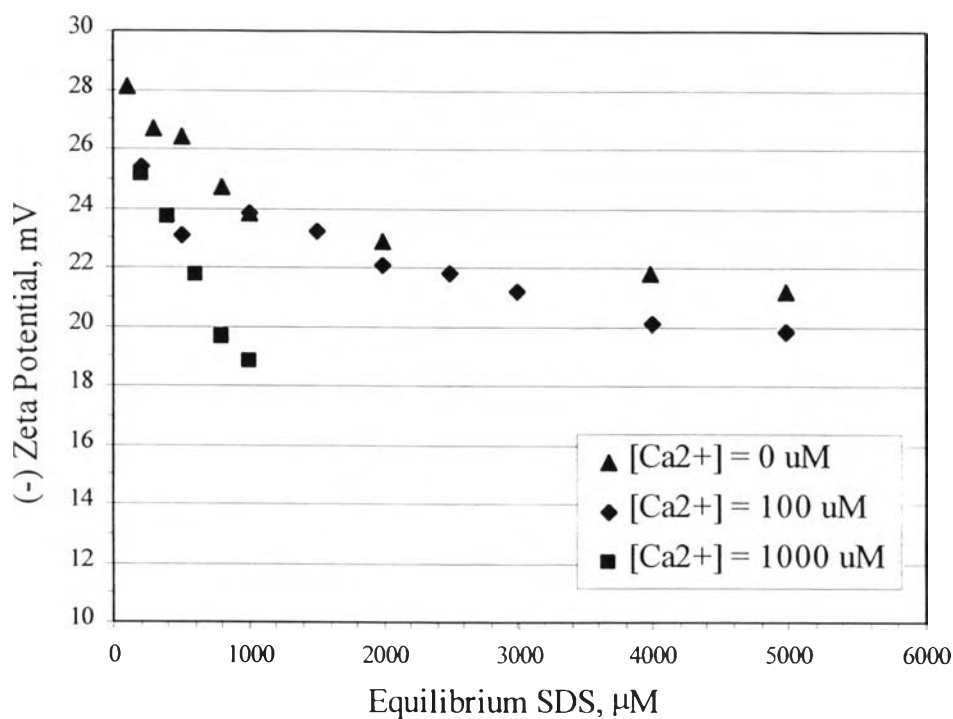**Figure 4.17** The schematic of the SDS adsorption on paper fiber (Scamehorn *et al.*, 1997).

Figure 4.18 Zeta potential of paper fiber as a function of equilibrium SDS concentration with varying calcium concentration at pH 7 at 30°C; (▲) varying initial SDS concentration, (◆) varying initial SDS concentration and constant calcium concentration 100 μM, (■) varying initial SDS concentration and constant calcium concentration 1,000 μM.

4.4 Effect of pH to the Zeta Potential of Paper Fiber

Figure 4.19 illustrates the zeta potential of the paper fiber in the absence of added calcium with varying pH. The ability of SDS adsorption at pH 7 was reduced by half compared to one at pH 9 in the range of equilibrium SDS concentration below CMC. At equilibrium SDS concentration above CMC, both SDS adsorption isotherms at pH 7 and at pH 9 were almost the same. The presence of 100 μM and 1000 μM of calcium ions are shown in Figures 4.20 and 4.21. The same tendency still occured in both presence and absence of Ca^{2+} concentration. At pH 9, decreasing in SDS adsorption caused the absolute magnitude of zeta potential increase by approximately 3 mV.

Beyond CMC, both SDS adsorption isotherms at pH 7 and 9 were almost the same, the absolute magnitude of zeta potential decreased by approximately 1 mV.
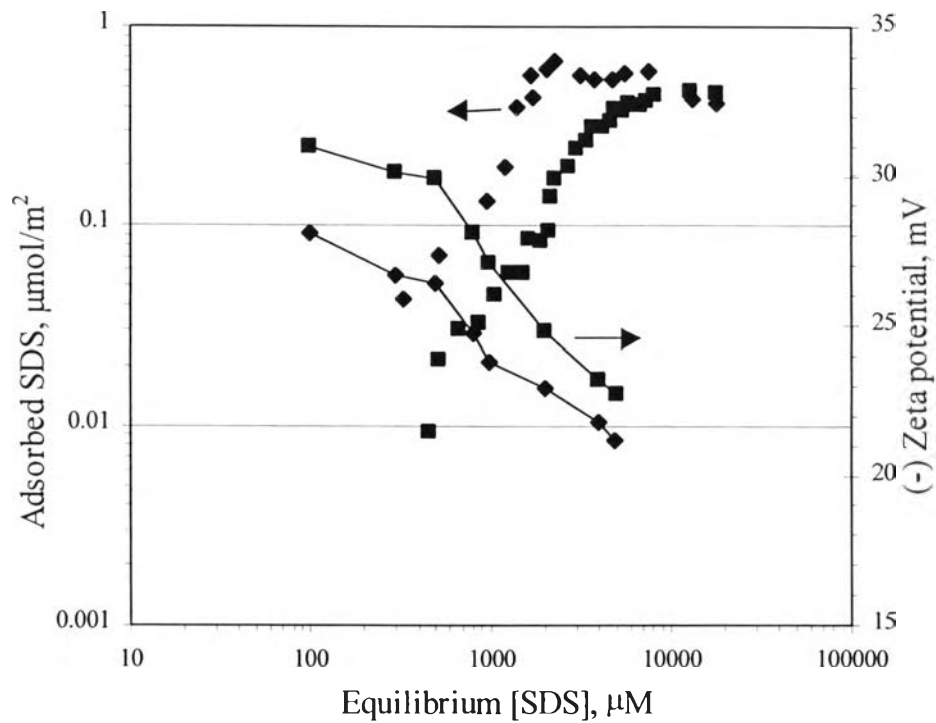

Figure 4.19 Adsorption isotherms of SDS and zeta potential of paper fiber with no calcium and varying pH at 30°C; (◆, ■) adsorption value of varying initial SDS concentration at pH 7 and 9 respectively, (—◆—,—■—) zeta potential value of varying initial SDS concentration at pH 7 and 9 respectively.

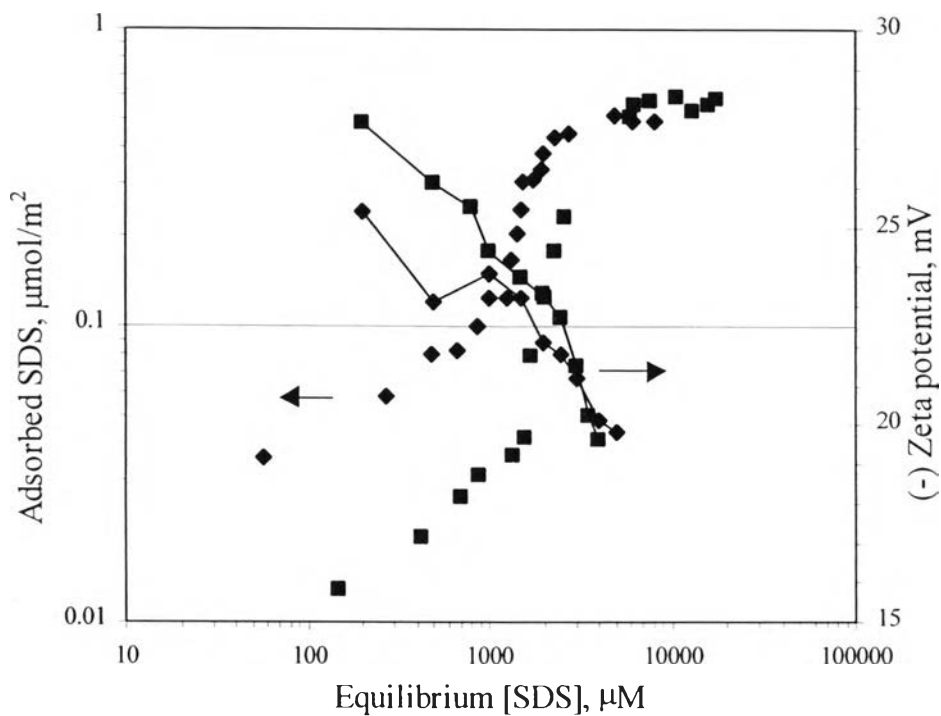**Figure 4.20** Adsorption isotherms of SDS and zeta potential of paper fiber with initial calcium concentration 100 μM and varying pH at 30°C; (◆, ■) adsorption value of varying initial SDS concentration at pH 7 and 9 respectively, (–◆–;–■–) zeta potential value of varying initial SDS concentration at pH 7 and 9 respectively.
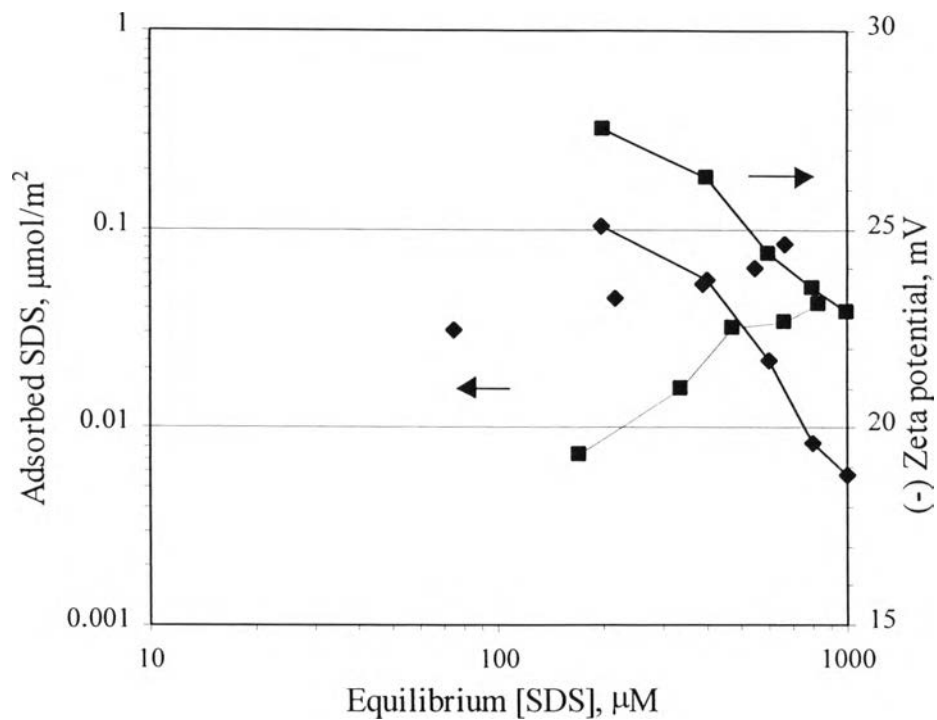
Figure 4.21 Adsorption isotherms of SDS and zeta potential of paper fiber with initial calcium concentration 1,000 μM and varying pH at 30°C; (◆, ■) adsorption value of varying initial SDS concentration at pH 7 and 9 respectively, (━◆━,━■━) zeta potential value of varying initial SDS concentration at pH 7 and 9 respectively.