CHAPTER IV
RESULTS AND DISCUSSION

4.1 Surfactant Adsorption Isotherms

There are several factors strongly influencing surfactant adsorption at the solid-liquid interface such as nature of structural groups on the surface, molecular structure of surfactant and the environment of aqueous solution. For this thesis, pH of system and electrolyte content (calcium concentration) were selected to elucidate the adsorption behavior of surfactant on carbon black.

4.1.1 Effect of pH of Suspension

In this section, pH of 7 and 9 were selected for moderate basic pH condition to imitate conditions of traditional deinking operations. Figure 4.1 illustrates the adsorption of sodium dodecyl sulfate (SDS) versus equilibrium concentration at pH of 7 and 9 in the absence of calcium. Comparing the adsorption isotherms, the adsorption at pH of 7 was slightly greater than the adsorption at pH of 9 in all regions. As the pH of the aqueous phase was reduced, the solid surface became more positive or less negative due to the adsorption of protons onto charged sites. This consequence led to increase in the adsorption of anionic surfactants. For carbon black in water, the point of zero charge (PZC) was determined to be approximately 2.3 indicating that the carbon black had a net negative charge at pH levels above 2.3 (Riviello, 1997).

Results of adsorption isotherms on carbon black at both pH of 7 and 9, plotted on log-log scale, were different from typical adsorption isotherms, which were observable the four distinct regions. At small

equilibrium SDS concentration (from point A to B shown in Figure 4.1), the isotherm shape was similar to Langmuir-type isotherm. The slope of isotherm from A to B was linear. It was expected that the monomeric surfactants adsorbed on the surface without significant association or aggregation of adsorbed surfactants. The horizontal or laying-down configuration of adsorbed surfactants was possible to occur, and the interaction of adsorbed surfactants might be hydrophobic chain/surface interaction. The adsorption of surfactants in this orientation might remain until complete monolayer coverage (from B to C). Beyond this stage, the slope of isotherm was steep again as surfactant concentration increased. The marked inflection point occurred at C. The adsorption of surfactants might be more close packing, and the interaction of adsorbed surfactants might be hydrophobic chain/chain interaction. However, from log-log adsorption isotherm at pH of 7 and 9, the slope of such area (from point C to D) was not greater than unity. It might be indicated that the adsorption of SDS on carbon black was mainly unassociative or at least not strongly associative. The plateau or maximum adsorption of SDS at pH of 7 and 9 was approximately 2.06 μmole/m^2 and occurred near CMC of SDS, 8300 μM (Mukerjee and Mysel, 1970).

The approximate adsorption corresponding to saturation of surface by either a monolayer or a bilayer can be determined from the area of single adsorbed surfactant molecule. The approximate value for area per molecule of SDS adsorbed in close-packed perpendicular orientation on surfaces such as carbon black was 53 A^{o2} (Rosen, 1989). Calculating this value, the close-packed monolayer coverage would require 3.13 μmole/m^2. Bilayer coverage would give in the double of this value. The plateau adsorption from the experiment corresponded to 65.73% of monolayer coverage for SDS.
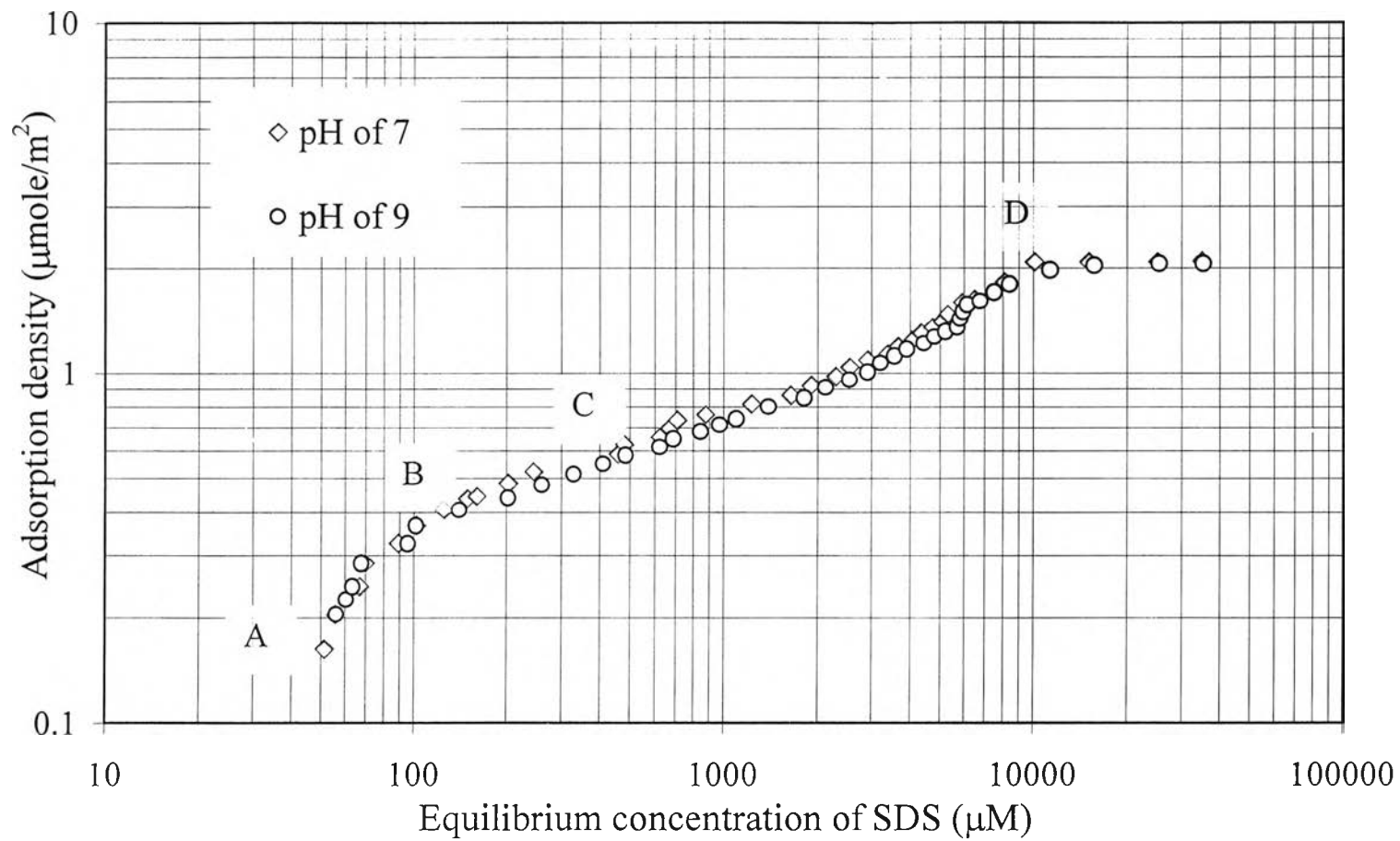
Figure 4.1 The adsorption isotherms of SDS versus equilibrium SDS concentration at pH of 7 and 9.

4.1.2 <u>Effect of Calcium Concentration</u>

In the adsorption and electrophoretic experiments, SDS and calcium concentrations were controlled so that no precipitation of calcium didodecyl sulfate complexes occurred. On the phase boundary, the precipitate phase is in equilibrium with dissolved surfactant and calcium. For systems consisting of a divalent cation such as Ca^{2+} and a monovalent anionic surfactant, the concentration-based solubility product constant (K_{sp}) is defined as follows;

$$K_{sp} = [Ca^{2+}][DS^-]^2 \qquad (4.1)$$

where the bracketed values represent the concentration of species in the solution at equilibrium with the calcium didodecyl sulfate precipitate. The concentration-based K_{sp} of calcium didodecyl sulfate at 30°C was $6.0 \times 10^{-10} M^3$ (Riviello, 1997) and the activity-based K_{sp} was $5.02 \times 10^{-10} M^3$ (Stellner and Scamehorn, 1989).

Figures 4.2 and 4.3 depict the adsorption of SDS on carbon black at constant pH of 7 and 9 as varying calcium concentrations. In all experiments, the initial calcium concentrations were varied from 100 to 1000 μM, and SDS concentrations were varied from 8000 to 60000 μM and from 14000 to 45000 μM for initial calcium concentration 100 and 1000 μM, respectively. Therefore the concentrations of calcium and SDS at equilibrium remained below the K_{sp} value. At increasing calcium concentration levels, the adsorption of SDS on carbon surfaces increased, because an increase in ionic salt led to a decrease in the repulsive forces between the head groups of surfactants. Moreover, decreasing the electrical repulsion between the similarly charged adsorbed ions permitted closer packing. From the experiments, the plateau adsorptions of SDS at initial calcium concentration of
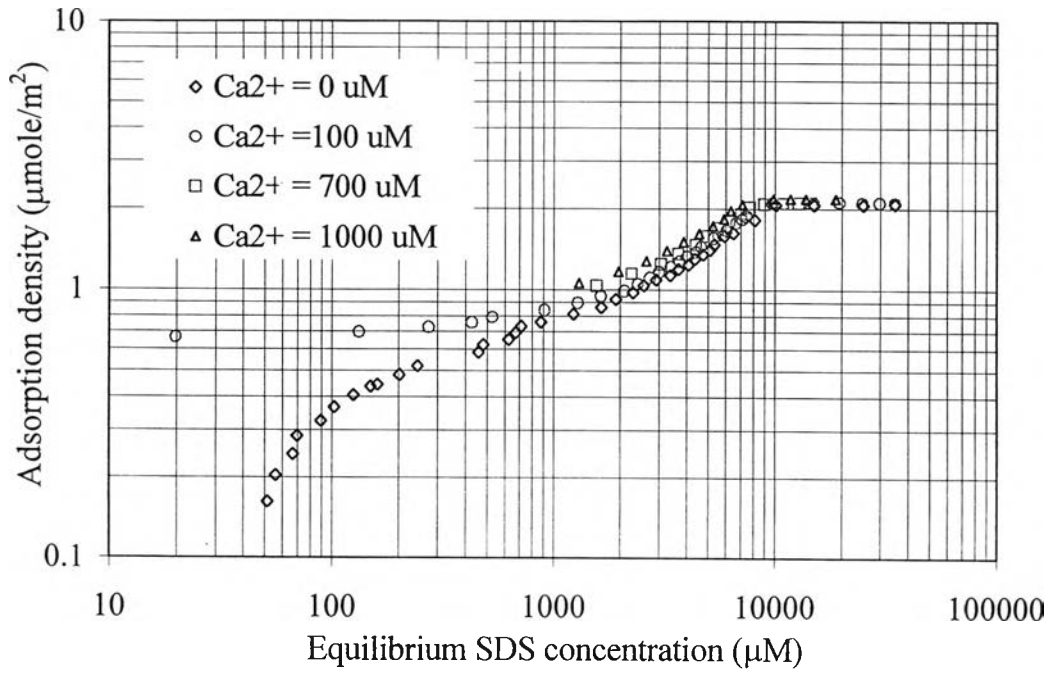
Figure 4.2 Adsorption isotherms of SDS on carbon black at pH of 7 with varying initial calcium concentration.
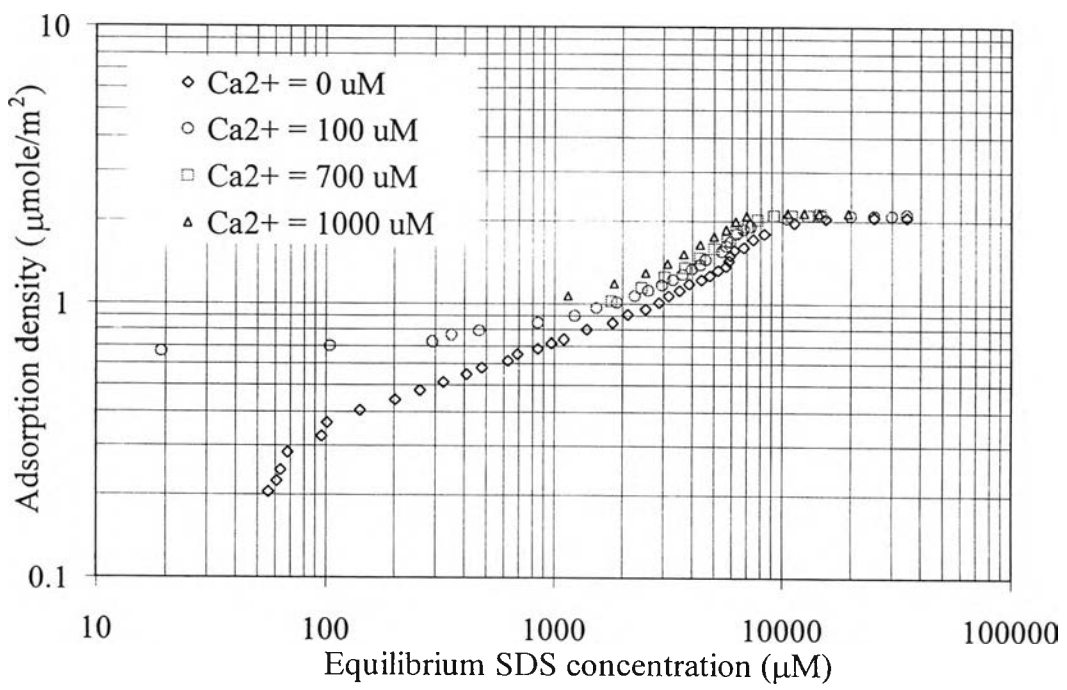

Figure 4.3 Adsorption isotherms of SDS on carbon black at pH of 9 with varying initial calcium concentration.

100, 700, and 1000 μM were 2.10, 2.11 and 2.18 μmole/m^2, respectively for pH of 7 and 2.08, 2.09, and 2.13 μmole/m^2, respectively for pH of 9.

Figures 4.4 and 4.5 demonstrate the relationship of calcium adsorption and SDS adsorption with varying equilibrium SDS concentration at pH of 7 and 9. The results showed that at constant equilibrium SDS concentration when the adsorption of calcium increased, the adsorption of SDS also increased. In the same way, when the adsorption of SDS increased, the adsorption of calcium also increased. This might indicate the cooperative adsorption with ionic surfactants in the presence of oppositely charged ions. The electrostatic repulsion was diminished among the head groups of surfactants by association of the counterion, and this association was not precipitation process.

The adsorption of calcium on the carbon black in the absence of SDS at pH of 7 and 9 is shown in Figure 4.6. The result of calcium adsorption isotherms was Langmurian shape, indicating that the adsorption of calcium was monolayer coverage. The adsorption of calcium ions was attracted by negatively charged sites on the carbon surfaces resulting from surface oxidation. The ionic radius of calcium was 0.099 nm (Russell, 1992). The close-packed monolayer coverage of adsorbed calcium from calculation was 167.8 μmole/m^2. The plateau adsorptions of calcium ions on carbon surface at pH of 7 and 9 were approximately 0.36 and 0.79 μmole/m^2 corresponding to 0.21% and 0.47% of close-packed monolayer coverage, respectively. Generally, bare cations are smaller than anions, and they bond tenaciously to hydrating water molecules (Oldham and Myland, 1994). The interaction between adsorbed calcium ions was not able to occur since aqueous molecules surrounded adsorbed ions and the lateral interactions were repulsive, not attractive. Consequently, it could be concluded that the adsorption of calcium on carbon surfaces was purely electrostatic and non-associative.
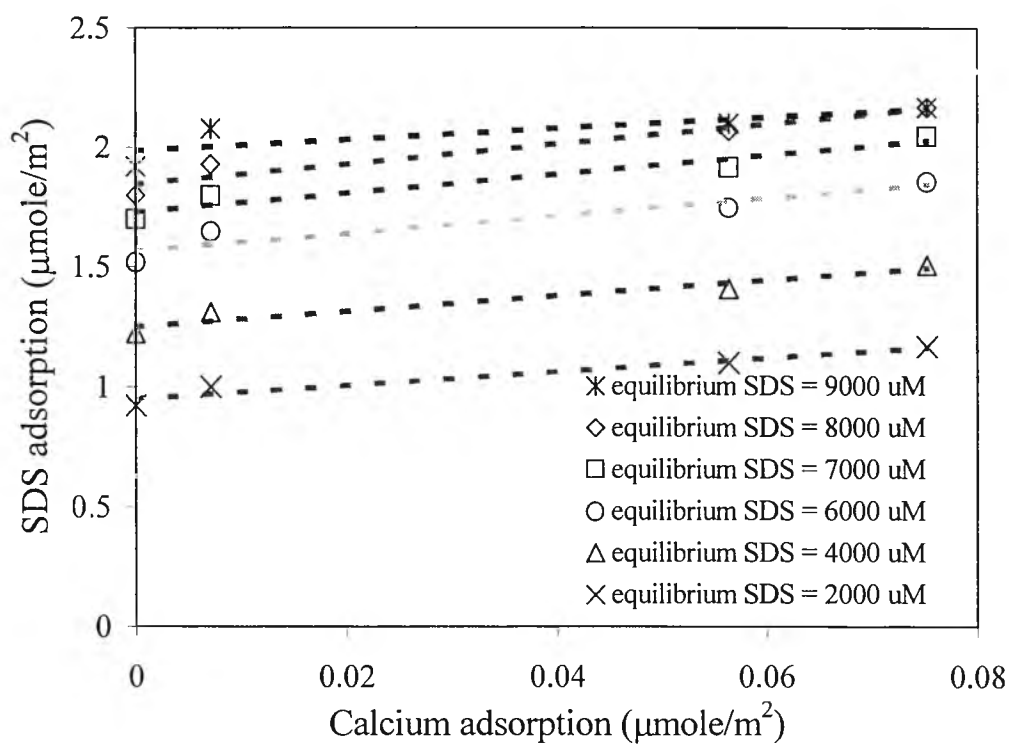
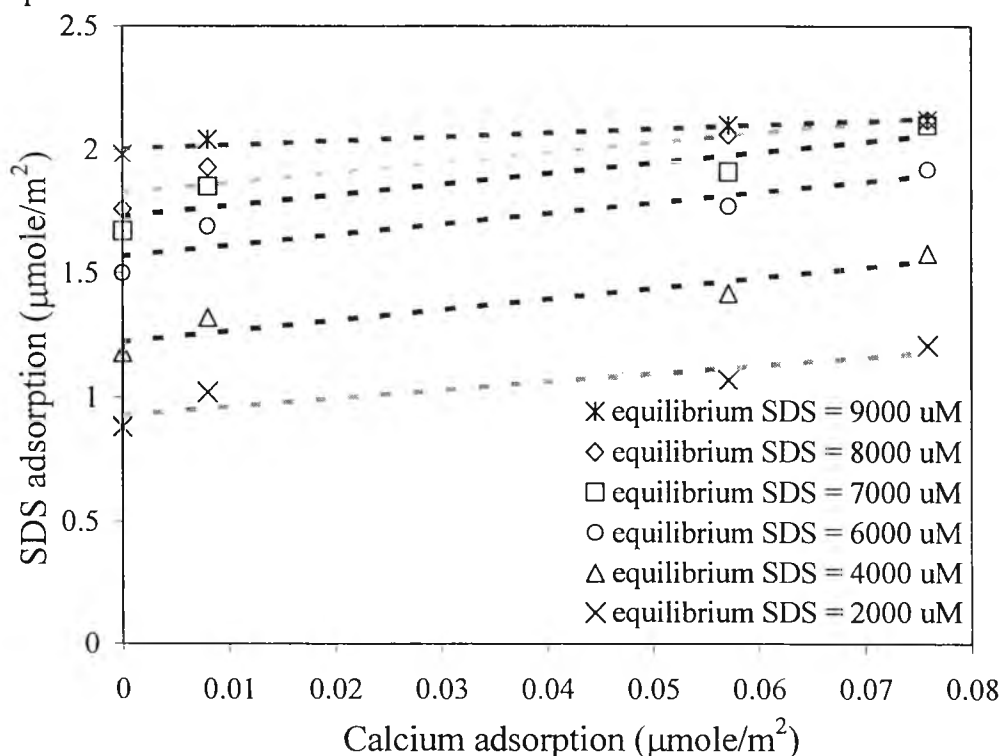**Figure 4.4** SDS adsorption versus calcium adsorption at pH 7 with varying equilibrium SDS concentration.

Figure 4.5 SDS adsorption versus calcium adsorption at pH 9 with varying equilibrium SDS concentration.
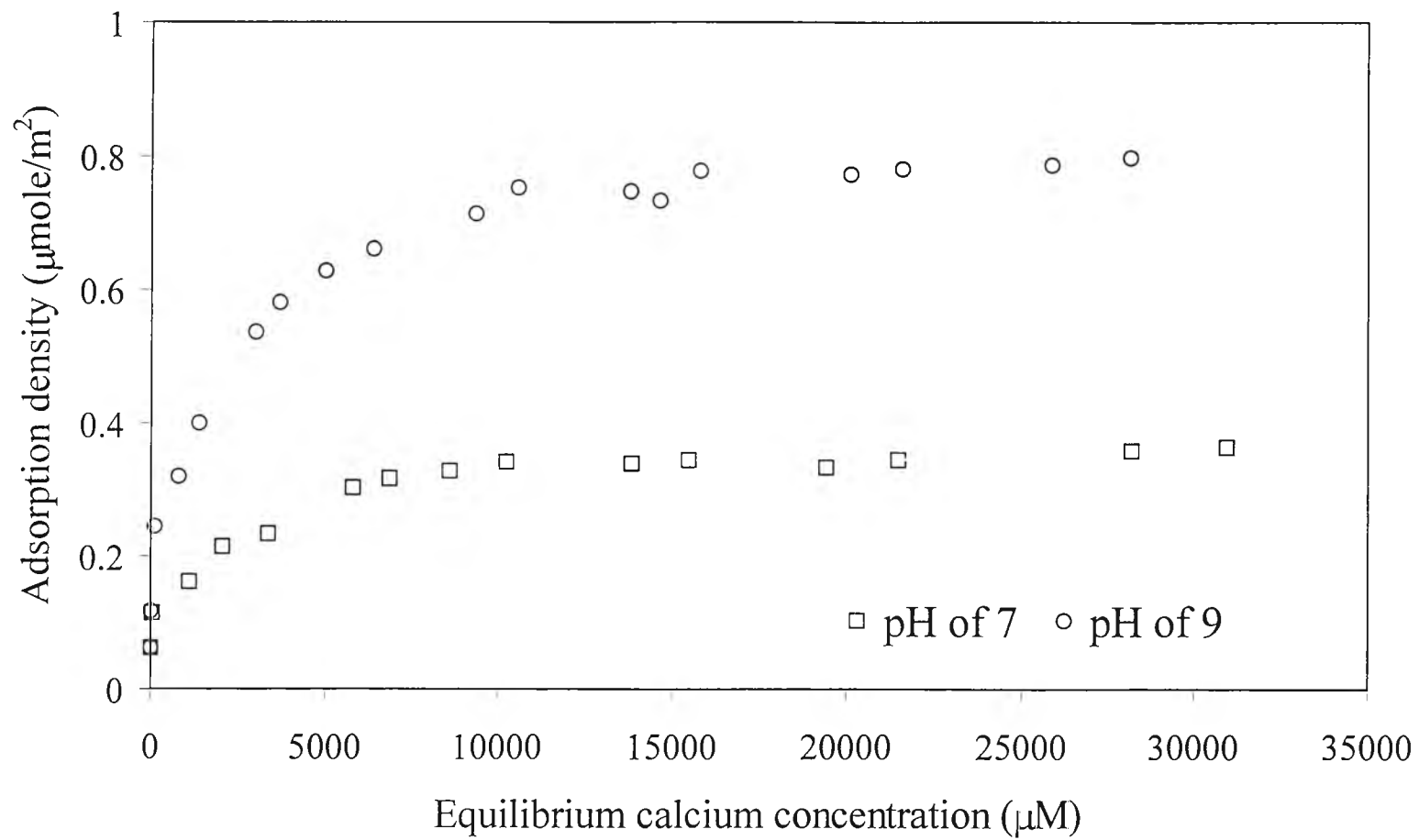
Figure 4.6 Adsorption isotherms of calcium on carbon black at pH of 7 and 9 in the absence of SDS.

4.1.3 Electrophoretic Determination

Zeta potential is an approximation of surface potential. It is the electrical potential at the shear plane between Stern layer and diffuse layer. It is an important feature because zeta potential can be measured in a fairly simple manner, while the surface potential cannot. Zeta potential is an effective tool for coagulation control because of changes in the repulsive force between colloids.

Figure 4.7 illustrates the zeta potential of carbon black as a function of equilibrium SDS concentration without calcium addition at pH of 7 and 9. The results indicated the positive effect of SDS on the measured zeta potential. While the equilibrium SDS concentration increased, the absolute zeta potential of carbon also increased. Since the adsorbed SDS on carbon exposed the negatively charged group to the solution, and the hydrophobic tail group interacted with the surface, therefore the absolute zeta potential of carbon increased with increasing SDS concentration. At constant equilibrium SDS concentration, the absolute zeta potential of carbon at pH of 9 was slightly greater than one at pH of 7. Because the effect of pH between 7 and 9 was not significant to the SDS adsorption on carbon surface, the net negative charge on carbon surface at pH of 9 remained higher than one at pH of 7.

Figures 4.8 and 4.9 depict the zeta potential of carbon versus equilibrium SDS concentration as varying calcium concentration at pH of 7 and 9. With constant equilibrium SDS concentration, the absolute zeta potential of carbon decreased at increasing calcium levels. It was probably because calcium ions neutralized the negatively charged sites on carbon surfaces and hydrophilic groups of SDS, consequently, the net negative charges on carbon adsorbents decreased.

Figure 4.10 shows the relationships of adsorption isotherms and zeta potential versus equilibrium SDS concentration at pH of 7 and 9 in the absence of calcium. At low SDS adsorption, the negative zeta potential
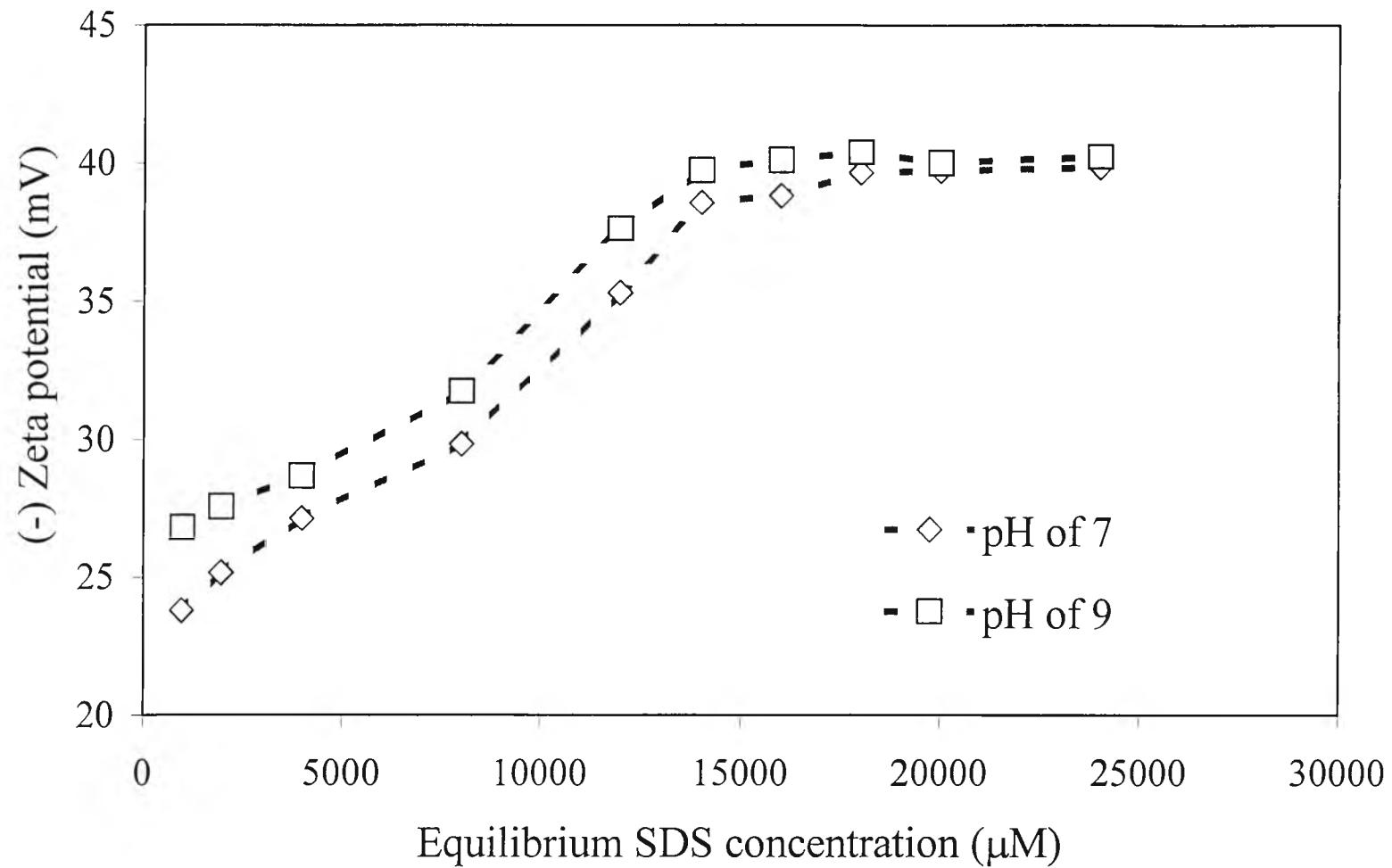
Figure 4.7 Zeta potential of carbon black versus equilibrium SDS concentration at pH of 7 and 9 without calcium addition.
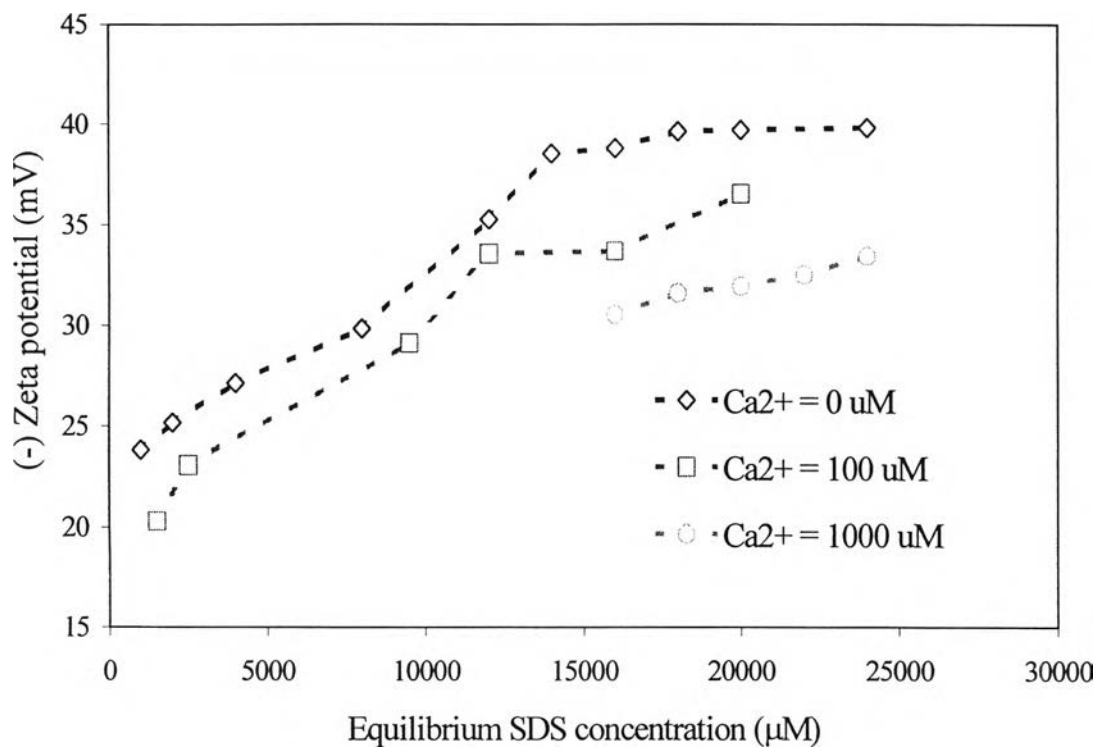
Figure 4.8 Zeta potential of carbon black versus equilibrium SDS concentration at pH of 7 with varying initial calcium concentration.
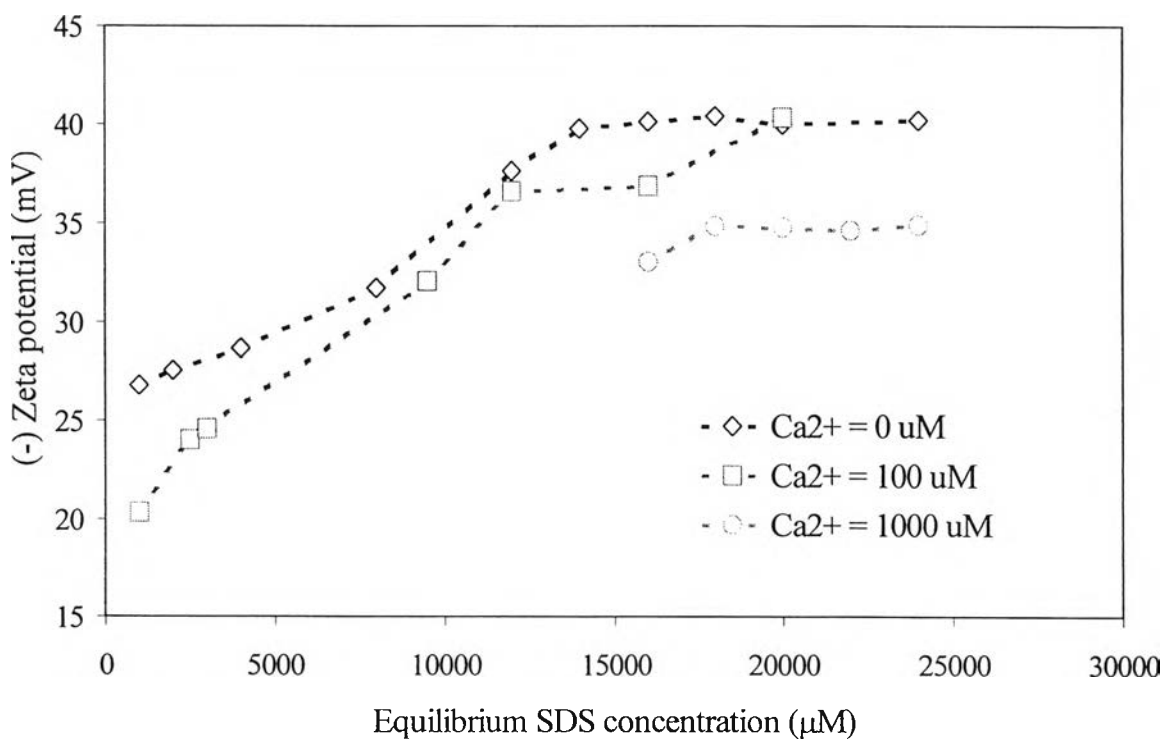

Figure 4.9 Zeta potential of carbon black versus equilibrium SDS concentration at pH of 9 with varying initial calcium concentration.
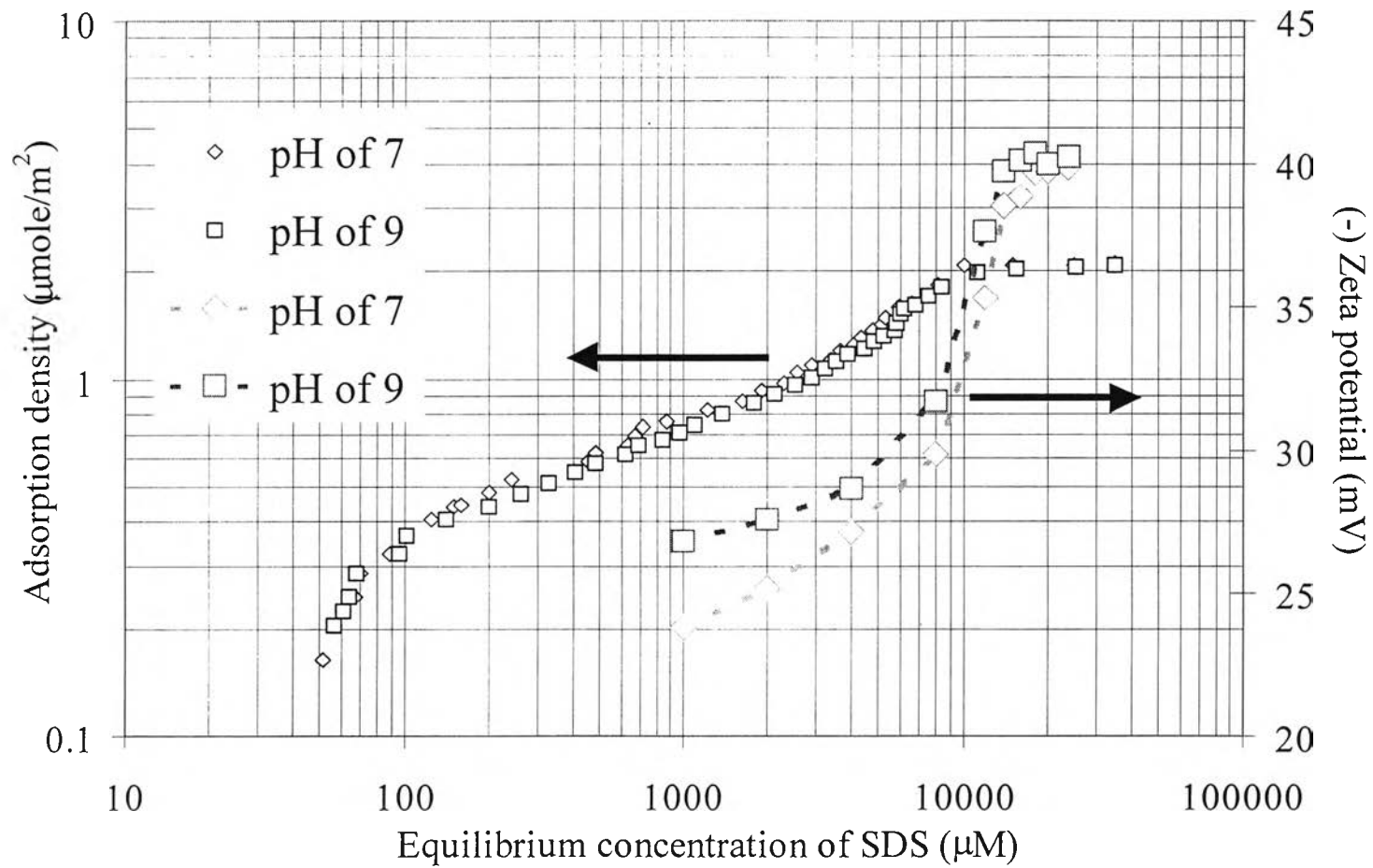
Figure 4.10 SDS adsorption and zeta potential of carbon versus equilibrium SDS concentration at pH of 7 and 9.

increased slightly from -23.8 to -27.1 mV at pH of 7 and from -26.8 to -28.7 mV at pH of 9. After that the negative zeta potential decreased significantly from -27.1 to -38.6 mV at pH of 7 and from -28.7 to -39.8 mV at pH of 9 as increasing SDS adsorption more. Finally, the zeta potential was fairly constant at SDS concentration slightly beyond the CMC of SDS.

4.2 Calcium Adsorption Isotherms

The purpose of this experimental part is to study the role of small concentrations of SDS to calcium adsorption on carbon black. Many research works indicate that electrolytes or counterions result dramatically on the adsorption of surfactants. Addition of neutral electrolyte such as NaCl or KBr causes a decrease in the adsorption of the ionic surfactants onto the oppositely charged adsorbents and an increase in their adsorption onto the similarly charged adsorbents. Conversely, the addition of surfactants such as anionic surfactants should obtain whether positive or negative effect on the adsorption of counterions.

4.2.1 Effect of Surfactant Concentration

Figures 4.11 and 4.12 illustrate the effect of SDS concentration on the adsorption of calcium at pH of 7 and 9. The results of calcium adsorption isotherms at varying SDS concentration were Langmurian curves, and the adsorption of calcium ion decreased at increasing SDS concentration. Because the monomeric SDS probably adsorbed onto carbon surface in the horizontal or laying-down configuration, some parts of hydrophobic tail group might locate at negatively charged sites, which might consequently be the barriers for calcium ions to be adsorbed on the remaining negatively charged sites as calcium adsorption decreased. Another possible reason to explain was that the amount of SDS added was very small, when the surfactant adsorbed
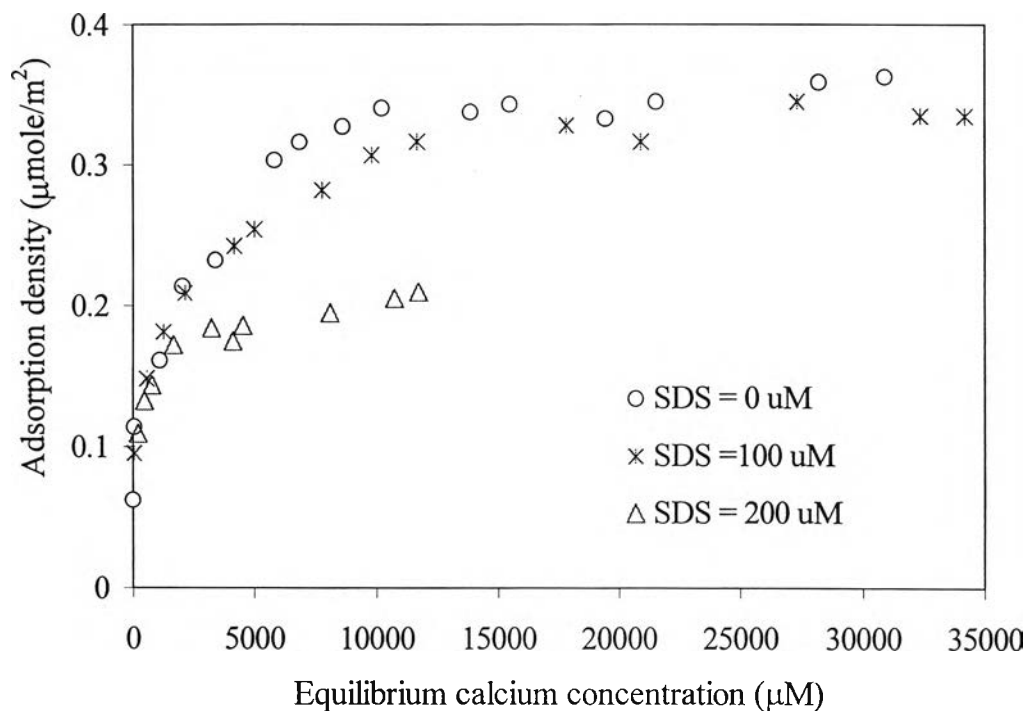
Figure 4.11 Calcium adsorption on carbon black at pH of 7 with varying initial SDS concentration.
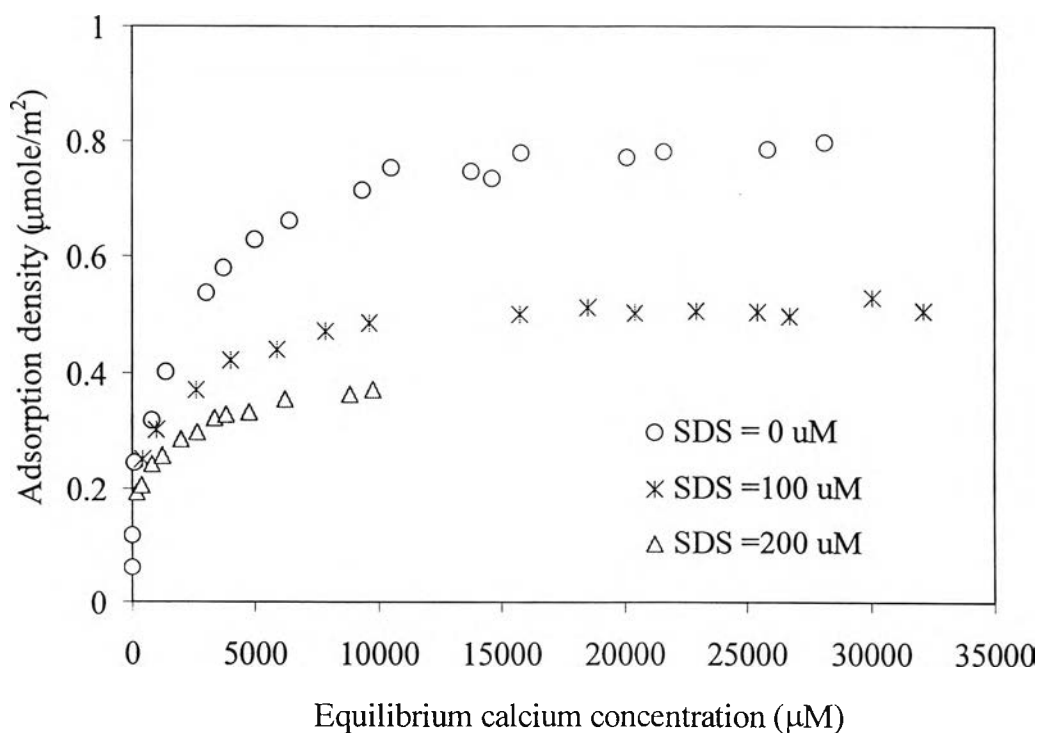

Figure 4.12 Calcium adsorption on carbon black at pH of 9 with varying initial SDS concentration.

on the surface without the interaction between individual adsorbed surfactants, the cooperative adsorption with ionic surfactants in the presence of ionic salt rarely occurred. From the result, the adsorption of calcium on the carbon in the presence of small amount of SDS was less than the adsorption of calcium without SDS addition.

4.2.2 Electrophoretic Determination

Figures 4.13 and 4.14 illustrate the zeta potential of carbon black versus equilibrium calcium concentrations as varying SDS concentration at pH of 7 and 9. When calcium was added to the system, the magnitude of zeta potential decreased dramatically because of the adsorption of calcium onto oppositely charged sites of carbon surfaces. However, at constant calcium concentration, the change in the magnitude of zeta potential was small with increasing amount of SDS. It was possibly because the amount of SDS added was too small to produce a net change in the zeta potential magnitude.
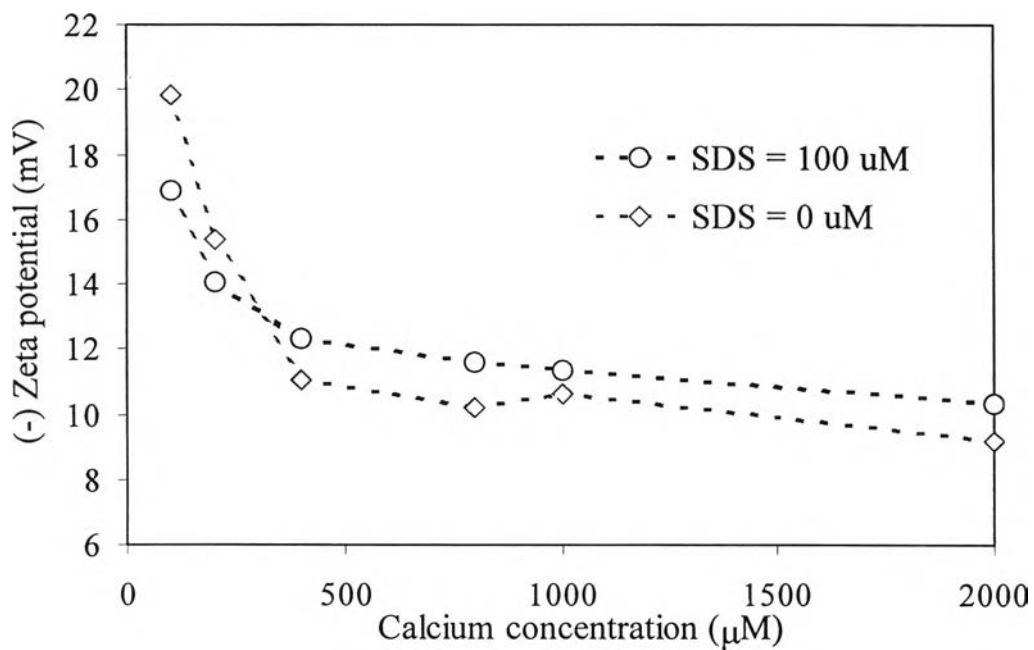
Figure 4.13 Zeta potential versus calcium concentration at pH of 7 with varying initial SDS concentration.
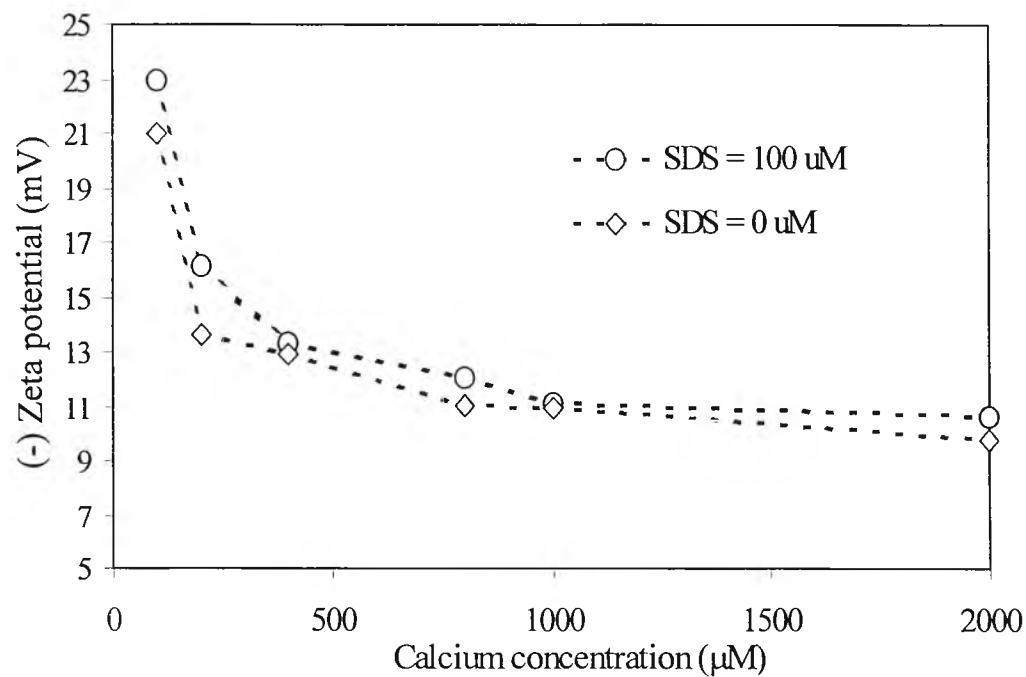

Figure 4.14 Zeta potential versus calcium concentration at pH of 9 with varying initial SDS concentration.