

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Solubility of Soap and SDS

The solubility limit of soap decreases with decreasing pH as shown in Table 4.1. The result showed the protonation of soap occurring as the pH decreased. Octanoic acid, which is the result of protonation of octanoate ions, has a lower solubility limit than soap at low pH (Lyman et. al.,1990). Therefore, the solubility of soap increases with increasing pH.

Table 4.1 The solubility limit of soap at different pH,  
temperature = 30 °C

pH	Solubility limit (M)
9	2
7	0.5
6	0.15
5	0.03

The solubility limit of SDS is about 0.8 M at 30°C. Decrease pH of the SDS solution has no effect on the solubility limit. If the concentration of SDS is higher than 0.8 M, the solution becomes sticky gel and SDS can not further dissolve in water.

The experiment to study the effect of SDS on hardness tolerance of SO was limited by its solubility. They could not be done in some concentrations and ratios. The solutions could be prepared as indicated in unshaded areas as shown in Table A-1 of appendix A.

#### **4.2 Composition of Precipitation in Mixed System**

HPLC was used to determine the composition of the precipitate obtained from different experiments. The results show that about 30 - 40 % of SO precipitated out and about 20-30 % of SDS precipitated out. It means that SO was the major component.

The hardness tolerance of a mixture containing more than one anionic surfactant is obtained when the solubility product of the least soluble surfactant is reached. Mixed precipitate is usually not seen along the precipitation phase boundary of mixed anionic surfactant unless  $K_{sp}$  values of the two surfactants are similar. For the conditions studied in this paper, SO is the precipitating species for the mixed SDS/SO system. Hence, this study documents the effect of SDS on SO precipitation.

The experiment can be done only at ratios of SDS/SO equal 5/95, 10/90, 20/80, and 40/60 because other ratios are beyond the solubility limit of SDS and SO.

### 4.3 Precipitation Phase Boundaries in Mixed System

Figure 4.1 is the phase boundary of pure SO at various pH. The precipitation phase boundaries for mixed systems shown in Figures 4.2-4.7 illustrate the effect of pH and mole ratio of the mixture on the precipitation phase boundaries. The precipitate is formed by soap and the counterion. A schematic diagram of this system is shown in Figure 2.2.

Above the phase boundary curve, precipitation forms. Solution with total concentration below the curve remains clear and no crystals appear. The minimum in these plots represent the CMC. Below the CMC, SDS and SO precipitated as  $\text{Ca}(\text{DS})_2$  and  $\text{Ca}(\text{O})_2$  respectively.

For SDS :

$$K_{\text{sp},\text{Ca}(\text{DS})_2} = [\text{Ca}^{+2}]_{\text{un}} [\text{DS}^-]_{\text{mon}}^2$$

where  $K_{\text{sp}}$  = The concentration - based solubility product,  $\text{M}^3$

$[\text{Ca}^{+2}]_{\text{un}}$  = The concentration of unbound calcium, M

$[\text{DS}^-]_{\text{mon}}$  = The monomer concentration of anionic surfactant, M

For SO :

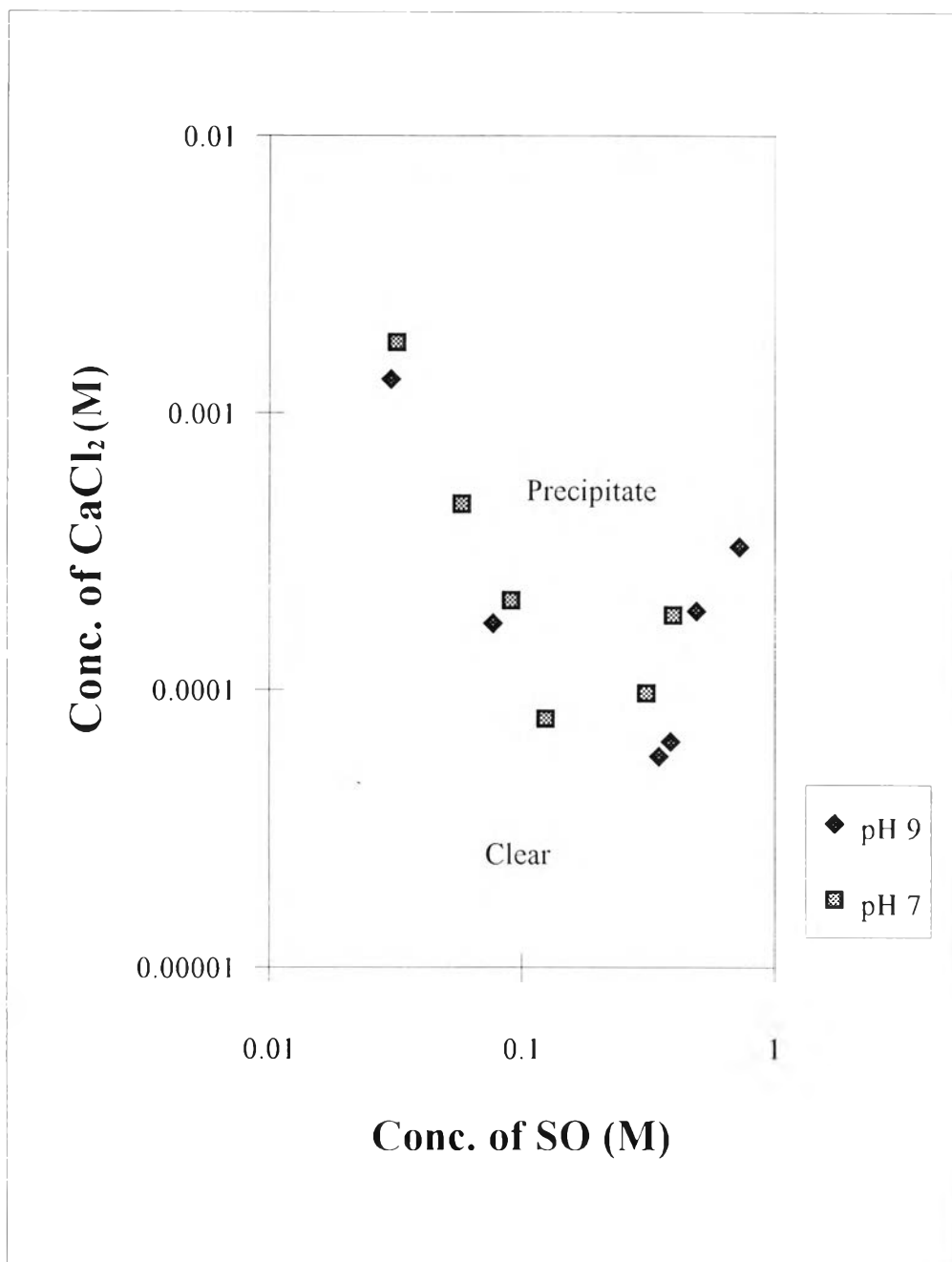
$$K_{\text{sp},\text{Ca}(\text{O})_2} = [\text{Ca}^{+2}]_{\text{un}} [\text{CH}_3(\text{CH}_2)_6\text{COO}^-]_{\text{mon}}^2$$

where  $K_{\text{sp}}$  = The concentration - based solubility product,  $\text{M}^3$

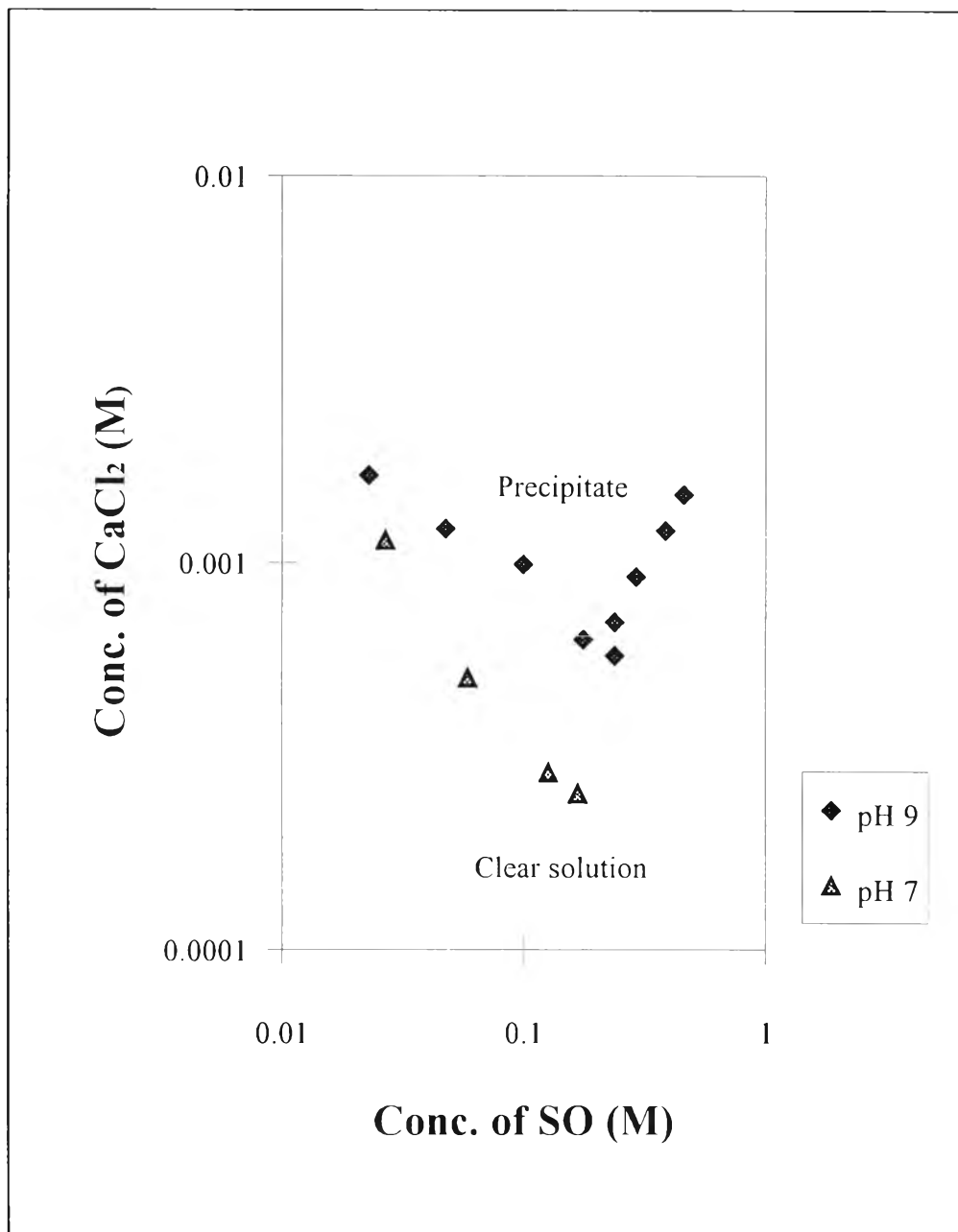
$[\text{Ca}^{+2}]_{\text{un}}$  = The concentration of unbound calcium, M

$[\text{CH}_3(\text{CH}_2)_6\text{COO}^-]_{\text{mon}}$  = The monomer concentration of soap, M

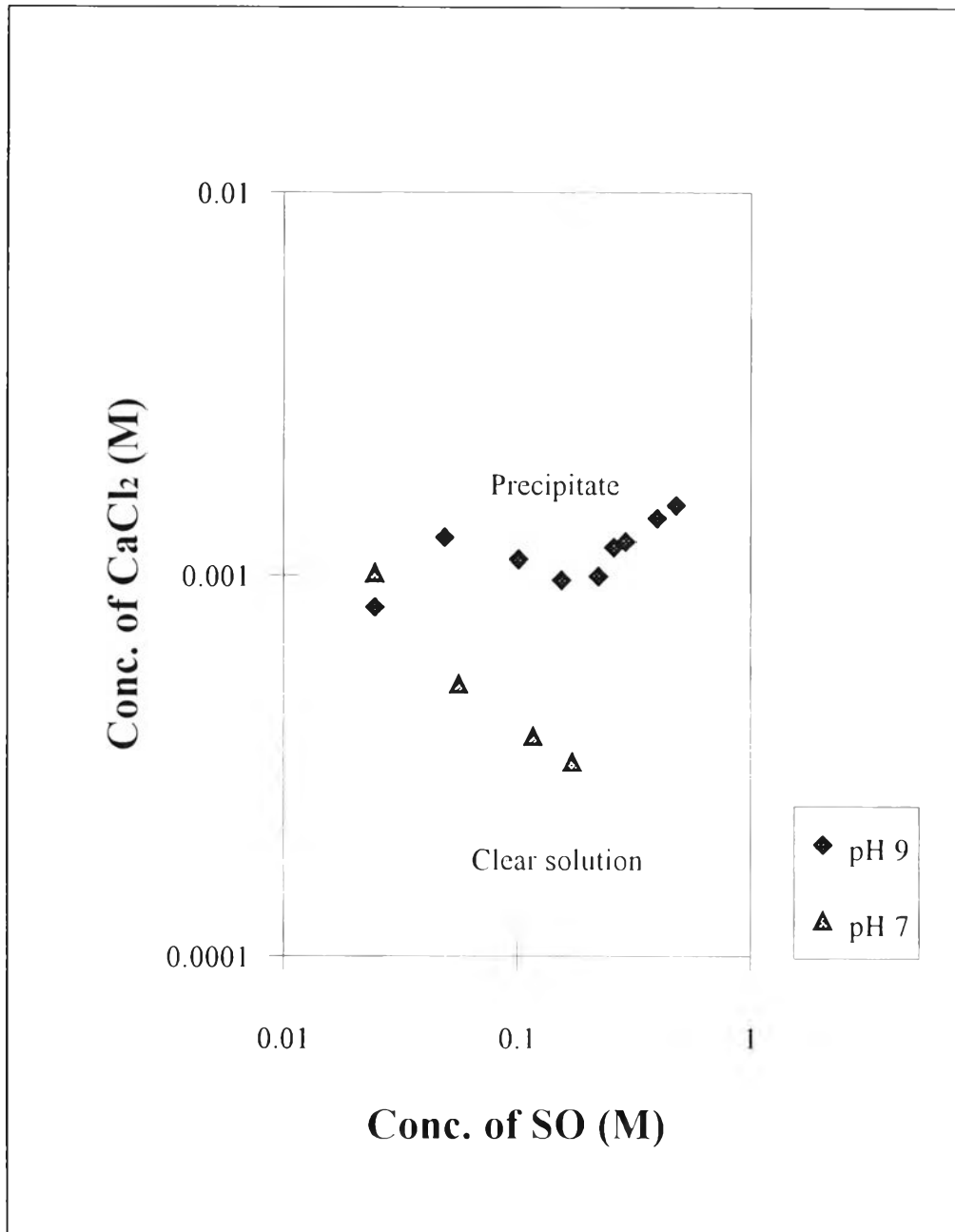
These equations show that SDS and SO concentrations increase below the CMC result in hardness tolerance decreasing. At the CMC, micelle begin to form and the precipitation phase boundary drastically changes. The hardness tolerance is minimum at the CMC. Above the CMC, when the concentrations of SDS and SO increase, the hardness tolerance increases. This is due to counterion binding of  $\text{Ca}^{+2}$  onto micelles.



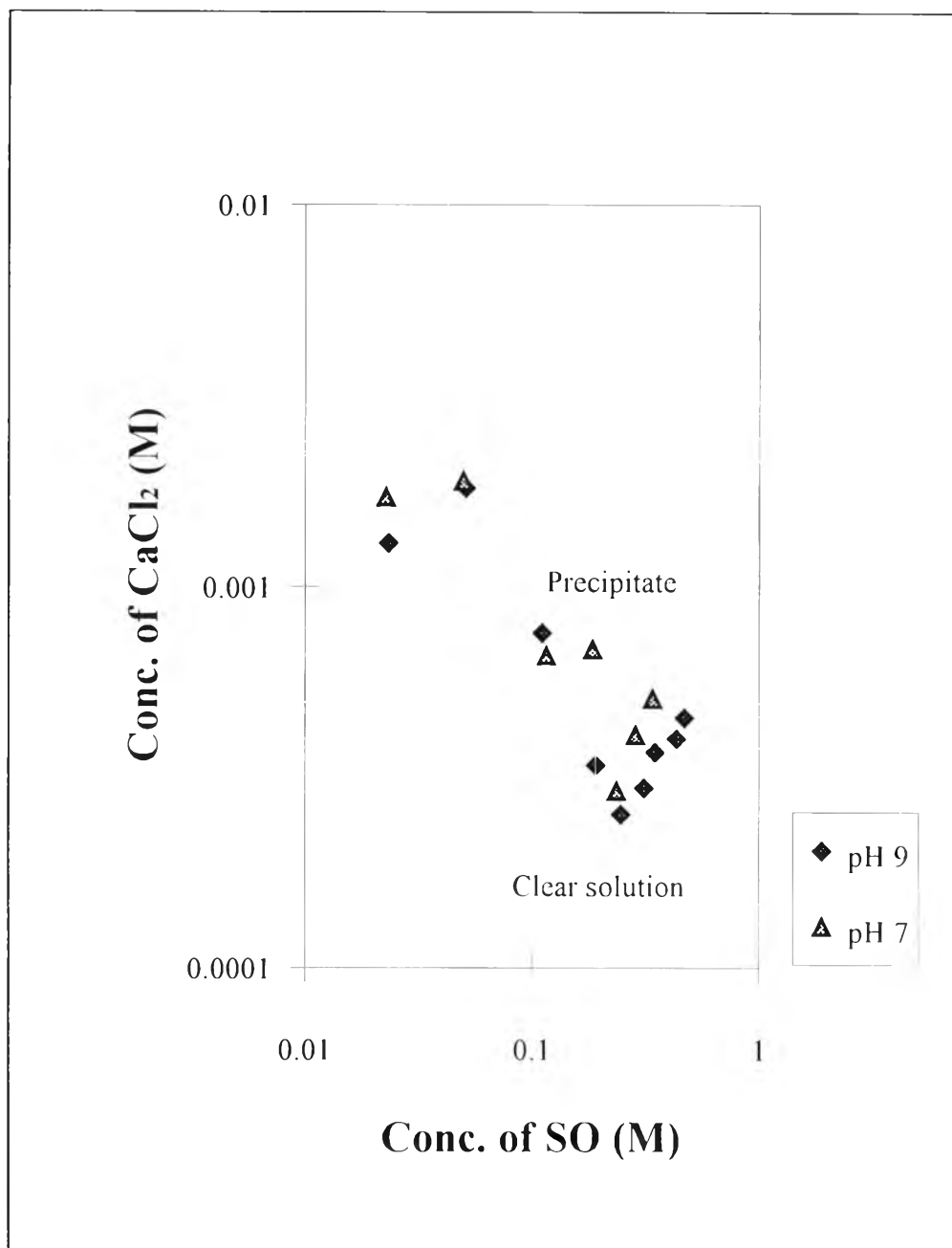
**Figure 4.1** Phase boundary of pure SO.



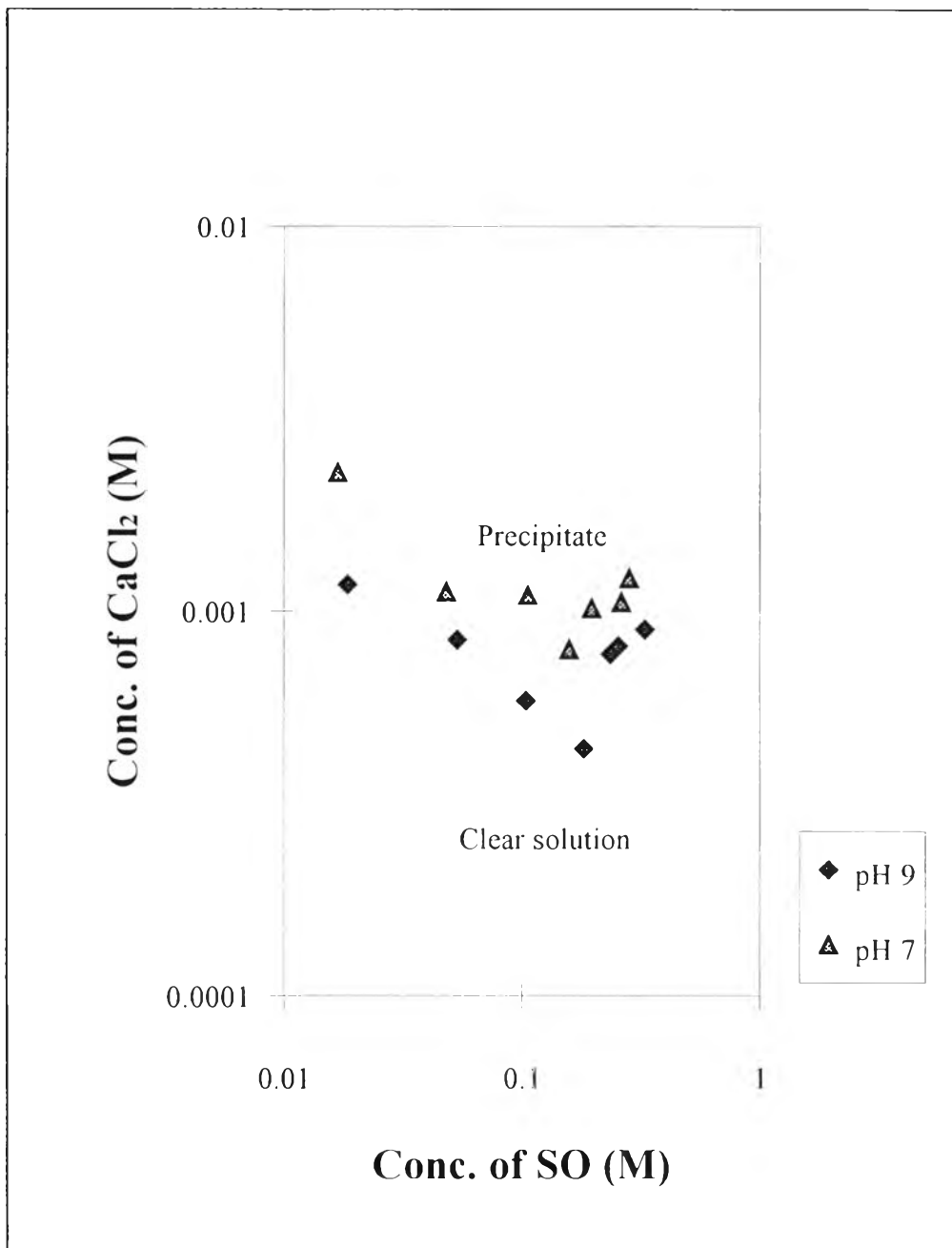
**Figure 4.2** Phase boundary of mixed SDS/SO at mole ratio of SDS/SO = 5/95.



**Figure 4.3** Phase boundary of mixed SDS/SO at mole ratio of SDS/SO = 10/90.

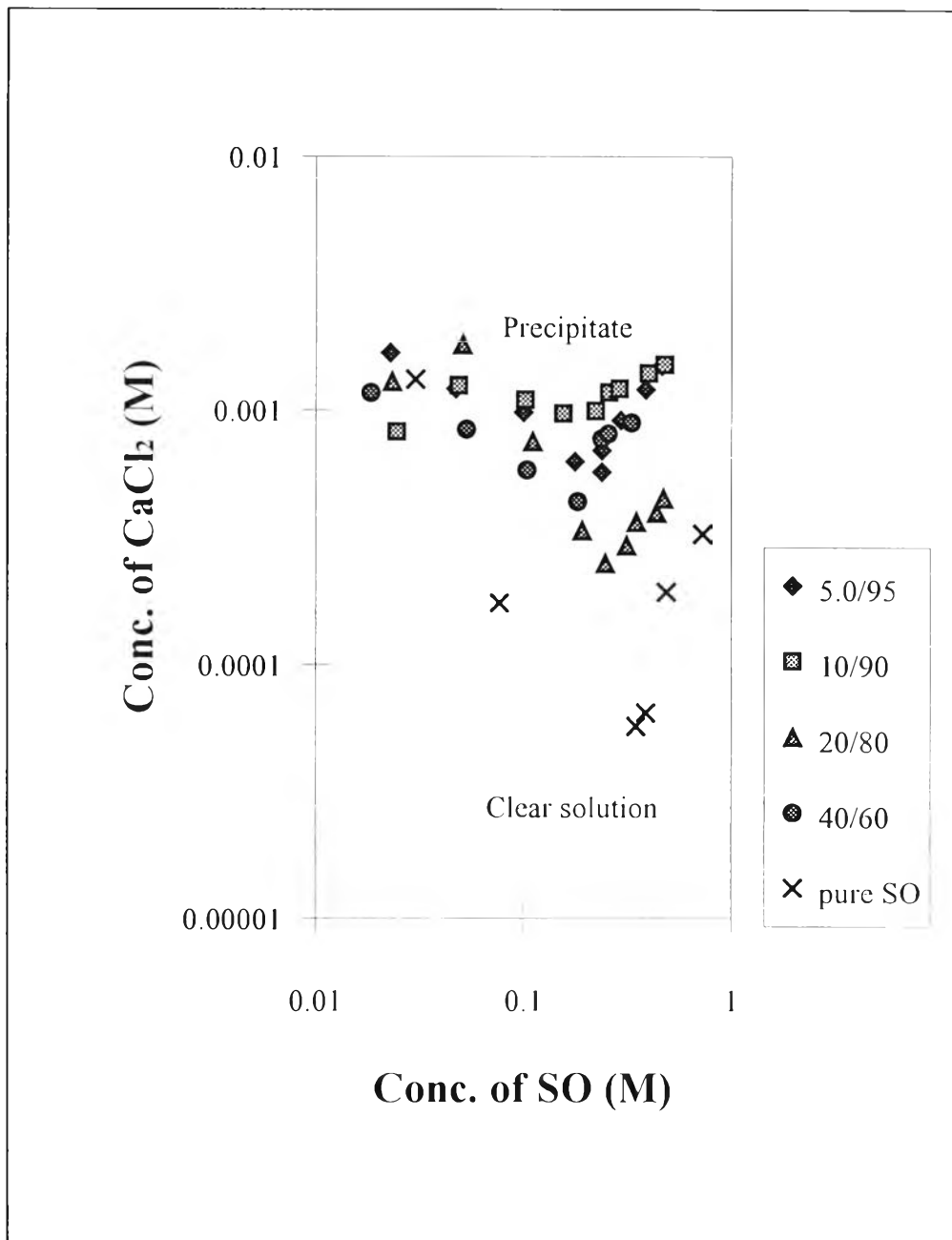


**Figure 4.4** Phase boundary of mixed SDS/SO at mole ratio of SDS/SO = 20/80.



**Figure 4.5** Phase boundary of mixed SDS/SO at mole ratio of SDS/SO = 40/60





**Figure 4.6** Phase boundary of mixed SDS/SO at pH9.

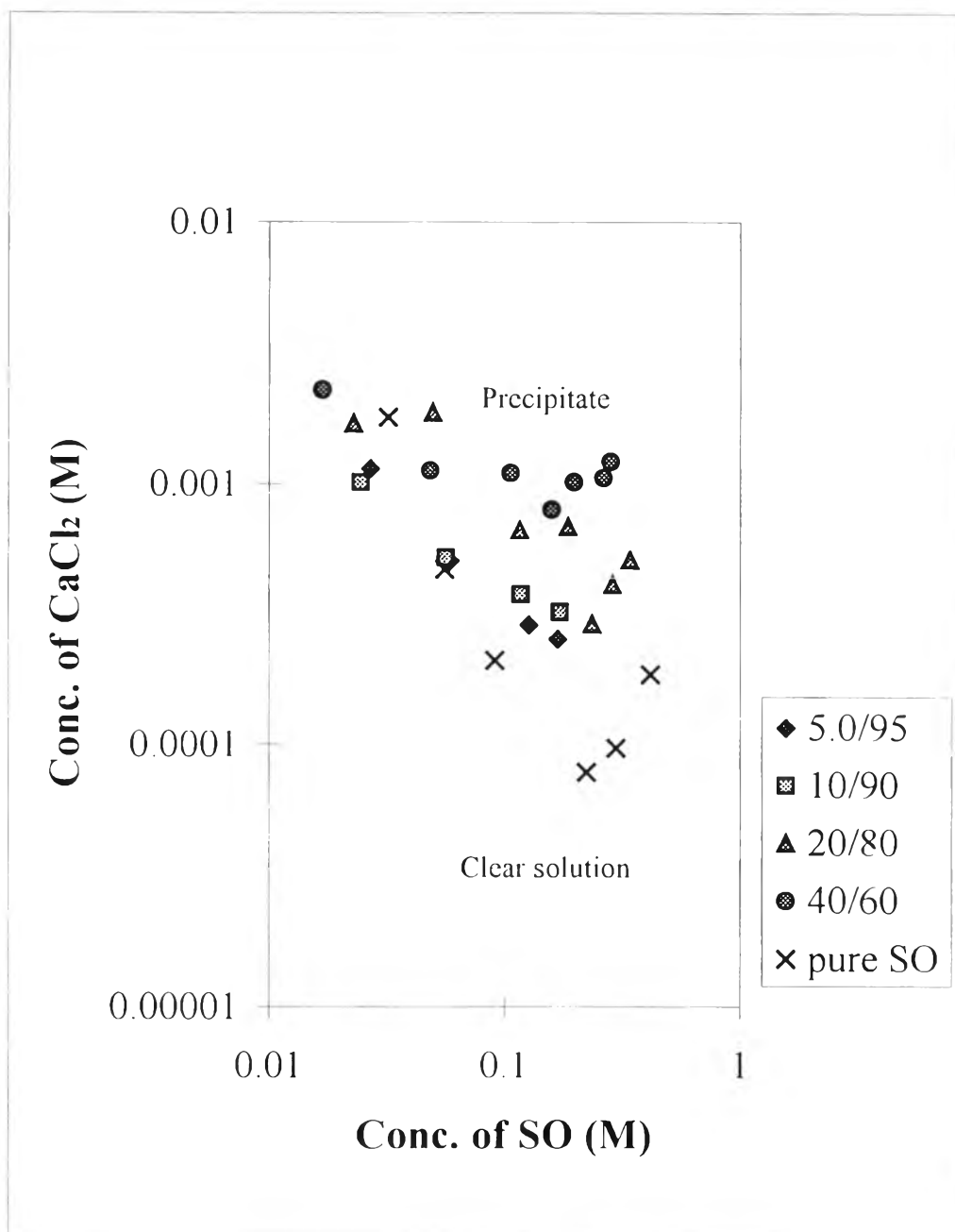
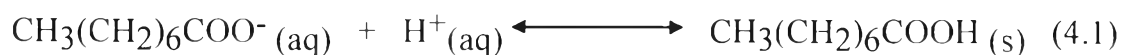


Figure 4.7 Phase boundary of mixed SDS/SO at pH7.

The effect of pH on the mixed system of SO and SDS are shown in Figure 4.2-4.5. At ratios 0.2:0.8 and 0.4:0.6 of SDS:SO, minimum hardness tolerance slightly increases as pH is lowered. The mixed micelles can form more easily at low pH than at high pH because a reduction of electrostatic repulsion in the mixed micelle at low pH caused by hydrogen ions. At ratios 0.05:0.95 and 0.1:0.9 of SDS:SO, the composition of SO is much higher than SDS. At low pH, SO can react with H<sup>+</sup> ion according to equation 4.1 resulting in the formation of protonated precipitate of organic acid. It makes the solution so turbid that the precipitation of SO and SDS with Ca<sup>2+</sup> ion can not be observed. So the experiment at high concentration can not be done. The protonated precipitate of organic acid occurs when initial concentration of SO is high .



The micelle-monomer-precipitate equilibrium diagram for SO is shown in Figure 4.8. There is an anionic, deprotonated form of SO (O<sup>-</sup>) which is precipitating with calcium in this figure. The deprotonated form is also present as monomer and in the micelles. There is also an uncharged, protonated form of SO(HO) which is present in the micelles and as monomer. Due to the presence of these two forms, SO is able to form nonideal mixed micelles without the presence of any other components. Precipitation of HO is also possible in these systems if the solubility limit is reached.

As the pH is decreased, a larger fraction of SO is present in the uncharged, protonated form. These HO monomers are inserted into the micelle between the negatively charged O<sup>-</sup> ions, creating a more nonideal mixed micelle. As the micelles become more nonideal, the SO monomer concentration decreases, resulting in a higher hardness tolerance. As the SO

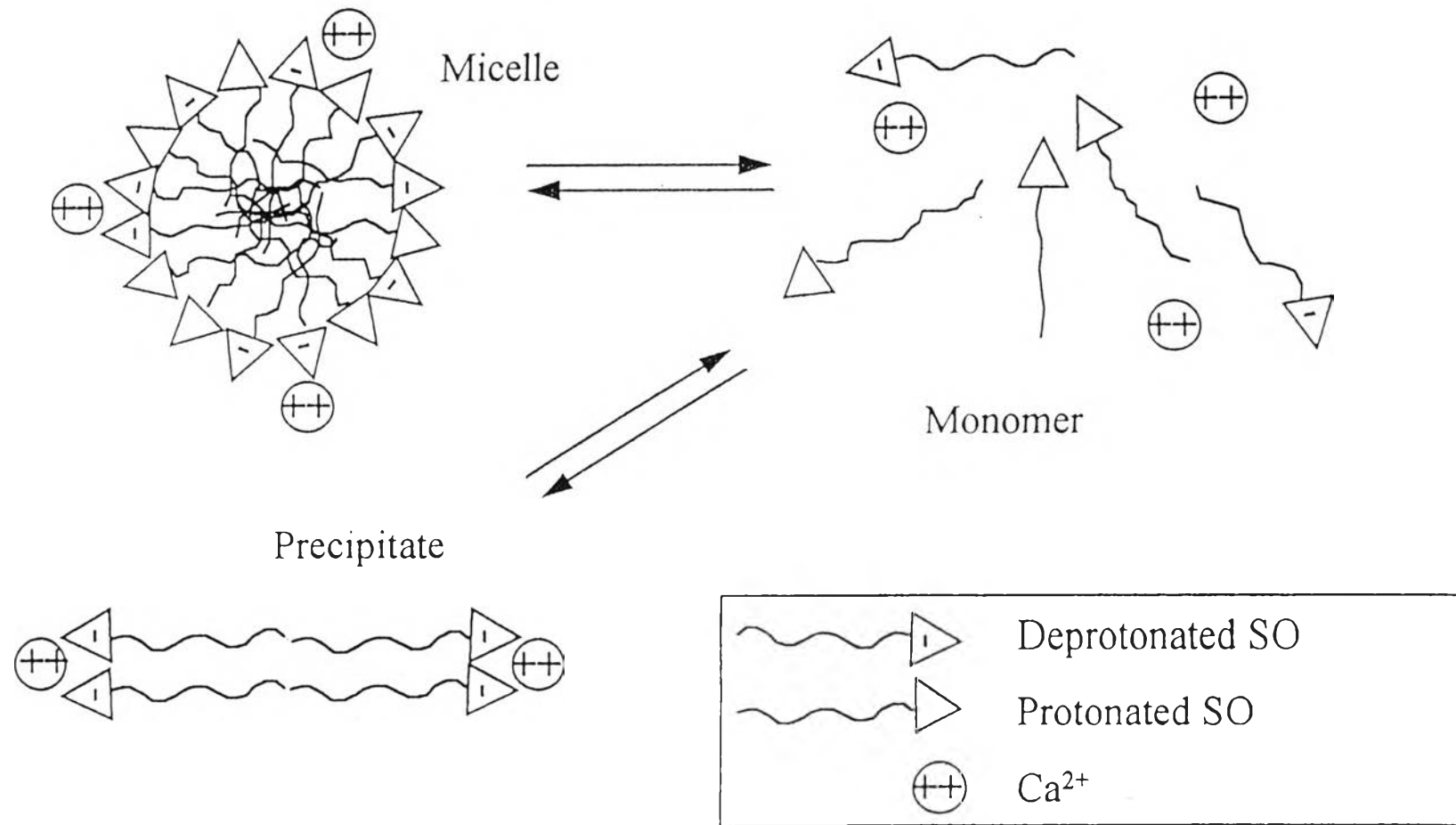


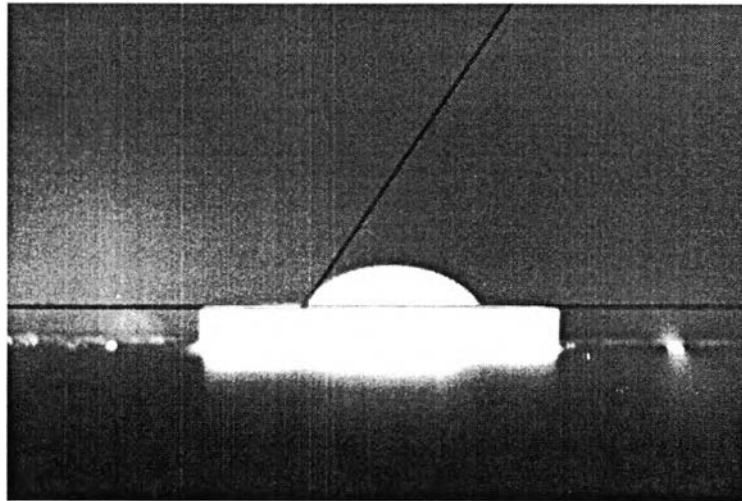
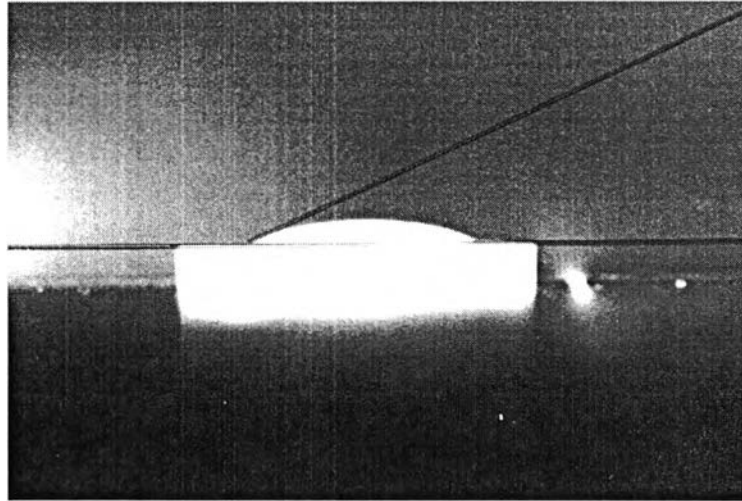
Figure 4.8 Schematic of equilibrium existing in pure SO system.

concentration increases and the pH decreases, the monomeric fatty acid concentration reaches its solubility limit.

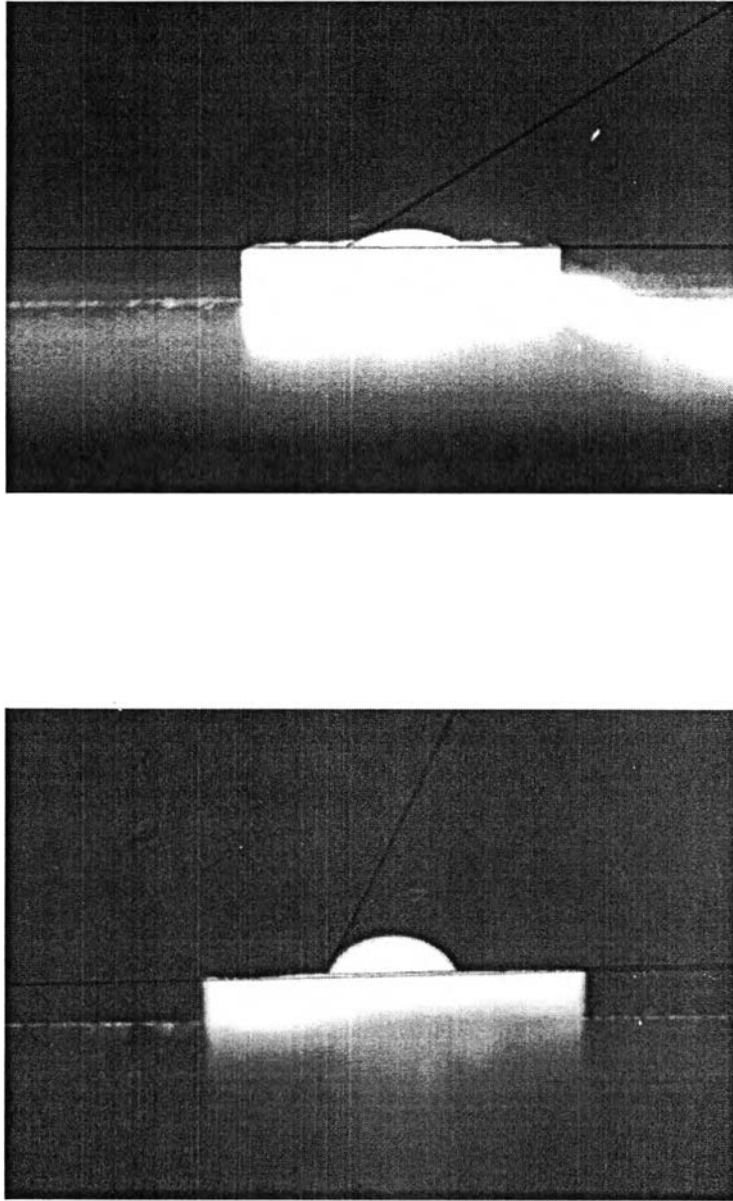
The effect of the mole ratio of the mixed system on the precipitation phase boundaries are illustrated in Figure 4.6-4.7. The hardness tolerance of mixed system is higher than the pure SO system. The CMC of the mixed system is lower than the CMC of pure system. Mixed micelle is more stable than the micelle of pure SO because SDS can help to stabilize the mixed micelle. Therefore, the minimum hardness tolerance of the mixed system increases when SDS is added in the SO system.

#### **4.4 Contact angle**

The contact angles measured from photographing are shown in Figure 4.9-4.10. The contact angles of SO and SDS are  $54^\circ$  and  $28^\circ$ , respectively. It indicates that SDS has more wettability than SO. The contact angles of  $\text{Ca(O)}_2$  and  $\text{Ca(DS)}_2$  precipitates are about  $60^\circ$  and  $30^\circ$ , respectively. The results show that the contact angle of SO is less than the contact angle of  $\text{Ca(DS)}_2$  precipitate and the contact angle of SDS is also less than the contact angle of  $\text{Ca(O)}_2$  precipitate. These results indicate that the contact angles of pure substrates are less than the contact angle of the precipitate. Therefore, pure substrates are more wettability than the precipitate  $\text{Ca(O)}_2$  and  $\text{Ca(DS)}_2$ .



**Figure 4.9** The contact angle measurement of SDS and SO.



**Figure 4.10** The contact angle measurement of Ca-SDS and Ca-SO